Electronic Supplementary Information to:

Photo-induced β-Elimination of 9-Fluorenymethanol Leading to Dibenzofulvene

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**Experimental**

**Materials.** 9-Fluorenylmethanol (FM) (TCI), potassium tert-butoxide (TCI) and 2,2,6,6-tetramethyl-4-piperidinol (Sigma-Aldrich) were used as obtained. Hexane (Kanto) was washed with conc. H₂SO₄, aq. NaOH, and water in this order and distilled over CaH₂ under N₂. Methanol (Kanto) was distilled over CaH₂ under N₂. Acetonitrile (Kanto) was dried on MS4A and distilled under N₂. Distilled H₂O was obtained through the purified water supply system at Institute for Catalysis, Hokkaido University. Dibenzofulvene (DBF), the pristine sample, was synthesized according to the literature.¹,²

**Instrumentation and measurements.** NMR spectra were recorded on JEOL JNM-ESC400 spectrometer (400 MHz for 1H, 100 MHz for 13C). Size-exclusion chromatography (SEC) measurements were carried out using a chromatographic system consisting of a JASCO DG-980-50 degasser, a HITACHI L-7100 pump, a HITACHI L-7420 UV-Vis detector and a HITACHI L-7490 RI detector, equipped with TOSOH TSKgel G3000H HR and G6000H HR columns (30 × 0.72 (i.d.) cm) connected in series (eluent: THF, flow rate: 1.0 mL/min). UV-Vis spectra were taken in quartz cells on JASCO V-550 and V-570 spectrophotometers, and fluorescence spectra were measured using quartz cells on a JASCO PF-8500 fluorescence spectrophotometer. FT-IR spectra were recorded on a JASCO FT/IR-6100 apparatus. Photo irradiation was conducted using a 300-W Xe lamp (Cermax Y-1089) in a R300-3J lamp house driven with a model CX-04E power source with a MR 60/90-ALM 45-deg reflecting mirror unit equipped with a CM2 UV cold mirror, an Asahi Spectra 1200 50x50 cold filter, and a quartz-made focus lens.

**Irradiation experiments.** Solutions at 3.9 x 10⁻⁵ M were prepared in the following manner (samples for the data in Table 1 in the main text). A hexane solution of FM at 3.9 x 10⁻⁵ M was prepared as follows (a sample for the data in Table 1). A hexane solution: a 10-mL solution of FM in hexane (3.78 mg, 1.9 x 10⁻³ M) was prepared in a volumetric flask from which a 2-mL portion was transferred using a 2-mL graduated pipette to a 100-mL volumetric flask where a solution at 3.9 x 10⁻⁵ M in hexane was made by dilution. A methanol solution: a 10-mL solution of FM in methanol (0.41 mg, 2.1 x 10⁻⁴ M) was prepared in a volumetric flask from which a 4.6-mL portion was transferred using a 5-mL graduated pipette to a 25-mL volumetric flask where a solution at 4 x 10⁻⁵ M in methanol was made by dilution. An acetonitrile solution: a 10-mL solution of FM in acetonitrile (1.57 mg, 8.0 x 10⁻⁴ M) was prepared in a volumetric flask from which a 1.2-mL portion was transferred using a 2-mL graduated pipette to a 25-mL volumetric flask where a solution at 3.9 x 10⁻⁵ M in acetonitrile was made by dilution. An H₂O solution: a 100-mL solution of FM in H₂O (9.81 mg, 5.0 x 10⁻⁴ M) was prepared in a volumetric flask from which a 0.77-mL portion was transferred using a 1-mL graduated pipette to a 10-mL volumetric flask where a solution at 3.9 x 10⁻⁵ M in H₂O was made by dilution. A sample solution in a 1-cm, two-face quartz cell was irradiated for a prescribed duration of time. The distance between the reflecting mirror and the focusing lens was 15 cm, and that between the lens and the sample cell was 10 cm. A home-made aluminum-foil reflecting chamber was placed behind the cell.

**Determination of molar absorptivities of FM in hexane, methanol, acetonitrile, and H₂O.** Absorbance values were measured at five to six different concentrations (SI, Figure S5), and molar absorptivities were estimated by a linear plot of absorbance against concentration. Sample solutions were prepared as follows and numerical data are summarized in Table S1. A 100-mL solution of FM (9.81 mg, 5 x 10⁻⁴ M) was prepared using volumetric flask from which 4.5-mL was transferred using a graduated pipette to a 25-mL volumetric flask to made 9.0 x 10⁻⁵ M by dilution. A 1.5-mL portion of the 5 x 10⁻⁴-M solution was transferred to 10-mL volumetric flask to made 7.5 x 10⁻⁵ M by dilution. A 3-mL portion of 5 x 10⁻⁴ M solution was transferred using a whole pipette to 25-mL volumetric flask to made 6.0 x 10⁻⁵ M by dilution. A 1-mL portion of this solution of the 5 x 10⁻⁴-M solution was transferred to 10-mL volumetric flask to made 5.0 x 10⁻⁵ M by dilution. A 2-mL portion of the 5 x 10⁻⁴-M solution was transferred using a graduated pipette to a 25-mL volumetric flask to made 4.0 x 10⁻⁵ M by dilution. A 3-mL portion of the 5 x 10⁻⁴-M solution was transferred to 5-mL volumetric flask to made 3 x 10⁻⁵ M by dilution. A 0.5-mL portion of the 5 x 10⁻⁴-M solution was transferred using a graduated pipette to a 10-mL volumetric flask to made 2.5 x 10⁻⁵ M by dilution. A 1-mL portion of 5 x 10⁻⁵ M solution was transferred using a graduated pipette to 5-mL volumetric flask to made 1 x 10⁻⁵ M by dilution, and then 1-mL
portion of this solution (1 \times 10^{-5} \text{ M}) was transferred using a whole pipette to 10-mL volumetric flask to made 1 \times 10^{-6} \text{ M} by dilution.

**Determination of molar absorptivities of DBF in hexane, methanol, and acetonitrile.** Molar absorptivities were estimated by absorbance spectra taken in the solvents where one spectrum was taken for each solvent at the concentrations indicated below. Sample solutions were prepared as follows and numerical data are summarized in Table S2. Molar absorptivity in H\textsubscript{2}O was not determined, and the value for methanol was used for the experiments in H\textsubscript{2}O. A hexane solution: a 50-mL solution of DBF in hexane (17.75 mg, 1.99 \times 10^{-3} \text{ M}) was prepared in volumetric flask from which a 1-mL was transferred using a whole pipette to a 100-mL volumetric flask where a solution at 1.99 \times 10^{-5} \text{ M} was made by dilution. A methanol solution: a 50-mL solution (18.35 mg, 2.06 \times 10^{-3} \text{ M}) was prepared in volumetric flask from which a 1-mL was transferred using a whole pipette to a 100-mL volumetric flask where a solution at 2.06 \times 10^{-5} \text{ M} was made by dilution. An acetonitrile solution: A 50-mL solution (15.13 mg, 1.70 \times 10^{-3} \text{ M}) was prepared in volumetric flask from which a 1-mL was transferred using a whole pipette to a 100-mL volumetric flask where a solution at 1.70 \times 10^{-5} \text{ M} was made by dilution.

**Fluorescence measurements of FM as well as 9,10-diphenylanthracene as a standard compound for emission quantum yield measurements in hexane, methanol, acetonitrile, and H\textsubscript{2}O.** Sample solutions were prepared as follows and numerical data are summarized in Table S3. FM solutions: a 100-mL solution of FM (9.81 mg, 5.0 \times 10^{-4} \text{ M}) was prepared using volumetric flask from which a 1-mL portion was transferred using a 1-mL whole pipette to a 5-mL volumetric flask where a solution at 1.0 \times 10^{-4} \text{ M} was made by dilution. A 1-mL of this solution (1.0 \times 10^{-4} \text{ M}) was transferred to a 10-mL volumetric flask and diluted to a solution at 1.0 \times 10^{-5} \text{ M}. A 1-mL portion of the solution (1.0 \times 10^{-5} \text{ M}) was transferred to a 10-mL volumetric flask and diluted to a solution at 1.0 \times 10^{-6} \text{ M}. 9,10-Diphenylanthracene solutions: a 10-mL solution (3.30 mg, 1.0 \times 10^{-3} \text{ M}) was prepared using a 10-mL volumetric flask from which a 1-mL portion was transferred using a 1-mL graduated pipette to a 10-mL volumetric flask where a solution at 1.0 \times 10^{-4} \text{ M} was made by dilution. A 1-mL portion of this solution (1.0 \times 10^{-4} \text{ M}) was transferred to a 10-mL volumetric flask and diluted to a solution at 1.0 \times 10^{-5} \text{ M}, and also a 1-mL portion of the solution (1.0 \times 10^{-5} \text{ M}) was transferred to a 10-mL volumetric flask and diluted to a solution at 1.0 \times 10^{-6} \text{ M}. Fluorescence spectra were measured on excitation at 265 nm in 1-cm, four-face quartz cell sealed with a screw cap using the solution which had been bubbled with N\textsubscript{2} gas for 20 min.

**Computational method.** Geometry optimization was carried out with the density functional theory (DFT) calculation with the B3LYP functional.\textsuperscript{3,4} For the basis functions, the 6-31G sets were used for all the atoms. This computational set up is accurate enough to investigate qualitative mechanism of organic reactions. Singlet excited states were calculated using time-dependent density functional theory (TDDFT).\textsuperscript{5} For the lowest triplet state, the ground-state DFT with single determinant was used. The Gaussian 09 package\textsuperscript{6} was used for the computations. For geometry optimization of the minimum energy intersystem crossing point, our in-house code was used.

To connect reactant and product states in triplet-state potential energy surface, the sphere contracting walk method (SCW)\textsuperscript{7} was used. To locate some transition states, the scaled hypersphere search method (2PSHS) was used.\textsuperscript{8} The SCW and 2SHS calculations were carried out using the GRRM14 package.\textsuperscript{9,10}
Figure S1. IR spectra of DBF (a), FM (b) and a photo-generated DBF-FM mixture (c) prepared in hexane (3.9 x 10^{-5} M) on irradiation for 70 min (KBr): full-range (A) and expanded (B) spectra.

Figure S2. ^1^H NMR spectra of FM (A) and DBF (B) (400 MHz, CDCl$_3$, 23°C).
**Figure S3.** SEC profiles of FM (a) and a reaction mixture of FM containing DBF ([FM]₀ = 3.9 x 10⁻⁵ M, irradiation time = 70 min) (b): full-range (A) and expanded chromatograms (B).

**Figure S4.** Conc. vs. initial reaction rate plots of photo-generated DBF in hexane at [FM]₀ = 7.5 x 10⁻⁵ M, 5.0 x 10⁻⁵ M, 3.9 x 10⁻⁵ M, 1.5 x 10⁻⁵ M, and 1.0 x 10⁻⁵ M for different durations of reaction. The data have been normalized to match the results reported in Table 1 and Figure 2 at [FM]₀ = 3.9 x 10⁻⁵ M in the main manuscript in order to minimize errors due to aging of the Xe lamp.
Figure S5. Absorbance spectra of FM in hexane (A), methanol (B), acetonitrile (C), and H$_2$O (D) at different concentrations (cell path length = 1 cm; temp. = 23°C).

Figure S6. Absorbance-vs.-concentration plots for FM in hexane (A), methanol (B), acetonitrile (C), and H$_2$O (D) (cell path length = 1 cm; temp. = 23°C).
Table S1. Molar absorptivities of FM in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (L mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>265.8</td>
<td>20000</td>
</tr>
<tr>
<td>Methanol</td>
<td>265.5</td>
<td>24700</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>265.0</td>
<td>18400</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>265.2</td>
<td>16000</td>
</tr>
</tbody>
</table>

Figure S7. Absorbance spectra of FM in hexane (1.99 x 10$^{-5}$ M) (A), methanol (2.06 x 10$^{-5}$ M) (B), and acetonitrile (1.70 x 10$^{-5}$ M) (C) in different solvents (cell path length = 1 cm; temp. = 23°C).
Table S2. Molar absorptivities of DBF in various solvents.\(^a\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(\lambda_{1,\text{max}})</th>
<th>(\varepsilon_1)</th>
<th>(\lambda_{2,\text{max}})</th>
<th>(\varepsilon_2)</th>
<th>(\lambda_{3,\text{max}})</th>
<th>(\varepsilon_3)</th>
<th>(\lambda_{4,\text{max}})</th>
<th>(\varepsilon_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>306.2</td>
<td>9080</td>
<td>295.4</td>
<td>8930</td>
<td>278.0</td>
<td>10100</td>
<td>268.0</td>
<td>11200</td>
</tr>
<tr>
<td>Methanol</td>
<td>305.4</td>
<td>7220</td>
<td>294.4</td>
<td>8040</td>
<td>276.8</td>
<td>9530</td>
<td>266.8</td>
<td>10400</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>305.4</td>
<td>8440</td>
<td>294.4</td>
<td>9420</td>
<td>277.0</td>
<td>11400</td>
<td>266.6</td>
<td>12400</td>
</tr>
</tbody>
</table>

\(^a\)Minimum wavelength resolution setting = 0.2 nm.

Figure S8. Emission spectra of FM in various solvents (excitation wavelength = 265 nm; cell path length = 1 cm).
Table S3. Fluorescence measurements of FM in various solvents at 23 °C.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Absorbance at 265 nm ($\lambda_{ex}$)</th>
<th>$\lambda_{max}$ (nm)</th>
<th>Intensity (a.u.)</th>
<th>$\Phi$\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>0.0395</td>
<td>304.2</td>
<td>1143.39</td>
<td>0.12</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0257</td>
<td>304.2</td>
<td>1815.95</td>
<td>0.29</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.0282</td>
<td>304.6</td>
<td>2362.57</td>
<td>0.35</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.0250</td>
<td>304.6</td>
<td>1855.03</td>
<td>0.33</td>
</tr>
</tbody>
</table>

\textsuperscript{a}[FM] = 1.0 x 10\textsuperscript{-6} M, $\lambda_{ex}$ = 265 nm. \textsuperscript{b}Determined using 9-10-diphenylanthracene as a standard compound (F = 0.90, ref. 11).

Figure S9. First-order rate plots for DBF production from FM on irradiation in hexane distilled under N$_2$ (A) and in hexane bubbled with air (B) ([FM]$_o$ = 3.9 x 10\textsuperscript{-5} M). The latter solution was bubbled for 10 min before starting the reaction, and further bubbled for 1 min after each spectral measurement. The data have been normalized to match the results reported in Table 1 and Figure 2 at [FM]$_o$ = 3.9 x 10\textsuperscript{-5} M in the main manuscript in order to minimize errors due to aging of the Xe lamp.
Reference