Supporting Information

Exploring photophysical properties of new Boron and Palladium(II) complexes with β-diketone pyridine type ligands: From liquid crystals to metal fluorescence probes

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Compounds 1-(2-pyridyl)-3-(4-n-alkyloxyphenyl)propane-1,3-dione [HLR(n)py] (R = C₆H₄OC₇H₂n+1, n = 12 (1), 14 (2)) and 2-[3-(4-n-alkyloxyphenyl)propane-1,3-dion-1-yl]pyridinium chloride [HLR(n)pyH]Cl (R = C₆H₄OC₇H₂n+1, n = 12 (3), 14 (4)).

[HLR(12)py] (1): yellow solid (85 %). Elemental analysis: Found: C, 75.9; H, 8.6; N, 3.5. C₂₆H₃₅NO₃ requires C, 76.2; H, 8.6; N, 3.4%.

ν_max(KBr)/cm⁻¹ 3389w (OH), 1602vs (C═O) + (C═C) and 785 m γ(CH)py.

δ_H (300 MHz, CDCl3, Me₄Si) 0.88 (t, J 6.6, CH₃), 1.27 (m, CH₂), 1.81 (m, CH₂), 4.04 (t, J 6.5, OCH₂), 4.80 (s, C(2)H₂), 6.96 (d, J 8.8, Hₘ), 7.45 (m, H₅), 7.55 (s, C(2)H), 7.89 (m, H₄), 8.06 (d, J 8.8, H₀), 8.16 (d, J 6.0, H₃), 8.72 (d, J 4.4, H₆), 15.32 (s, OH).

[HLR(14)py] (2): yellow solid (86 %). Elemental analyses: Found: C, 76.4; H, 8.9; N, 3.3%. C₂₈H₄₀NO₃ requires C, 76.8; H, 9.0; N, 3.2%.

ν_max(KBr)/cm⁻¹ 3390w (OH), 1602vs (C═O) + (C═C) and 787 m γ(CH)py.

δ_H (300 MHz, CDCl3, Me₄Si) 0.88 (t, J 6.6, CH₃), 1.27 (m, CH₂), 1.81 (m, CH₂), 4.05 (t, J 6.5, OCH₂), 4.80 (s, C(2)H₂), 6.97 (d, J 8.9, Hₘ), 7.45 (m, H₅), 7.55 (s, C(2)H), 7.89 (m, H₄), 8.06 (d, J 8.8, H₀), 8.16 (d, J 6.0, H₃), 8.72 (d, J 4.4, H₆), 15.32 (s, OH).

[HLR(12)pyH]Cl (3): yellow solid (88 %). Elemental analyses: Found: C, 70.2; H, 8.5; N, 3.2%. C₂₆H₃₆NO₃Cl requires C, 70.0; H, 8.1; N, 3.1%.

ν_max(KBr)/cm⁻¹ 3343vw (NH), 1605s, 1580s, 1510s (C═O) + (C═C) and 782 m γ(CH)py.

δ_H (300 MHz, CDCl3, Me₄Si) 0.88 (t, J 6.8, CH₃), 1.27 (m, CH₂), 1.84 (m, CH₂), 4.09 (t, J 6.6, OCH₂), 7.03 (d, J 9.0, Hₘ), 8.01 (m, H₅), 8.39 (d, J 9.0, H₀), 8.48 (s, C(2)H), 8.56 (m, H₃, H₄), 8.99 (d, J 4.9, H₆), 15.37 (s, OH).

[HLR(14)pyH]Cl (4): yellow solid (89 %). Elemental analyses: Found: C, 70.7; H, 8.3; N, 3.0%. C₂₈H₄₀NO₃Cl requires C, 70.9; H, 8.5; N, 2.9%.

ν_max(KBr)/cm⁻¹ 3375w (NH), 1600s, 1536s, 1465s (C═O) + (C═C) and 785 m γ(CH)py.

δ_H (300 MHz, CDCl3, Me₄Si) 0.88 (t, J 6.8, CH₃), 1.26 (m, CH₂), 1.81 (m, CH₂), 4.04 (t, J 6.5, OCH₂), 7.03 (d, J 8.8, Hₘ), 8.01 (m, H₅), 8.39 (d, J 8.8, H₀), 8.48 (s, C(2)H), 8.56 (m, H₃, H₄), 8.99 (d, J 4.5, H₆), 15.41 (s, OH).

Complexes [Pd(η³-C₃H₅)(HLR(14)py)][PF₆] (7) and [Pd(η³-C₃H₅)(L₆(R₁⁴pyH))[PF₆] (8).

To a solution of [Pd(μ-Cl)(η³-C₃H₅)]₂ (100 mg, 0.273 mmol) in dry acetone (25 mL) was added AgPF₆ (138.1 mg, 0.546 mmol) under nitrogen atmosphere. The mixture was stirred overnight in the absence of light and then filtered over Celite. The corresponding [HLR(14)py] or [HLR(14)pyH]Cl (0.546 mmol) in dichloromethane (20 mL) was added to
the resulting solution and let stirring overnight at room temperature. Then the solvent was removed in vacuo and the solid recrystallized in dichloromethane/hexane leading to the precipitation of a yellow solid, which was filtered off, washed with hexane and dried in vacuo.

\[\text{[Pd(} \eta^3-\text{C}_3\text{H}_5)(\text{HL}^{\text{R(14)}\text{py}})\text{][PF}_6] \] (7): yellow solid (66 %). Elemental analyses: Found: C, 51.4; H, 5.9; N, 2.1. \( \text{C}_{31}\text{H}_{44}\text{NO}_3\text{PdPF}_6 \) requires C, 51.0; H, 6.1; N, 1.9%. \( \nu_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3410w (OH), 1600s (C=O) + (C=), 780m \( \gamma \)(CH)py, 842 \( \nu \)(P– F), 558 \( \gamma \)(F–P–F). \( \delta \)H (300 MHz, CDCl3, Me4Si) 0.88 (t, \( J \) 6.9, CH3), 1.26 (m, CH2), 1.82 (m, CH2), 3.41 (d, \( J \) 12.4, H_anti), 4.07 (t, \( J \) 6.5, OCH2), 4.39 (br, H_syn), 5.83 (m, H_meso), 7.05 (d, \( J \) 9.0, H_m), 7.34 (s, C(2)H), 7.71 (m, H5), 8.22 (d, \( J \) 9.0, H_o), 8.28 (m, H4), 8.71 (d, \( J \) 8.4, H3), 8.72 (d, \( J \) 4.8, H6).

\[\text{[Pd(} \eta^3-\text{C}_3\text{H}_5)(\text{LR}^{\text{R(14)}\text{pyH}})\text{][PF}_6] \] (8): yellow solid (55 %). Elemental analyses: Found: C, 51.4; H, 5.8; N, 2.0. \( \text{C}_{31}\text{H}_{44}\text{NO}_3\text{PdPF}_6 \) requires C, 51.0; H, 6.1; N, 1.9%. \( \nu_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3549w, 3487w, 3415s (NH), 1602vs (C=O) + (C=C), 783m \( \gamma \)(CH)py, 844 \( \nu \)(P– F), 558 \( \gamma \)(F–P–F). \( \delta \)H (300 MHz, CDCl3, Me4Si) 0.89 (t, \( J \) 6.9, CH3), 1.28 (m, CH2), 1.81 (m, CH2), 3.38 (d, \( J \) 12.5, H_anti), 4.07 (t, \( J \) 6.5, OCH2), 4.36 (d, \( J \) 7.1, H_syn), 5.80 (m, H_meso), 7.05 (d, \( J \) 9.0, H_m), 7.39 (s, C(2)H), 7.71 (m, H5), 8.22 (d, \( J \) 9.0, H_o), 8.26 (m, H4), 8.65 (d, \( J \) 8.6, H3), 8.75 (d, \( J \) 3.8, H6).

Fig. S1 Absorption and fluorescence emission in dichloromethane solution of the compound [HL^{2R(4)}].
Fig. S2 (a) Absorption and (b) normalized fluorescence emission titration spectra of compound 5 in freshly dichloromethane solution in the presence of increased amounts of Zn\(^{2+}\) (\(\lambda_{ex} = 404 \text{ nm} \)); Room Temperature.