Highly Fluorescent Pyreno[2,1-b]pyroles: First Syntheses, Crystal Structure, and Intriguing Photophysical Properties

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A series of pyrrole analogues of benzo[a]pyrene have been synthesized in which pyreno[2,1-b]pyrrole exhibits highly fluorescent properties. While these compounds show strong π–π stacking, the π-stacking-induced fluorescence spectral changes lead to future applications such as molecular recognition feasible upon chemical modification.

For further extension of pyrrole systems, heterocyclic pyrrole analogues such as pyreno[2,1-b]furan,16 pyrreno[2,1-b]thiophene,17 pyrreno[2,1-b]pyrrole, CO2H, 4
H
4

Results and Discussion

Pyreno[2,1-b]pyrrole (1) was efficiently prepared by using a Hemetsberger−Knittl reaction19 (Scheme 1) that incorporated a Knoevenagel condensation of pyrene-1-aldehyde A and methyl azidocetate in the presence of

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The oxidative coupling product of cumyl hydroperoxide in the presence of Mo(CO)\textsubscript{6} offered bis(pyrenopyrrole) \(8\) synthesis of pyreno[2,1-\(b\)]pyrrole-7-Sn between solution, giving 2-substituted products. The Stille coupling reaction with electrophiles such as trimethylsilyl chloride, tributyltin chloride, and iodine to afford the corresponding derivative of pyrene-fused pyrene \(2\) was realized with \(7\)-I\(\text{Si} \) and 

\[ \text{Scheme 1}\]

\[ \text{Scheme 2}\]

\( ^a \) Reagents and reaction conditions: (i) \( \text{N}_2\text{CH}_2\text{CO}_2\text{CH}_3, \text{NaOCH}_3, \text{THF}, -15 \text{ to } 0 \text{ °C, 6 h, 87%} \) (ii) \( \text{PhCH}_3, 110 \text{ °C, 4 h, 92%} \) (iii) \( \text{KOH, THF, H}_2\text{O, reflux, 2 h, 97%} \) (iv) \( \text{Cu, quinoline, 220 °C, 2 h, 91%} \) (v) \( \text{LiAlH}_4, \text{THF, 25 °C, 3 h, 96%} \) (vi) \( \text{MnO}_2, \text{C}_6\text{H}_5\text{CO}_2\text{H, 80 °C, 5 h, 78%} \).

sodium methoxide at \(-15 \text{ to } 0 \text{ °C}, \) forming \(B\). Further pyrolysis of \(B\) in toluene afforded the methyl ester derivative of pyrrole-fused pyrene \(2\). Saponification of \(2\) using aqueous KOH in THF gave acid \(3\), which upon decarboxylation by catalysis of copper in redistilled quinoline afforded \(1\). Thus, pyrene-1-aldehyde was obtained by a four-step sequence to give pyreno[2,1-\(b\)]-pyrrole \((1)\) in 71% overall yield. On the other hand, reduction of ester \(2\) with \(\text{LiAlH}_4\) afforded alcohol \(4\), which on oxidation with \(\text{MnO}_2\) yielded aldehyde \(5\). The synthesis of pyreno[2,1-b]pyrroles \(1-5\) was achieved with >80% yield at each step.

The fused-pyrrole ring also exhibits versatile chemistry of indole types.\(^{20}\) Lithiation reactions of the N-Boc derivative of pyrro[2,1-b]pyrrole \(7\) occurred smoothly at \(-78 \text{ °C} \). Thus, \(7\) was lithiated with \(\text{t-BuLi}\) and reacted with electrophiles such as trimethylsilyl chloride, tributyltin chloride, and iodine to afford the corresponding 2-substituted products \(7\)-\(\text{Si}\), \(7\)-\(\text{Sn}\), and \(7\)-\(\i\). The N-Boc group was readily removed by heating \(110 \text{ °C}\) in DMF solution, giving \(\text{6}\) from \(7\). The Stille coupling reaction between \(7\)-\(\text{Sn}\) and \(7\)-\(\i\) also proceeded smoothly by catalysis of palladium under standard conditions,\(^{21}\) yielding bis(pyrro[2,1-b]pyrrole) \(8\) (Scheme 2). Oxidation of \(1\) with cumyl hydroperoxide in the presence of \(\text{Mo(CO)}_6\) offered the oxidative coupling product \(9\) of indigo-type structure.\(^{22}\)

The appearance of characteristic pattern of a pyrrole NH signal, e.g., at \(\delta 8.54\) for \(1\), and other signals in the \(^1\)H NMR spectra are consistent with their assigned structures. Further structural information for \(1\) and \(2\) was rendered by the single-crystal X-ray diffraction analyses. Compound \(1\) in EtOAc solution and compound \(2\) in benzene solution were slowly evaporated to grow the single crystals suitable for X-ray analyses. Compound \(1\) crystallized in an orthorhombic configuration. It is clear that pyrenopyrrole energetically favors an offset parallel \(\pi\) stacking between two proximal molecular planes separated by a distance of 3.46 Å (Figure 1), e.g., the B-ring of one molecule stacking on top of the E-ring of the other molecule (referring structure \(1\) for ring assignments). The intercentroid distance is 3.65 Å, e.g., from the B-ring center of one molecule to the E-ring center of the other parallel molecule. The packing is analogous to that of pyrene,\(^{23}\) which also shows an offset parallel stacking with the hydrogens roughly over ring centers with an interplanar distance of 3.5 Å.

Ester \(2\) crystallizes as a triclinic configuration, which shows a salient dimeric feature due to the formation of dual hydrogen bonds between the pyrrole NH of one molecule and the ester carbonyl group of the other molecule with an NH-...O-C distance of 2.06 Å.

\[ \text{FIGURE 1. Molecular packing diagram of 1 showing } \pi-\pi \text{ interaction with an interplanar distance of 3.46 Å.} \]


Compounds 1–3 were screened for their mutagenic properties relative to benzo[a]pyrene\(^{24}\) to ascertain their toxicity before further studies and were found to be in no way comparable with benzo[a]pyrene.

The detailed photophysical properties of 1–9 are listed in Table 1, while typical absorption and emission spectra in solution and crystal are included in the Supporting Information. The peak wavelength of the lowest \(\pi \rightarrow \pi^*\) absorption for 1–9 shows a significant bathochromic shift of \(>50\) nm with respect to that of pyrene. Table 1 also clearly indicates that C(2) substitution with a carbonyl group decreases the energy gap, whereas N(1) functionalization by Boc results in an opposite trend. Molecular modeling for 1 based on the ZINDO/S method\(^{25}\) (eight occupied and unoccupied molecular levels) gave an allowed singlet HOMO \(\rightarrow\) LUMO excitation (\(\sim 0.78\)), indicating that the breakdown of symmetry from D\(_{2h}\) (pyrene) to C\(_{s}\) (pyrenyl[2,1-b]pyrrole) drastically facilitates the optical transition. The calculated energy gap of 27 778 cm\(^{-1}\) for 1 is qualitatively consistent with the experimental value of 26 455 cm\(^{-1}\). Theoretical approaches also reveal that \(\pi\) electrons are spread over the entire molecular framework for both HOMO and LUMO levels (see the Supporting Information). Thus, a key contribution for the substituent effect is believed to be the modulation of \(\pi\)-electron conjugation, consistent with the experimental results, in which aldehyde 5 has the lowest energy gap among 1–5 due to its greatest tendency of extending the \(\pi\) electron delocalization. Conversely, an electron-withdrawing Boc group at the N(1) position (e.g., 7) localizes the N(1) lone pair electrons and hence increases the energy gap.

All analogues except for 9 exhibit strong fluorescence with quantum efficiency of \(\Phi_1 > 0.27\) in EtOAc or THF. In the cases of 1, 4, and 6, \(\Phi_1\) is even near unity. Unlike the remarkable excimer formation for pyrene in solution,\(^{26}\) the emission spectra of 1–9 turned out to be virtually concentration independent in the range of \(10^{-5}\) to \(10^{-4}\) M. In contrast, the emission resulting from the \(\pi\) stacking is obvious in the solid, as supported by the \(>100\) nm red shift of the peak wavelength (\(\lambda_{\text{max}} \approx 538\) nm) in a single crystal relative to that in solution for 1. The lack of excimer emission for 1 in solution can plausibly be rationalized by the much shorter radiative lifetime of \(<5\) ns, i.e., the more allowed transition, for the pyreno[2,1-b]pyrrole moiety than that for pyrene (<200 ns).\(^{26}\) Therefore, the rate of bimolecular excimer formation is too slow to compete with the intramolecular decay processes. Support of this viewpoint is given by increasing the concentration of 1 up to \(\sim 10^{-3}\) M, the emission of which exhibited a shoulder with a peak wavelength at \(\sim 510\) nm and is tentatively ascribed to the excimer emission (see the Supporting Information). Unfortunately, due to the highly emissive monomer fluorescence in EtOAc as well as in other solvents, further resolution of the excimer emission for compound 1 is not possible at this stage.

Finally, it is noteworthy that 9 is treated as an analogue of indigo with extended \(\pi\) conjugation. The absorption and emission peak maxima were measured to be 687 and 710 nm, respectively, in ethyl acetate, which, to our knowledge, possesses the lowest energy gap among current existing indigo derivatives. The small emission energy gap, along with a relatively low \(\Phi_1\), can be qualitatively explained by the energy gap law pertaining to the radiationless decay, concluding that the radiationless deactivation should increase upon decreasing the energy gap of the transition.\(^{27}\) Nevertheless, 9 is particularly intriguing in the photovoltaic/dye application due to its high extinction coefficients covering the entire visible range.

**Conclusion**

We have developed a new series of pyrrole analogues of benzo[a]pyrene. All monomeric pyreno[2,1-b]pyrrole and derivatives are highly emissive in solution. Despite the strong \(\pi\) stacking interaction, the fluorescence yield in the crystal, e.g., 1, is anomalously high and can be tentatively rationalized by its intact packing structure so that the defective sites are obscure. The difficulty in forming excimer emission in solution for the pyrenyl[2,1-b]pyrrole moiety renders a superiority in developing, e.g., a dual pyreno[2,1-b]pyrrole sensor based on the intramolecular excimer formation upon binding the analytes. In this case, the probe concentrations can be maximized free from the intermolecular excimer perturbation. From this work, we have established structural groundwork to aid in the further design of new materials applicable in various areas such as supramolecular science, optoelectronics, and biological probe.

### Table 1. Photophysical Parameters of Pyreno[2,1-b]pyrroles 1–9

<table>
<thead>
<tr>
<th>compd</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\varepsilon_{\text{max}}) (M(^{-1}) cm(^{-1}))</th>
<th>(\lambda_{\text{em}}) (nm)</th>
<th>(\Phi_1)</th>
<th>lifetime (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>384 (456)(^{c})</td>
<td>37 300</td>
<td>398 (538)(^{c})</td>
<td>0.95 (0.15)(^{d})</td>
<td>2.80 (2.63)(^{c})</td>
</tr>
<tr>
<td>2</td>
<td>400 (458)(^{c})</td>
<td>53 400</td>
<td>404 (590)(^{c})</td>
<td>0.82</td>
<td>2.29 (2.33)(^{c})</td>
</tr>
<tr>
<td>3</td>
<td>398 (493)(^{c})</td>
<td>52 600</td>
<td>404 (594)(^{c})</td>
<td>0.82</td>
<td>2.31 (1.32)(^{c})</td>
</tr>
<tr>
<td>4</td>
<td>388(^{b})</td>
<td>34 800</td>
<td>404(^{b})</td>
<td>0.96</td>
<td>2.64(^{p})</td>
</tr>
<tr>
<td>5</td>
<td>416(^{b})</td>
<td>23 600</td>
<td>438(^{b})</td>
<td>0.61</td>
<td>2.55(^{p})</td>
</tr>
<tr>
<td>6</td>
<td>392(^{b})</td>
<td>24 100</td>
<td>404(^{b})</td>
<td>0.95</td>
<td>2.41(^{p})</td>
</tr>
<tr>
<td>7</td>
<td>371(^{b})</td>
<td>51 300</td>
<td>401(^{b})</td>
<td>0.27</td>
<td>8.29(^{p})</td>
</tr>
<tr>
<td>8</td>
<td>473(^{a})</td>
<td>88 475</td>
<td>482(^{a})</td>
<td>0.50</td>
<td>1.40(^{p})</td>
</tr>
<tr>
<td>9</td>
<td>687(^{a})</td>
<td>11 150</td>
<td>707(^{a})</td>
<td>0.0076(^{f})</td>
<td>0.42(^{a})</td>
</tr>
</tbody>
</table>

\(^{a}\) \(\Phi_1\) calculated relative to coumarins at 298 K for compounds 1–8. \(^{b}\) Data acquired in 1 \(\times 10^{-5}\) M EtOAc. \(^{c}\) Data acquired in crystal.


Experimental Section

Methyl 2-Azido-3-(1-pyrrenyl)propenoate (B). Sodium methoxide (2.16 g, 40 mmol) was taken in a flask fitted with a pressure equalizer. The system was evacuated and kept under argon atmosphere. Methanol (30 mL) was introduced, and the flask was cooled to −15 °C. The pressure equalizer was charged with a THF solution (40 mL) of pyrrole-1-aldehyde (2.3 g, 10 mmol) and methyl azidoacetate (4.6 g, 40 mmol). The mixture was stirred at −15 °C with a magnetic stirrer for 2 h under an argon atmosphere, to a stirred suspension of LiAlH₄ under argon atmosphere. Methanol (30 mL) was introduced, stirred filtered, washed with water, and dried. The reaction mixture was cooled to −15 °C, filtered through a plug of silica gel to give compound B (2.84 g, 87%) which was used for the next step without further purification. ³¹P NMR (CDCl₃, 68 MHz) δ 151.9, 151.7, 132.3, 132.2, 129.7, 129.6, 129.4, 129.2, 128.6, 128.4, 128.3, 126.8, 126.6, 126.0, 125.8, 124.9, 124.7, 124.6, 124.5, 124.4, 122.7, 122.6, 121.0, 53.2; HR-FAB-MS calcd for C₃₉H₃₇NO₅ 327.1013 (M⁺).

Pyreno[2,1-b]pyrrole-2-carboxaldehyde (5). Activated MnO₂ (165 mg, 1.9 mmol) was added to a solution of alcohol 5 (271 mg, 1 mmol) in anhydrous CH₂Cl₂ (100 mL). The mixture was stirred at room temperature for 3 h and filtered through Celite, which was subsequently washed with CH₂Cl₂ (100 mL) followed by THF (100 mL). After removal of the solvents, the addition was purified by column chromatography using EtOAc/hexane (1:3) to yield pure aldehyde 5 (220 mg, 82%). mp 265 °C dec; ¹H NMR (DMSO-d₆, 400 MHz) δ 12.63 (s, 1 H), 10.03 (s, 1H), 9.89 (d, J = 9.2 Hz, 1 H), 8.33–8.38 (m, 2 H), 8.29 (d, J = 8.0 Hz, 1 H), 8.25 (s, 1 H), 8.18 (d, J = 7.2 Hz, 1 H), 8.11 (d, J = 9.2 Hz, 1 H), 7.93–8.01 (m, 2 H); ¹³C NMR (DMSO-d₆, 100 MHz) δ 132.0, 131.0, 130.5, 129.5, 129.4, 128.9, 124.9, 124.3, 124.2, 123.8, 123.6, 123.6, 123.2, 119.8, 107.6, 101.1; HR-FAB-MS calcd for C₂₀H₁₈N₂O₂ 341.1290 (M⁺), found m/z 341.1290 (M⁺).

(2-(Trimethylsilyl)pyrreno[2,1-b]pyrrole (6). Under an argon atmosphere, a solution of 7 (341 mg, 1 mmol) in THF (20 mL) was cooled to −78 °C. To this solution was added tert-butyl lithium (1.1 mmol, 0.7 mL of 1.6 M pentane solution) dropwise. The mixture was stirred for 3 h at −78 °C, and the electrophile of trimethylsilyl chloride (1.2 mmol, 0.15 mL) in THF (10 mL) was added dropwise. After being stirred for 2 h at −78 °C, the reaction mixture was poured into cold water and extracted with EtOAc. The organic phase was dried over Na₂SO₄ and evaporated to dryness. The crude N-[t-butyl-2-(trimethylsilyl)pyrreno[2,1-b]pyrrole (7-5i) was dissolved in DMF (15 mL) and heated at 110 °C for 5 h. The solution was cooled, poured into water, and extracted with EtOAc. The organic layer was washed with water, dried over Na₂SO₄, and concentrated in vacuo. The crude material was purified by column chromatography using EtOAc/hexane (2:8) to afford compound 6 (244 mg, 78%): mp 161–163 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.64 (s, 1 H), 8.59 (d, J = 8.8 Hz, 1 H), 8.20 (d, J = 8.8 Hz, 1 H), 8.16 (d, J = 7.6 Hz, 1 H), 8.13 (s, 1 H), 8.08 (d, J = 7.6 Hz, 1 H), 8.01 (d, J = 8.8 Hz, 1 H), 7.86–7.95 (m, 2 H), 7.54 (d, J = 8.4 Hz, 2 H); ¹³C NMR (CDCl₃, 100 MHz) δ 146.0, 134.8, 134.8, 129.5, 128.6, 127.5, 127.3, 126.8, 125.9, 124.7, 124.4, 124.3, 124.1, 123.1, 122.9, 122.1, 119.9, 118.9, 118.8, 118.5, 118.0, 108.6, 51.9; HR-FAB-MS calcd for C₃₂H₂₄N₂O₃ 509.1691, found m/z 509.1694 (M⁺).
butoxycarbonyl)-2-iodopyrro[2,1-b]pyrrole (7-1, 415 mg, 89%) and N-(tert-butoxycarbonyl)-2-(tributylstannyl)pyrro[2,1-b]pyrrole (7-Sn, 448 mg, 71%). A mixture of 7 (234 mg, 0.5 mmol), 7-Sn (378 mg, 0.6 mmol), and Pd(PPh3)4Cl2 (11 mg, 0.015 mmol, 3 mol %) in DMF (20 mL) was heated at 110 °C. After 5 h, the reaction mixture was cooled and poured into water. The dark green precipitates were collected by filtration, washed with a small amount of EtOAc and 50 mL of water, and then dried in vacuo to yield compound 8 (149 mg, 62%); mp > 340 °C; 1H NMR (DMSO-d6, 400 MHz) δ 12.53 (s, 2 H), 8.66 (d, J = 8.9 Hz, 2 H), 8.37 (s, 2 H), 8.32 (d, J = 8.9 Hz, 2 H), 8.9 Hz, 2.3 Hz, 9 Hz, 2 H), 8.13–8.21 (m, 4 H), 8.04 (s, 2 H), 7.91–7.99 (m, 4 H). 13C NMR (DMSO-d6, 100 MHz) δ 135.5, 133.0, 130.5, 130.3, 128.3, 127.1, 126.9, 125.3, 125.3, 125.0, 124.8, 124.6, 124.1, 123.5, 123.0, 119.6, 108.2, 98.4; HR-FAB-MS calcd for C29H19NO2; 480.1626, found m/z 480.1623 (M+).

**Indigoid Derivative of Pyrro[2,1-b]pyrrole (9).** A mixture of pyrro[2,1-b]pyrrole (205 mg, 0.85 mmol), benzoic acid (10 mg, 0.085 mmol), molybdenum hexacarbonyl (2.3 mg, 0.0085 mmol), and cumyl hydroperoxide (0.46 mL, 3 mmol) in cumene (10 mL) was heated at 110 °C for 5 h. The reaction mixture was cooled, filtered, and washed successfully with cumene and methanol. The black solid was dried in vacuo to yield compound 9 (152.5 mg, 70%), mp > 300 °C. The NMR spectrum was not recorded due to insufficient solubility of 9 in various solvents: FT-IR (KBr) cm⁻¹ 3430, 3045, 1726, 1633, 1587, 1547, 1434, 1129, 1089, 851, 678, 638; HR-FAB-MS calcd for C14H11N2O; 235.0910 (M+).

**Spectroscopic and Dynamic Measurements.** Steady-state absorption and emission spectra were recorded at 298 K. The excitation light source of the fluorimeter has been calibrated by recording the corrected excitation light from the scattered light spectrum of the corrected excitation light. Two different concentrations ranging from 5 × 10⁻³ to 5 × 10⁻² M were measured. Coumarin 102 in ethanol was used as a reference, assuming a yield of 0.93 with a 400-nm excitation, to determine the fluorescence quantum yields of compounds 1–7 in solution. For compound 8, coumarin 480 was used as a reference (λem = 480 nm, Exciton, Inc.), assuming a quantum yield of 0.93 in ethanol.²⁸ 4-(Dicyanomethylene) 2-ethyl-6-p-dimethylaminostyryl) 4H-pyran (CH3Cl2, λem = 615 nm) in methanol was used as a reference for compound 9, assuming a quantum yield of 0.43 with a 400-nm excitation.²⁹

Fluorescence quantum yields were calculated according to the following equation:³⁰

\[ \Phi_{\text{sample}} = \Phi_{\text{std}} \left( \frac{I_{\text{sample}}}{I_{\text{std}}} \right)^{2} \]  

In this equation, \( \Phi_{\text{sample}} \) and \( \Phi_{\text{std}} \) are the quantum yields of sample and standard, respectively; \( I_{\text{sample}} \) and \( I_{\text{std}} \) are the integrated emission intensities of the sample and the standard, respectively; \( n_{\text{sample}} \) and \( n_{\text{std}} \) are the refractive indices of the sample and standard solutions, respectively.

A configuration of front-face excitation was used to measure the emission of the solid sample in which the cell was made by assembling two edge-polished quartz plates with various Teflon spacers. A combination of appropriate filters was used to avoid the interference from the scattering light. An integrating sphere (300 K) was applied to measure the quantum yield in the solid state, in which the solid sample film was prepared via either the spin-coating or vapor-deposition method and was excited by a 365-nm Ar⁺ laser line. The resulting luminescence was acquired by an intensified charge-coupled detector for subsequent quantum yield analyses.

Nonsecond lifetime studies were performed by a photomultiplier system with a hydrogen-filled/for a nitrogen lamp as the excitation source. Data were analyzed using the nonlinear least-squares method in combination with an iterative convolution method. The emission decays were analyzed by the sum of exponential functions, which allows partial removal of the instrument time broadening and consequently renders a temporal resolution of ~200 ps. For dynamic measurements, sample solution was degassed via three freeze–pump–thaw cycles to avoid the oxygen-quenching interference.

**Theoretical Calculation Method.** Vertical transition energies (S₁ – S₀) of compound 1 were obtained by the semiempirical Zerner’s spectroscopic parameterization for intermediate neglect of differential overlap (ZINDO/S) method,²⁵ coupled with a single configuration interaction (SCI) technique, which involved eight occupied and unoccupied molecular levels, corresponding to the first branches of \( \pi \)- and \( \pi^* \)-type molecular orbitals. Hereby, the geometry was optimized with the AM1 (Austin Model 1) method.³¹ All semiempirical AM1 and ZINDO/S calculations were conducted with the HYPERCHEM program.³² As a result, the \( \pi \) electrons are spread over the entire molecular framework for both HOMO and LUMO levels (see the Supporting Information).

**X-ray Analysis.** The crystals were mounted on a glass fiber. Crystal data were collected on a diffractometer installed with monochromatized Mo Kα radiation, λ = 0.71073 Å at T = 295 K. All structures were solved by using the SHELXS-97³³ and refined with SHELXL-97³⁴ by full-matrix least-squares methods on \( F^2 \) values. Hydrogen atoms were fixed at calculated positions and refined using a riding mode.

Crystal data of 1 (from EtOAc): C₂₃H₁₈NO₂, M = 241.3, orthorhombic P2₁2₁2₁, a = 4.4960(2) Å, b = 14.4730(7) Å, c = 16.4550(8) Å, \( \alpha = \beta = \gamma = 90^\circ \), V = 1188.81(9) Å³, Z = 4, Dc = 1.347 g cm⁻³, 7379 reflections collected, unique 2710 (\( R_{\text{int}} = 0.0860 \)), final indices [1 > 2σ(l)], \( R_{1} = 0.0748, wR_{2} = 0.1487 \). Crystal data of 2 (from benzene): C₂₃H₁₇O₂N₂, M = 338.4, triclinic P, a = 8.3820(3) Å, b = 8.7820(3) Å, c = 15.7570(5) Å, α = 94.7160(11)°, β = 96.5930(11)°, γ = 92.2920(11)°, V = 852.39(8) Å³, Z = 2, Dc = 1.318 g cm⁻³, 5876 reflections collected, unique 3786 (\( R_{\text{int}} = 0.0593 \)), final indices [1 > 2σ(l)], \( R_{1} = 0.0646, wR_{2} = 0.1678 \).

**Acknowledgment.** We thank Mr. Yi-Hung Liu (Instrumentation Center, National Taiwan University) for X-ray analyses and the National Science Council for financial support.

**Supporting Information Available:** Absorption, emission, ¹H NMR and ¹³C NMR spectra, theoretical calculation, ORTEP drawings, crystal data, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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30 (a) J. Chem. Soc. 107, 75, 991.