

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 [$\text{HL}^{\text{R(n)py}}$] ($\text{R} = \text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $n = 12$ (1), 14 (2)) and 2-[3-(4-n-alkyloxyphenyl)propane-1,3-dione-1-yl]pyridinium chloride [$\text{HL}^{\text{R(n)pyH}}\text{Cl}$] ($\text{R} = \text{C}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}$, $n = 12$ (3), 14 (4)).

[$\text{HL}^{\text{R(12)py}}$] (1): yellow solid (85 %). Elemental analysis: Found: C, 75.9; H, 8.6; N, 3.5. $\text{C}_{26}\text{H}_{35}\text{NO}_3$ requires C, 76.2; H, 8.6; N, 3.4%. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3389w (OH), 1602vs (C=O) + (C=C) and 785 m $\gamma(\text{CH})\text{py}$. δ_{H} (300 MHz, CDCl_3 , Me_4Si) 0.88 (t, J 6.6, CH_3), 1.27 (m, CH_2), 1.81 (m, CH_2), 4.04 (t, J 6.5, OCH_2), 4.80 (s, $\text{C}(2)\text{H}_2$), 6.96 (d, J 8.8, H_m), 7.45 (m, H_5), 7.55 (s, $\text{C}(2)\text{H}$), 7.89 (m, H_4), 8.06 (d, J 8.8, H_o), 8.16 (d, J 6.0, H_3), 8.72 (d, J 4.4, H_6), 15.32 (s, OH).

[$\text{HL}^{\text{R(14)py}}$] (2): yellow solid (86 %). Elemental analyses: Found: C, 76.4; H, 8.9; N, 3.3%. $\text{C}_{28}\text{H}_{39}\text{NO}_3$ requires C, 76.8; H, 9.0; N, 3.2%. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3390w (OH), 1602vs (C=O) + (C=C) and 787 m $\gamma(\text{CH})\text{py}$. δ_{H} (300 MHz, CDCl_3 , Me_4Si) 0.88 (t, J 6.6, CH_3), 1.27 (m, CH_2), 1.81 (m, CH_2), 4.05 (t, J 6.5, OCH_2), 4.80 (s, $\text{C}(2)\text{H}_2$), 6.97 (d, J 8.9, H_m), 7.45 (m, H_5), 7.55 (s, $\text{C}(2)\text{H}$), 7.89 (m, H_4), 8.06 (d, J 8.9, H_o), 8.16 (d, J 6.0, H_3), 8.72 (d, J 4.4, H_6), 15.30 (s, OH).

[$\text{HL}^{\text{R(12)pyH}}\text{Cl}$] (3): yellow solid (88 %). Elemental analyses: Found: C, 70.2; H, 8.5; N, 3.2. $\text{C}_{26}\text{H}_{36}\text{NO}_3\text{Cl}$ requires C, 70.0; H, 8.1; N, 3.1%. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3343vw (NH), 1605s, 1580s, 1510s (C=O) + (C=C) and 782 m $\gamma(\text{CH})\text{py}$. δ_{H} (300 MHz, CDCl_3 , Me_4Si) 0.88 (t, J 6.8, CH_3), 1.27 (m, CH_2), 1.84 (m, CH_2), 4.09 (t, J 6.6, OCH_2), 7.03 (d, J 9.0, H_m), 8.01 (m, H_5), 8.39 (d, J 9.0, H_o), 8.48 (s, $\text{C}(2)\text{H}$), 8.56 (m, H_3 , H_4), 8.99 (d, J 4.9, H_6), 15.37 (s, OH).

[$\text{HL}^{\text{R(14)pyH}}\text{Cl}$] (4): yellow solid (89 %). Elemental analyses: Found: C, 70.7; H, 8.3; N, 3.0. $\text{C}_{28}\text{H}_{40}\text{NO}_3\text{Cl}$ requires C, 70.9; H, 8.5; N, 2.9%. $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3375w (NH), 1600s, 1536s, 1465s (C=O) + (C=C) and 785 m $\gamma(\text{CH})\text{py}$. δ_{H} (300 MHz, CDCl_3 , Me_4Si) 0.88 (t, J 6.8, CH_3), 1.26 (m, CH_2), 1.81 (m, CH_2), 4.04 (t, J 6.5, OCH_2), 7.03 (d, J 8.8, H_m), 8.01 (m, H_5), 8.39 (d, J 8.8, H_o), 8.48 (s, $\text{C}(2)\text{H}$), 8.56 (m, H_3 , H_4), 8.99 (d, J 4.5, H_6), 15.41 (s, OH).

Complexes [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{HL}^{\text{R(14)py}})]\text{[PF}_6\text{]}$ (7) and [$\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\text{L}^{\text{R(14)pyH}})]\text{[PF}_6\text{]}$ (8).

To a solution of [$\text{Pd}(\mu\text{-Cl})(\eta^3\text{-C}_3\text{H}_5)_2$] (100 mg, 0.273 mmol) in dry acetone (25 mL) was added AgPF_6 (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 [$\text{HL}^{\text{R(14)py}}$] or [$\text{HL}^{\text{R(14)pyH}}\text{Cl}$] (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.

[Pd(η^3 -C₃H₅)(HL^{R(14)py})](PF₆) (7): yellow solid (66 %). Elemental analyses: Found: C, 51.4; H, 5.9; N, 2.1. C₃₁H₄₄NO₃PdPF₆ requires C, 51.0; H, 6.1; N, 1.9%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3410w (OH), 1600s (C=O) + (C=C), 780m $\gamma(\text{CH})\text{py}$, 842 $\nu(\text{P}-\text{F})$, 558 $\gamma(\text{F}-\text{P}-\text{F})$. δ_{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).

[Pd(η^3 -C₃H₅)(L^{R(14)pyH})](PF₆) (8): yellow solid (55 %). Elemental analyses: Found: C, 51.4; H, 5.8; N, 2.0. C₃₁H₄₄NO₃PdPF₆ requires C, 51.0; H, 6.1; N, 1.9%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3549w, 3487w, 3415s (NH), 1602vs (C=O) + (C=C), 783m $\gamma(\text{CH})\text{py}$, 844 $\nu(\text{P}-\text{F})$, 558 $\gamma(\text{F}-\text{P}-\text{F})$. δ_{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).

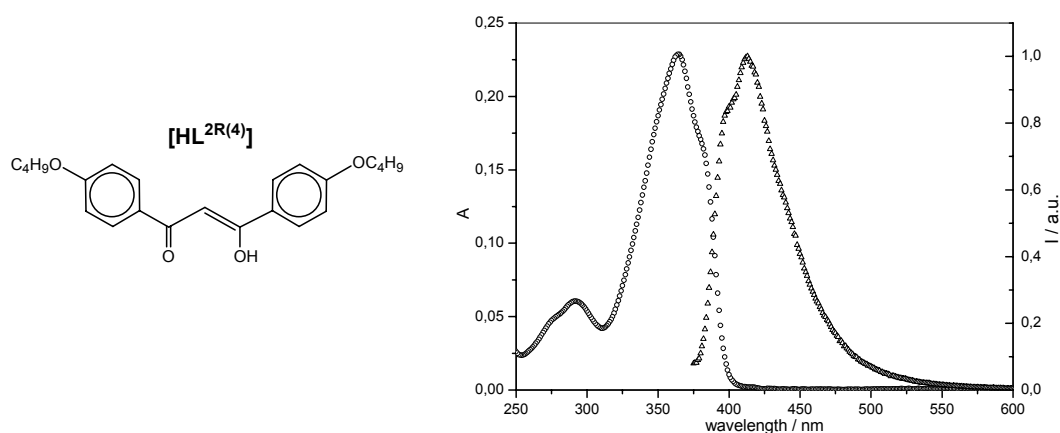


Fig. S1 Absorption and fluorescence emission in dichloromethane solution of the compound [HL^{2R(4)}]

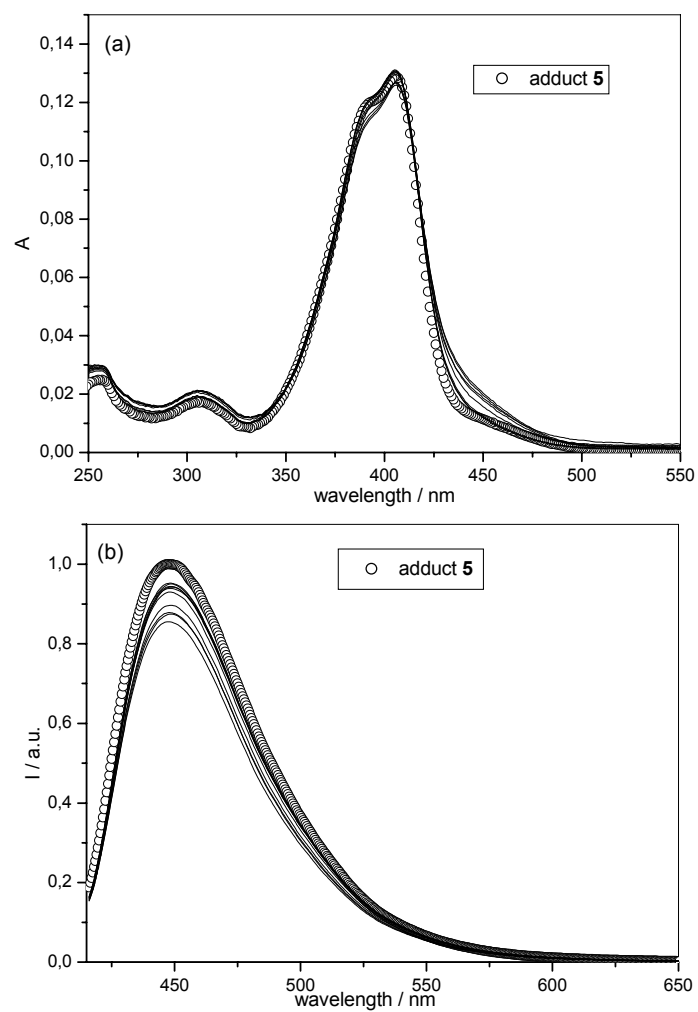


Fig. S2 (a) Absorption and (b) normalized fluorescence emission titration spectra of compound **5** in freshly dichloromethane solution in the presence of increased amounts of Zn²⁺ ($\lambda_{\text{ex}} = 404$ nm; Room Temperature).