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Pyridine-fused coumarins: a new class of ligands for ruthenium complexes with enhanced spectral absorption

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Abstract

New 2,4-diaryl chromeno[3,4*c*]pyridin-5-ones were prepared starting from β-ketoester, salicylacylaldehydes and 2-acetylpyridine. Some ruthenium(II) complexes using these cyclometallating ligands were also synthesized.

Keywords: coumarins; pyridines; dyes; ruthenium and compounds.

Coumarins are widely used as flash pumpable laser dyes or for photographic purposes because the triplet excited state often occurs in high yield.[1,2] Tridentate ligands such as 2,2′-6′,2′′-terpyridines or cyclometallating analogues such as 6-phenyl-2,2′-bipyridine or 1,3-bis(pyrid-2-yl)benzene are well known for transition metals complexation.[3–7] We have combined them as fused rings with 2,4-diaryl-chromeno[3,4*c*]pyridin-5-ones to obtain ligands which have not been described until now.

The synthesis starts with the condensation of a β-ketoester and a salicylaldehyde to give a 3-aroylcoumarin.[8] Nucleophilic addition of the anion from 2-acetylpyridine with the latter results in the formation of a 1,5-diketone in a Michael type reaction. The resulting diketone is cyclized using ammonium acetate in acetic acid to give the expected ligands and several by-products which have been isolated and characterized in certain cases (Fig. 1).[9]

For example, cyclization of **1** at room temperature did not give the bipyridine but two partially reduced pyridines **2** and **3**, together with a small amount of the retro-Michael product **4** (Fig. 2).

Compound **2** was successfully aromatized using sulfur as oxidant to afford only **5** in moderate yield (Fig. 3).[10]

Ligand **6** was prepared using the same procedure as described in Fig. 2, except for the conditions (boiling acetic acid/acetic anhydride: 5/2), which produced directly 5% of the aromatized product

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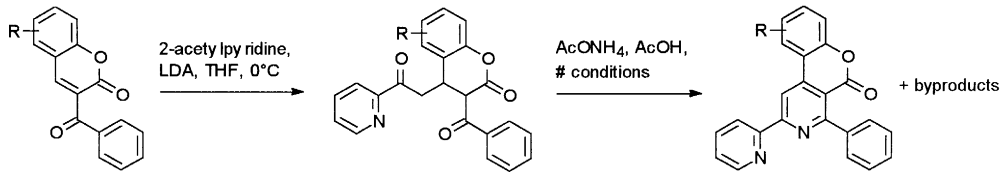


Fig. 1.

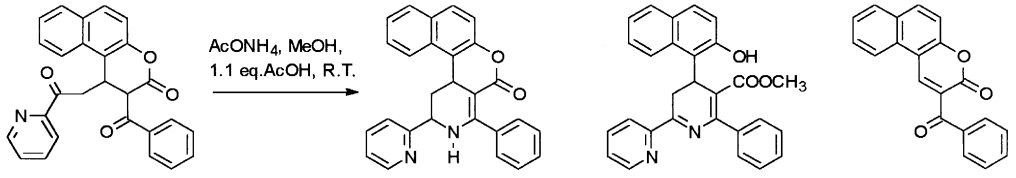


Fig. 2.

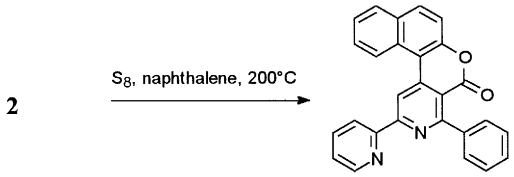
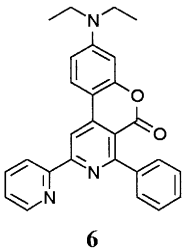


Fig. 3.

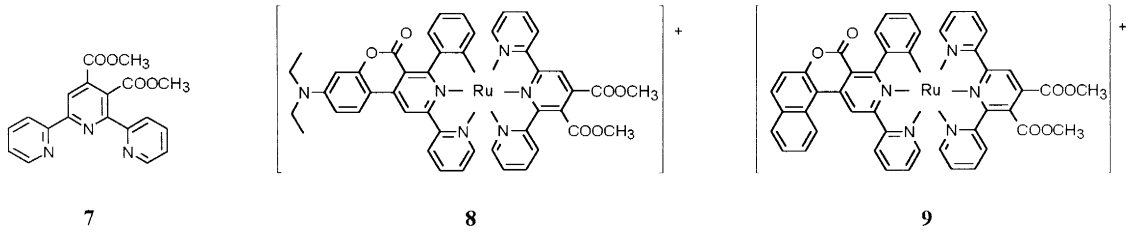
(Scheme 1).[11] This ligand was separated from the reaction mixture by column chromatography. Ligand **7** was prepared by another route.[12]



Scheme 1.

Ruthenium(II) was coordinated by the cyclometallating ligands **5** or **6** and terpyridine **7** carrying methoxycarbonyl groups starting from $RuCl_3 \cdot 3H_2O$ (Scheme 2). The first step was the coordination of one equivalent of ligand **7** with $RuCl_3 \cdot 3H_2O$. Treatment by $AgBF_4$ in acetone followed by addition of the cyclometallating pyridine-fused coumarine **5** or **6** and reflux under argon in DMF in the dark for 5 h afforded the coordination compounds **8** and **9**. The expected complexes were not obtained at lower temperatures. These complexes exhibit strong absorption in the visible spectrum with molar extinction coefficients up to 70 000.[13,14] The ε values are about seven times the coefficients observed for compounds published earlier.[4]

The photophysical and electrochemical properties of these ruthenium(II) complexes are under investi-



7 **8** **9**

Scheme 2.

gation. Preliminary results show intense emission bands for compounds **8** and **9** between 400 to 820 nm at room temperature.

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10. **5**: ^{1}H NMR: δ (ppm) $CDCl_3$ 9.62 (s, 1H), 8.94–8.91 (d, 4.9 Hz, 1H), 8.79–8.76 (ddd, 4.7, 1.7 and 1.0 Hz, 1H), 8.68–8.63 (ddd, 8.0, 1.0 and 1.0 Hz, 1H), 8.04–8.00 (d, 8.8 Hz, 1H), 8.00–7.76 (dd, 8.0 and 1.2 Hz, 1H), 7.90–7.81 (ddd, 8.0, 7.2 and 1.7 Hz, 1H), 7.86–7.77 (dd, 7.9 and 1.5 Hz, 1H), 7.77–7.72 (m, 2H), 7.65–7.58 (ddd, 8.0, 7.1 and 1.0 Hz, 1H), 7.56–7.53 (m, 3H), 7.49–7.45 (d, 8.8 Hz, 1H), 7.43–7.36 (ddd, 7.4, 4.7 and 1.2 Hz, 1H). ^{13}C NMR: δ (ppm) $CDCl_3$ 163.8, 158.7, 157.8, 154.7, 152.0, 149.5, 145.0, 141.0, 137.0, 133.8, 131.4, 129.7, 129.4, 129.4, 128.9, 128.7, 127.8, 125.7, 124.8, 124.8, 122.4, 117.1, 115.5, 114.4, 111.4. EI/MS: 400.3 ($M^{+\cdot}$, 100%), 322.1 ($M-C_5H_5N^+$, 57%), 200 (M^{++}, 29%), 78.1 ($C_5H_5N^+$, 4%). Abs. λ_{max} (nm), [ε (L mol^{-1} cm^{-1})] CH_3CN: 364 (37 620); m.p. 224°C.
11. **6**: ^{1}H NMR: δ (ppm) $CDCl_3$ 8.86 (s, 1H), 8.76–8.75 (dd, 4.3 and 1.5 Hz, 1H), 8.62–8.58 (d, 7.8 Hz, 1H), 8.12–8.08 (d, 9.1 Hz, 1H), 7.87–7.80 (ddd, 7.8, 7.7 and 1.5 Hz, 1H), 7.67–7.63 (m, 2H), 7.50–7.47 (m, 3H), 7.40–7.35 (dd, 7.7 and 4.3 Hz, 1H), 6.70–6.66 (dd, 9.1 and 2.4 Hz, 1H), 6.52–6.51 (d, 2.4 Hz, 1H), 3.49–3.41 (q, 7.0 Hz, 4H), 1.27–1.22 (t, 7.0 Hz, 6H). ^{13}C NMR: δ (ppm) $CDCl_3$ 163.7, 159.7, 157.1, 155.1, 155.0, 151.1, 149.1, 145.5, 141.4, 137.0, 128.9, 128.5, 127.7, 125.5, 124.5, 122.4, 111.7, 109.7, 108.8, 104.7, 97.8, 44.7, 12.5. Abs. λ_{max} (nm), [ε (L mol^{-1} cm^{-1})] CH_3CN: 353 (14 950); 402 (8210); m.p. 180°C.
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13. **8**: ^{1}H NMR: δ (ppm) CD_3CN 9.10 (s, 1H), 8.87 (s, 1H), 8.76–8.72 (d, 8.1 Hz, 1H), 8.61–8.57 (d, 8.1 Hz, 1H), 8.38–8.33 (d, 9.1 Hz, 1H), 8.29–8.25 (dd, 8.4 and 1.0 Hz, 1H), 8.16–8.11 (d, 8.6 Hz, 1H), 7.99–7.90 (ddd, 8.2, 7.6 and 1.4 Hz, 1H), 7.88–7.76 (m, 2H), 7.62–7.58 (d, 5.7 Hz, 1H), 7.53–7.50 (d, 5.7 Hz, 1H), 7.48–7.46 (d, 5.7 Hz, 1H), 7.21–7.09 (m, 3H), 6.97–6.91 (d, 2.5 Hz, 1H), 6.69–6.63 (m, 2H), 6.53–6.45 (ddd, 7.4, 7.4 and 1.5 Hz, 1H), 5.64–5.60 (dd, 7.6 and 1.2 Hz, 1H), 4.20 (s, 3H), 4.10 (s, 3H), 3.63–3.52 (q, 7.0 Hz, 4H), 1.31–1.24 (t, 7.0 Hz, 6H). FAB/MS: (m/z), 1016.3 ($[M]^+$, 3%), 871.4 ($[M-PF_6]^+$, 100%), 841.3 ($[M-PF_6-C_2H_4]^+$, diacid, 7%), 823.1 ($[M-PF_6-C_2H_6O]^+$, anhydride, 8%), 813.3 ($[M-PF_6-CO_2CH_3]^+$, 11%), 754.2 ($[M-PF_6-2CO_2CH_3]^+$, 5%), 521.9 ($[M-(32)]^+$, 8%), 436.1 ($[M]^{2+}$, 10%). Abs. λ_{max} (nm), [ε (L mol^{-1} cm^{-1})] CH_3CN: 368 (72 810); 435 (70 070); 523 (70 990).
14. **9**: ^{1}H NMR: δ (ppm) CD_3CN 9.37 (s, 1H), 9.12 (s, 1H), 9.07–9.04 (d, 8.6 Hz, 1H), 8.69–8.66 (d, 8.3 Hz, 1H), 8.61–8.58 (d, 8.2 Hz, 1H), 8.41–8.38 (d, 7.4 Hz, 1H), 8.27–8.24 (d, 9.0 Hz, 1H), 8.19–8.16 (d, 8.8 Hz, 1H), 8.16–8.12 (d, 8.9 Hz, 1H), 7.97–7.72 (m, 5H), 7.69–7.65 (d, 8.9 Hz, 1H), 7.62–7.60 (d, 5.3 Hz, 1H), 7.57–7.54 (d, 6.2 Hz, 1H), 7.54–7.52 (d, 6.5 Hz, 1H), 7.22–7.11 (m, 3H), 6.76–6.69 (dd, 7.6 and 7.6 Hz, 1H), 6.57–6.51 (dd, 7.4 and 7.2 Hz, 1H), 5.72–5.69 (d, 6.9 Hz, 1H), 4.19 (s, 3H), 4.09 (s, 3H). FAB/MS: (m/z), 850.3 ($[M-PF_6]^+$, 100%), 822.3 ($[M-PF_6-C_2H_4]^+$, diacid, 5%), 733.3 ($[M-PF_6-2CO_2CH_3]^+$, 4%). Abs. λ_{max} (nm), [ε (L mol^{-1} cm^{-1})] CH_3CN: 391 (49 150); 515 (71 000).