[Supporting information]

Photocrystallographic Analysis for Elucidation of the Effect of the Crystal Packing for the Molecular Structure and the Photophysical Property of [AuCl(PPh$_3$)$_2$]

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Fig. S1. Wilson-type plot: (a) $(2\sin\theta/\lambda)^2$ vs. $-\ln(I_{\text{on}}/I_{\text{off}})$; (b) $(2\sin\theta/\lambda)^2$ vs. $-\ln(I_{\text{off2}}/I_{\text{off1}})$.

The increment from the linear-fit to the Wilson type plot means change of the averaged temperature factor ($\Delta B/2$). The value of $\Delta B/2$ from $(2\sin\theta/\lambda)^2$ vs. $-\ln(I_{\text{on}}/I_{\text{off}})$ (Fig. 1(a)) is approximately same as one from $(2\sin\theta/\lambda)^2$ vs. $-\ln(I_{\text{off2}}/I_{\text{off1}})$ (Fig. 1(b)), which $I_{\text{off2}}$ is measured after the data collection of the light-on stage and $I_{\text{off1}}$ is corresponding to the light-off stage. It indicates that the difference of temperature between the light-on and light-off stage can be regarded as almost zero and had little effect on the examining structural change by photoexcitation.

Data collected at 118 K were used to plot above. At this temperature, because the cell volume was hardly changed by photoexcitation, the ratios of diffraction intensity ($I_{\text{on}}/I_{\text{off}}$) to every $(2\sin\theta/\lambda)^2$ were obtainable.
Table S1. Geometric parameters of [AuCl(PPh$_3$)$_2$] at every temperature (Å, °)

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</tr>
<tr>
<td>P2—C231—C236—C235</td>
<td>−175.26 (15) −175.32 (15) −176.0 (2) −176.1 (2)</td>
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Table S2. Difference of bond lengths (Å), bond angles (deg) and torsion angles (deg) between the light-on and the light-off stages at 177 K

<table>
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<tr>
<th>Bond angle</th>
<th>P1–Au1–P2</th>
<th>+0.07(16)</th>
<th>C113–C112–C111</th>
<th>+0.09(18)</th>
<th>C231–C236–C235</th>
<th>−0.1(2)</th>
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</thead>
<tbody>
<tr>
<td>P1–Au1–C11</td>
<td>+0.02(17)</td>
<td>C114–C115–C116</td>
<td>−0.05(18)</td>
<td>C233–C234–C235</td>
<td>−0.3(3)</td>
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<tr>
<td>P2–Au1–C11</td>
<td>+0.13(17)</td>
<td>C114–C113–C112</td>
<td>+0.2(19)</td>
<td>C234–C235–C236</td>
<td>+0.4(3)</td>
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<tr>
<td>C121–P1–Au1</td>
<td>+0.18(7)</td>
<td>C115–C114–C113</td>
<td>−0.24(18)</td>
<td>C234–C233–C232</td>
<td>−0.2(3)</td>
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<tr>
<td>C111–P1–Au1</td>
<td>−0.03(6)</td>
<td>C121–C122–C123</td>
<td>+0.4(2)</td>
<td>C236–C231–C232</td>
<td>+0.1(2)</td>
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<tr>
<td>C131–P1–Au1</td>
<td>−0.12(6)</td>
<td>C121–C126–C125</td>
<td>−0.0(2)</td>
<td>Au1–P1–C111–C112</td>
<td>−0.03(14)</td>
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<tr>
<td>C211–P2–Au1</td>
<td>+0.09(7)</td>
<td>C122–C121–C126</td>
<td>−0.2(2)</td>
<td>Au1–P1–C111–C116</td>
<td>−0.05(17)</td>
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<tr>
<td>C221–P2–Au1</td>
<td>−0.09(6)</td>
<td>C124–C125–C126</td>
<td>+0.2(3)</td>
<td>Au1–P1–C121–C122</td>
<td>−0.1(2)</td>
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<tr>
<td>C231–P2–Au1</td>
<td>−0.11(7)</td>
<td>C124–C123–C122</td>
<td>−0.4(3)</td>
<td>Au1–P1–C121–C126</td>
<td>+0.2(2)</td>
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<tr>
<td>C111–P1–C121</td>
<td>−0.07(9)</td>
<td>C125–C124–C123</td>
<td>0.0(2)</td>
<td>Au1–P1–C131–C132</td>
<td>+0.07(16)</td>
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<tr>
<td>C111–P1–C131</td>
<td>+0.10(8)</td>
<td>C133–C132–C131</td>
<td>−0.1(2)</td>
<td>Au1–P1–C131–C136</td>
<td>−0.25(16)</td>
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<tr>
<td>C121–P1–C131</td>
<td>−0.07(9)</td>
<td>C133–C134–C135</td>
<td>+0.1(2)</td>
<td>Au1–P2–C211–C212</td>
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<tr>
<td>C221–P2–C211</td>
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<td>C134–C133–C132</td>
<td>−0.1(2)</td>
<td>Au1–P2–C211–C216</td>
<td>+0.14(17)</td>
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<tr>
<td>C231–P2–C211</td>
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<td>C135–C136–C131</td>
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<td>Au1–P2–C221–C222</td>
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<tr>
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<td>C136–C131–C132</td>
<td>+0.20(18)</td>
<td>Au1–P2–C221–C226</td>
<td>+0.16(19)</td>
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<tr>
<td>Torsion angle</td>
<td>C112-C111-P1</td>
<td>C116-C111-P1</td>
<td>C122-C121-P1</td>
<td>C126-C121-P1</td>
<td>C132-C131-P1</td>
<td>C136-C131-P1</td>
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<td>0.00(14)</td>
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<td>+0.21(16)</td>
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<td>−0.04(15)</td>
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<td>+0.17(17)</td>
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<td>+0.12(17)</td>
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<th>Distortion</th>
<th>Bond Sequence</th>
<th>Distortion</th>
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<td>C131–P1–C111–C112</td>
<td>-0.14(18)</td>
<td>C122–C121–C126–C125</td>
<td>+0.4(4)</td>
</tr>
<tr>
<td>C131–P1–C111–C116</td>
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<td>C123–C124–C125–C126</td>
<td>-0.4(6)</td>
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<td>C131–P1–C121–C122</td>
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<td>C124–C125–C126–C121</td>
<td>-0.2(5)</td>
</tr>
<tr>
<td>C131–P1–C121–C126</td>
<td>+0.3(2)</td>
<td>C126–C121–C122–C123</td>
<td>-0.1(4)</td>
</tr>
<tr>
<td>C131–P1–C121–C126</td>
<td>+0.3(2)</td>
<td>C126–C121–C122–C123</td>
<td>-0.1(4)</td>
</tr>
<tr>
<td>C232–C231–C236–C235</td>
<td>-0.4(4)</td>
<td>C233–C234–C235–C236</td>
<td>+0.6(6)</td>
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<td>C234–C235–C236–C231</td>
<td>0.0(5)</td>
<td>C236–C231–C232–C233</td>
<td>+0.2(5)</td>
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Table S3. Wavelengths of emission band (λ_{max}) and lifetimes (τ) at every temperature

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<th>Temperature / K</th>
<th>λ_{max} / nm</th>
<th>τ / μs</th>
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<tr>
<td>295</td>
<td>502.2</td>
<td>3.69</td>
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<td>275</td>
<td>507.8</td>
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<td>255</td>
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<tr>
<td>235</td>
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<td>21.5</td>
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<td>195</td>
<td>515.8</td>
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<td>175</td>
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<td>155</td>
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<td>135</td>
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