Electronic Supplementary Information

Photoinduced hydrogen evolution with new tetradentate cobalt(II) complexes based on the TPMA ligand.

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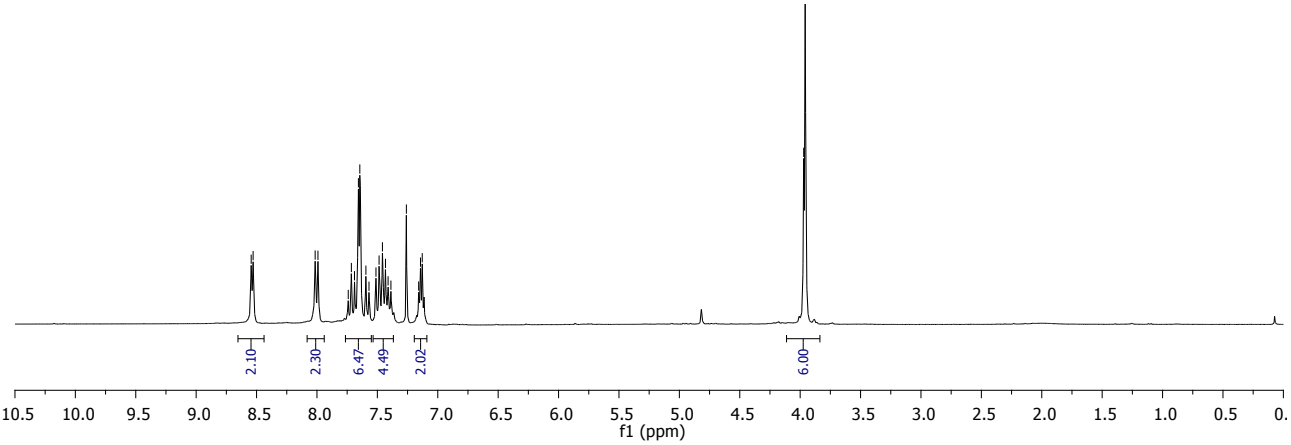
Characterization of the ligands

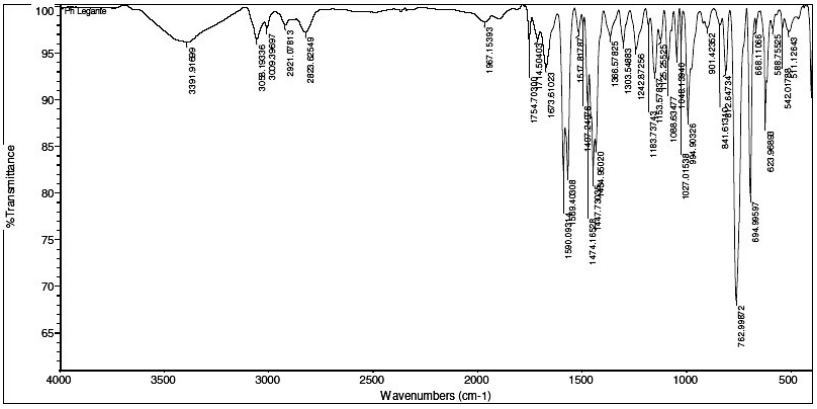
L0: (6-phenyl-2-pyridylmethyl)bis(2-pyridylmethyl)-amine

The final yield was 97%. ^{1}H-NMR, ^{13}C-NMR and ESI-MS are according to data reported in the literature (see C. L. Chuang, K. Lim, J. W. Canary, *Supramol. Chem.* **1995**, *5*, 39-43).

^{1}H-NMR (300 MHz, CD_3Cl,)



IR (KBr, cm^{-1})



L1: [6-(3-formylphenyl)-2-pyridylmethyl]bis(2-pyridylmethyl)-amine

The compound was obtained as a brownish oil (97% yield). ^{1}H-NMR, ^{13}C-NMR and ESI-MS are according to data reported in the literature (see F. A. Scaramuzzo, G. Licini, C. Zonta, *Chem. Eur. J.* **2013**, *19*, 16809-16813).

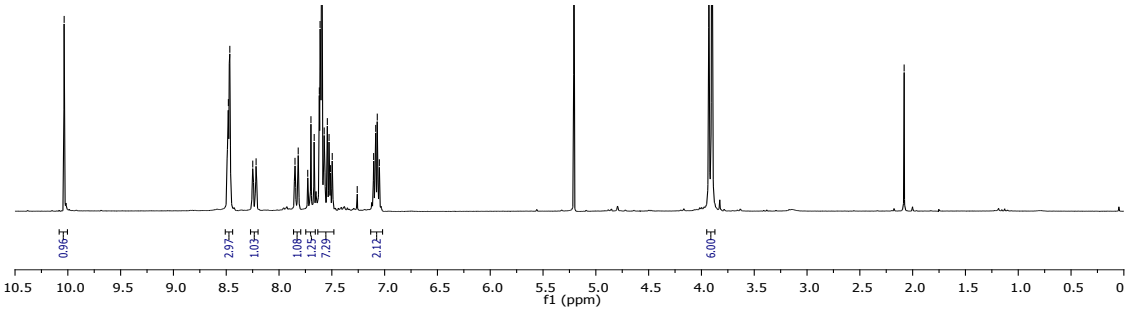
^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 10.03 (s, 1H, CHO), 8.47 (m, 3H, PyrH + ArH), 8.23 (d, 1H, *J* = 9.0 Hz, Ar H), 7.83 (d, 1H, *J* = 9.0 Hz, Ar H), 7.61 (m, 8H, Pyr H + Ar H), 7.08 (dd, 2H, *J* = 6.0 Hz Pyr H), 3.93 (s, 2H, CH_2), 3.90 (s, 4H, CH_2).

^{13}C-NMR (62 MHz, $CDCl_3$) δ (ppm): 191.96, 159.11, 159.04, 154.58, 148.71, 139.95, 137.05, 136.44, 136.18, 132.39, 129.39, 129.07, 127.95, 122.60, 121.73, 121.65, 118.37, 59.88, 59.73.

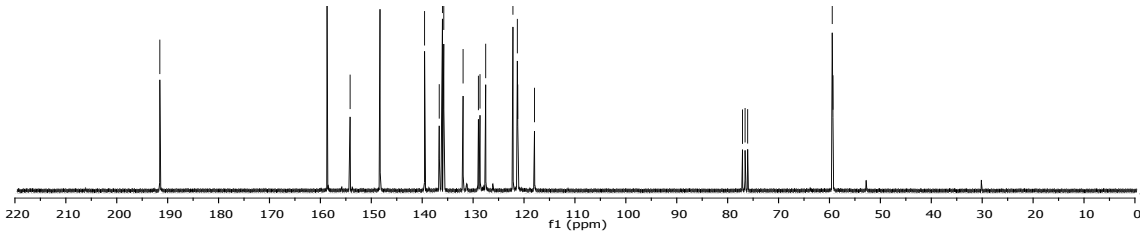
IR (KBr, cm^{-1}): 3384, 2824, 1698, 1580, 1570, 1474, 1434, 1184.

ESI + MS (m/z) Calc. $C_{25}H_{22}N_4O$ 394.2, Found 395.4 ($M+H^+$).

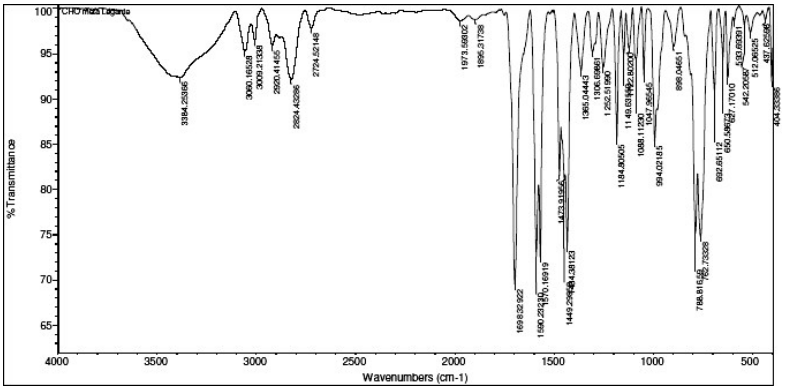
^{1}H-NMR (300 MHz, CD_3Cl,)



^{13}C-NMR (62 MHz, $CDCl_3$)



IR (KBr, cm^{-1})



L2:[6-(3-carboxyaminophenyl)-2-pyridylmethyl)bis(2-pyridylmethyl)-amine

The final product is a yellow solid and the yield was 87%.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.71 (s, 1H, ArH), 8.53 (d, 2H, PyrH, J = 2.5Hz), 8.08 (d, 1H, ArH), 7.96 (d, 1H, ArH), 7.66 (m, 7H), 7.39 (d, 1H),7.15 (dd, 2H, PyrH),3.98 (s, 6H, CH_2).

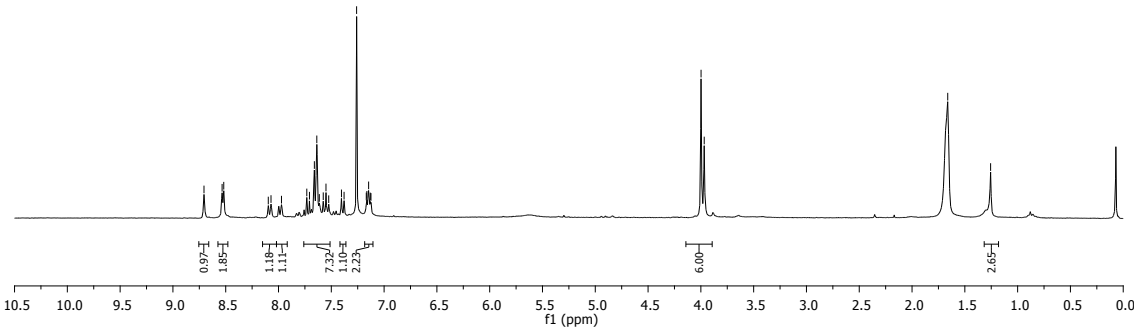
^{13}C-NMR (62 MHz, $CDCl_3$) δ (ppm): 169.30, 159.67, 158.74, 155.70, 149.18, 139.62, 137.47, 136.65, 133.94, 129.97, 129.14, 128.54, 126.39, 123.25, 122.39, 122.24, 118.79, 60.27, 59.48.

IR (KBr, cm^{-1}): 3359, 2821, 1667, 1591, 1570, 1433, 1381, 1121.

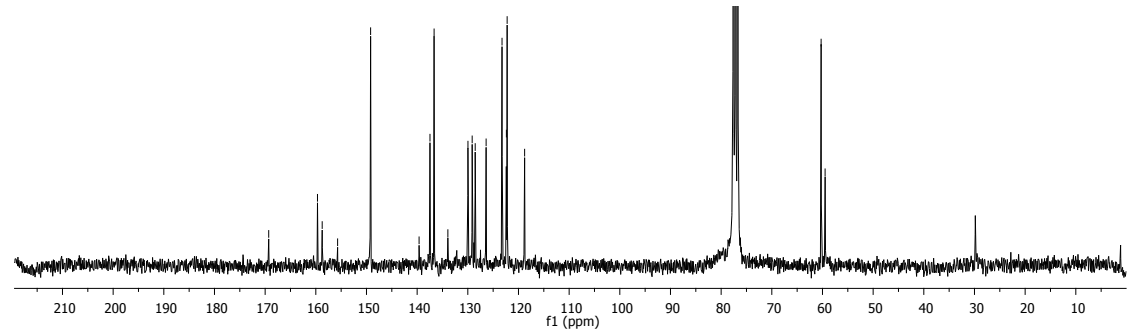
ESI+ MS (m/z) Calc. $C_{25}H_{23}N_5O$ 409.2, Found 410.1 ($M+H^+$).

Anal. Calcd. ($C_{25}H_{23}N_5O + H_2O$): C, 70.24; H, 5.89; N, 16.38. **Found:** C, 70.92; H, 6.02; N, 16.54.

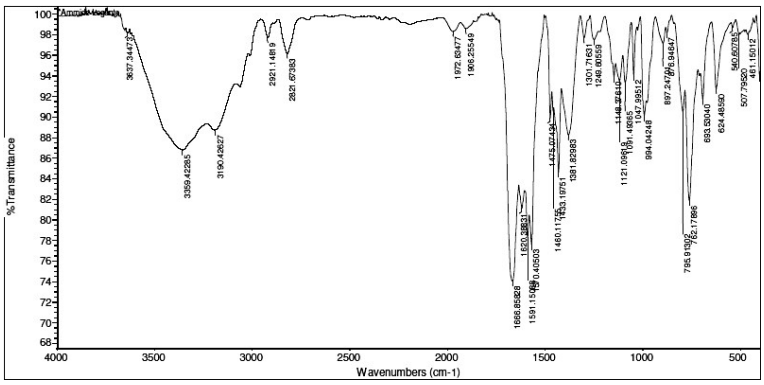
^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (62 MHz, $CDCl_3$)



IR (KBr, cm^{-1})



L3:[6-(3-hydroxyphenyl)-2-pyridylmethyl)bis(2-pyridylmethyl)-amine

The product is a brownish solid and the final yield was 80%.

^{1}H-NMR (300 MHz, CD_3CN) δ (ppm): 8.58 (d, 2H, *J* = 4.24 Hz, PyrH), 7.75-7.43 (m, 9H, PyrH + ArH), 7.12-7.40 (m, 3H, PyrH + ArH), 6.94(d, 1H, *J* = 7.1 Hz), 3.82 (s, 2H, CH_2), 3.84 (s, 4H, CH_2).

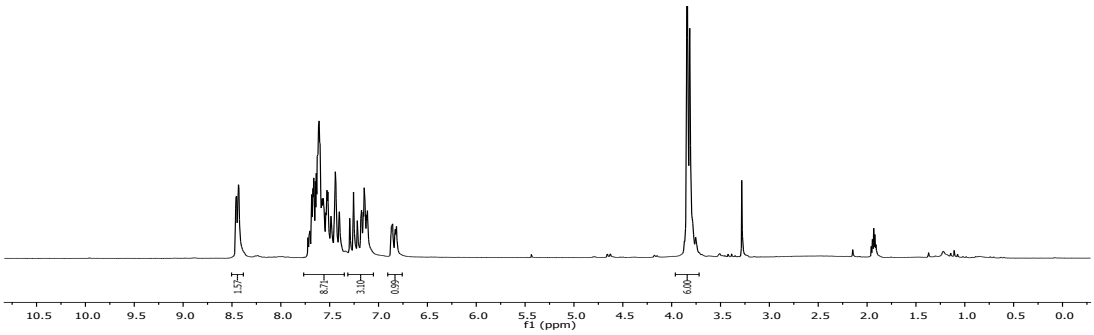
^{13}C-NMR (62 MHz, CD_3CN) δ (ppm): 159.76, 159.33, 157.82, 156.03, 148.98, 141.02, 137.48, 136.72, 129.98, 123.17, 122.72, 122.30, 121.76, 117.52, 116.16, 113.84, 60.18.

IR (KBr, cm^{-1}): 3393, 3055, 2918, 1569, 1449, 1436, 1308, 1245, 1151, 1121, 1083, 1048.

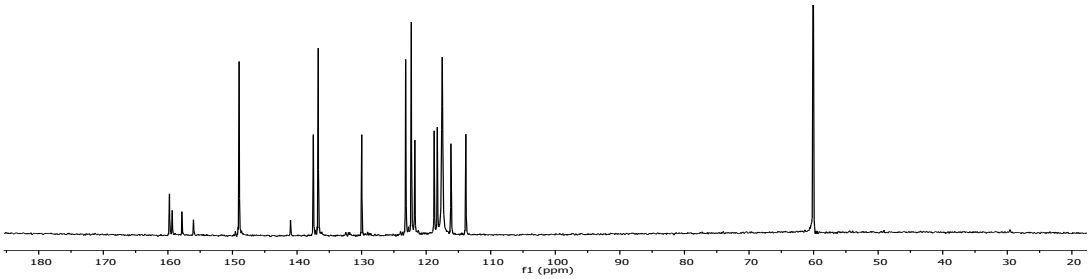
ESI+ MS (m/z) Calc. $C_{24}H_{22}N_4O$ 382.4, Found 383.5 ($M+H^+$).

Anal. Calcd. ($C_{24}H_{22}N_4O$): C, 75.70; H, 5.80; N, 14.65. **Found:** C, 75.32; H, 5.65; N, 14.33.

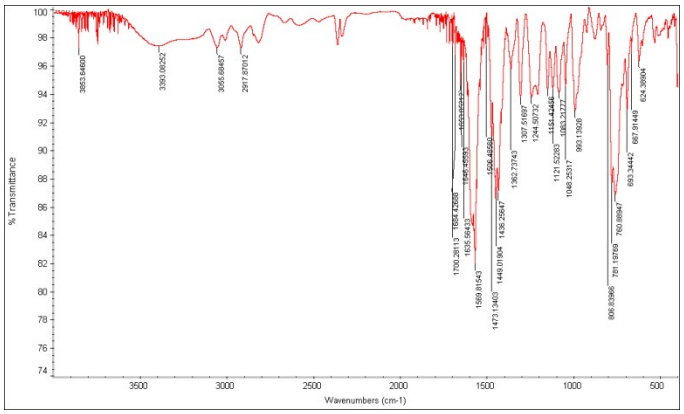
^{1}H-NMR (300 MHz, CD_3CN)



^{13}C-NMR (62 MHz, CD_3CN)



IR (KBr, cm^{-1})



L4:[6-(3-hydroxymethylphenyl)-2-pyridylmethyl)bis(2-pyridylmethyl)-amine

The product is a brownish solid and the final yield was 90%.

^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.54 (d, 2H, PyrH), 8.06 (s, 1H, ArH), 7.90 (d, 1H, ArH), 7.62 (m, 6H), 7.45 (m, 3H),7.15 (dd, 2H, PyrH), 4.78 (s, 2H, CH_2OH), 3.96 (s, 6H, CH_2).

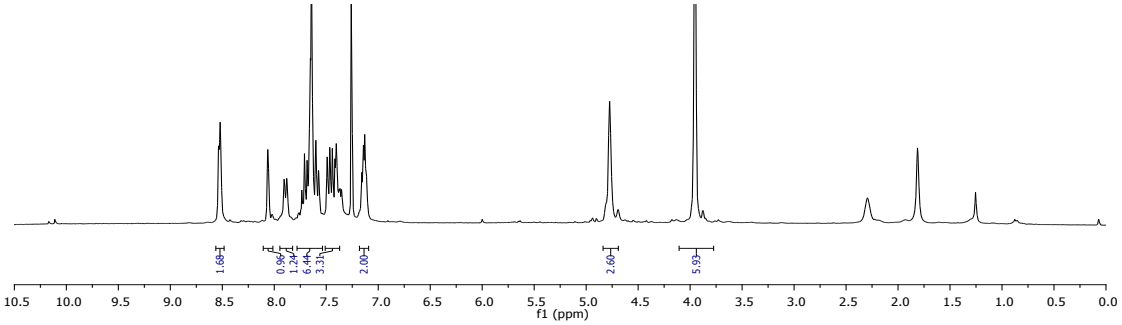
^{13}C-NMR (62 MHz, $CDCl_3$) δ (ppm): 159.77, 159.27, 156.59, 149.22, 141.70, 137.25, 136.57, 129.02, 127.52, 126.23, 125.77, 123.06, 122.11, 121.50, 118.85, 65.46, 60.36, 60.20.

IR (KBr, cm^{-1}): 3411, 2921, 2850, 1592, 1570, 1449, 1434, 1123, 1048.

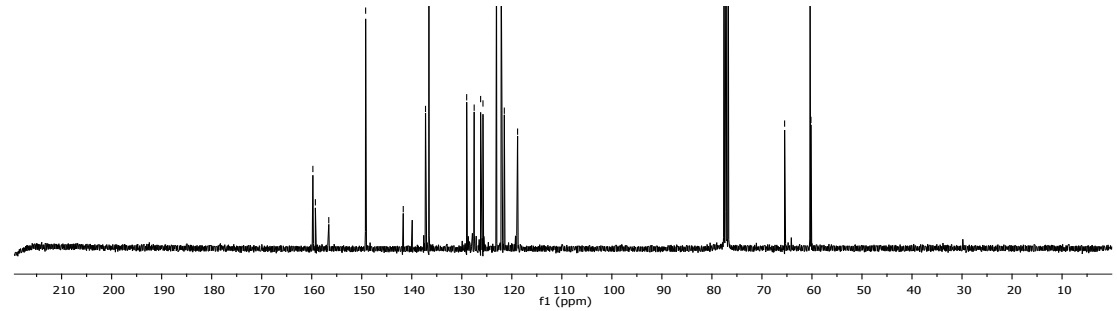
ESI+ MS (m/z) Calc. $C_{25}H_{24}N_4O$ 396.2, Found 397.2 ($M+H^+$).

Anal. Calcd. ($C_{25}H_{24}N_4O + H_2O$): C, 72.44; H, 6.32; N, 13.52. **Found:** C, 72.57; H, 6.41; N, 13.58.

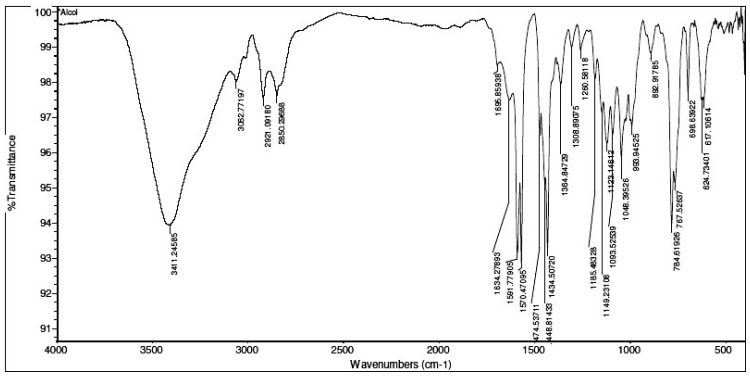
^{1}H-NMR (300 MHz, $CDCl_3$)



^{13}C-NMR (62 MHz, $CDCl_3$)



IR (KBr, cm^{-1})



Characterization of the complexes

CoL0: (6-phenyl-2-pyridylmethyl)bis(2-pyridylmethyl)-amine Cobalt complex

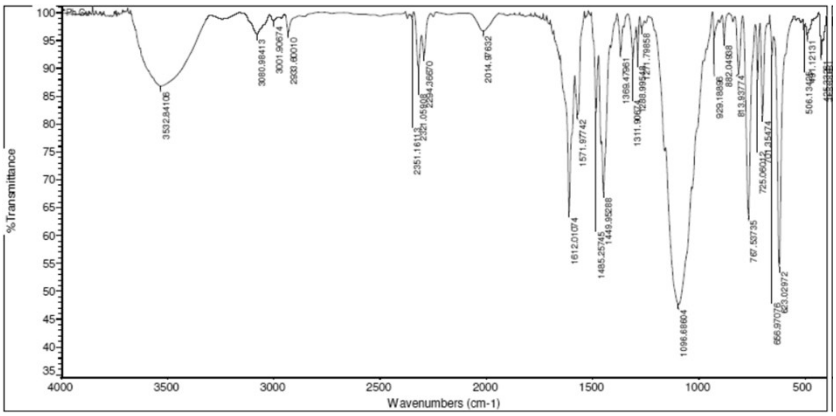
The product is a green solid and the final yield was 84%.

IR (KBr, cm^{-1}): 3523, 3081, 1612, 1572, 1485, 1450, 1096.

ESI+ MS(m/z): Calc. $C_{24}H_{22}N_4Co$ 425.11, Found 212.5 ($M^{2+}/2$).

Anal. Calcd. ($C_{24}H_{22}Cl_2N_4O_8Co$): C, 46.17; H, 3.55; N, 8.97. **Found:** C, 45.98; H, 3.49; N, 8.12.

IR (KBr, cm^{-1})



CoL1: [6-(3-formylphenyl)-2-pyridylmethyl]bis(2-pyridylmethyl)-amine Cobalt complex

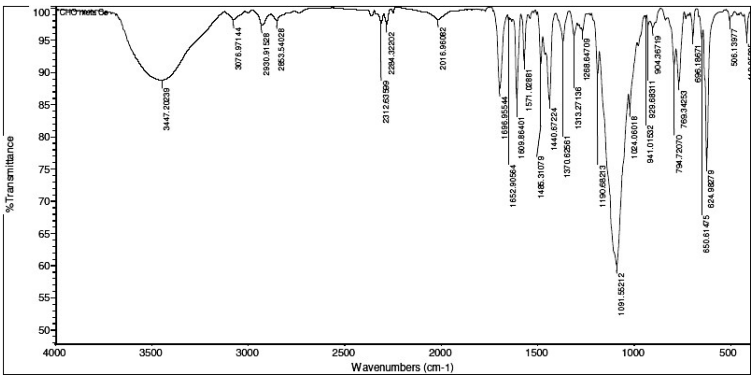
The product is a red-brownish solid and the final yield was 80%.

IR (KBr, cm^{-1}): 3447, 1697, 1610, 1571, 1441, 1092.

ESI+ MS(m/z): Calc. $C_{25}H_{22}N_4OCo$ 453.4, Found 226.5 ($M^{2+}/2$).

Anal. Calcd. ($C_{25}H_{22}Cl_2N_4O_9Co$): C, 46.03; H, 3.40; N, 8.59. **Found:** C, 45.88; H, 3.21; N, 8.46.

IR (KBr, cm^{-1})



CoL2: 6-(3-carboxyaminophenyl)-2-pyridylmethyl)bis(2-pyridylmethyl)-amine Cobalt complex

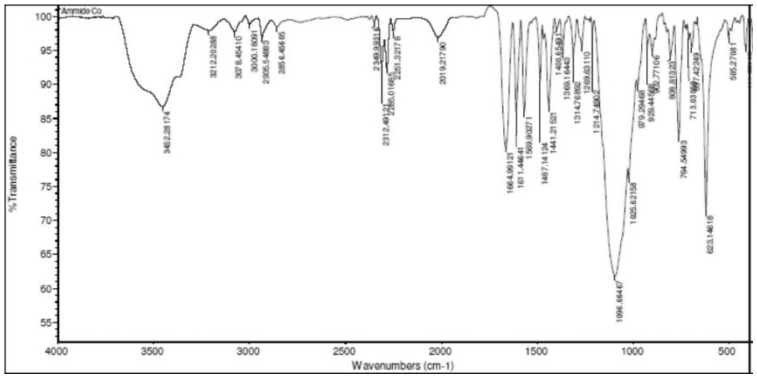
The product is a green solid and the final yield was 85%.

IR (KBr, cm^{-1}): 3452, 3078, 1665, 1611, 1570, 1487, 1441, 1096.

ESI+ MS(m/z): Calc. $C_{25}H_{23}N_5OCo$ 468.12, Found 234.0 ($M^{2+}/2$).

Anal. Calcd. ($C_{25}H_{23}Cl_2N_5O_9Co + H_2O$): C, 43.81; H, 3.68; N, 10.22. **Found:** C, 43.94; H, 3.71; N, 10.35.

IR (KBr, cm^{-1})



CoL3: [6-(3-hydroxyphenyl)-2-pyridylmethyl)bis(2-pyridylmethyl)-amine Cobalt complex

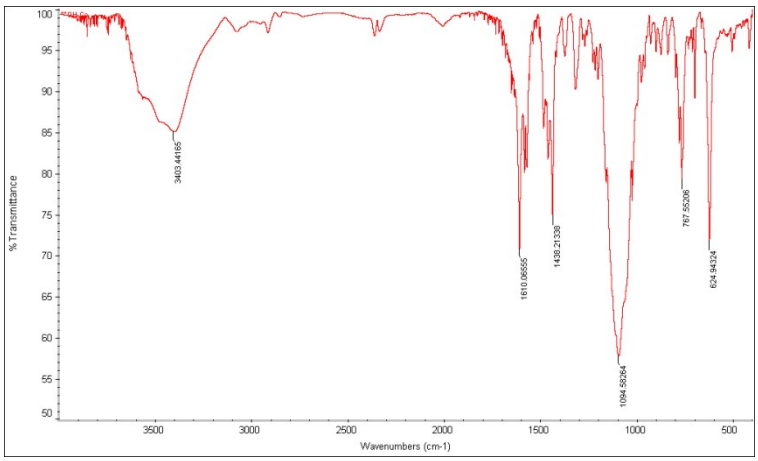
The product is a brown solid and the final yield was 89%.

IR (KBr, cm^{-1}): 3403, 1610, 1573, 1495, 1438, 1094.

ESI+ MS(m/z): Calc. $(C_{24}H_{22}N_4OCo + ClO_4)^+$ 540.06, Found 540.0 (M^+).

Anal. Calcd. ($C_{24}H_{22}Cl_2N_4O_9Co$): C, 45.02; H, 3.46; N, 8.75. **Found:** C, 45.33; H, 2.97; N, 8.66.

IR (KBr, cm^{-1})



CoL4:6-(3-hydroxymethylphenyl)-2-pyridylmethyl)bis(2-pyridylmethyl)-amine Cobalt complex

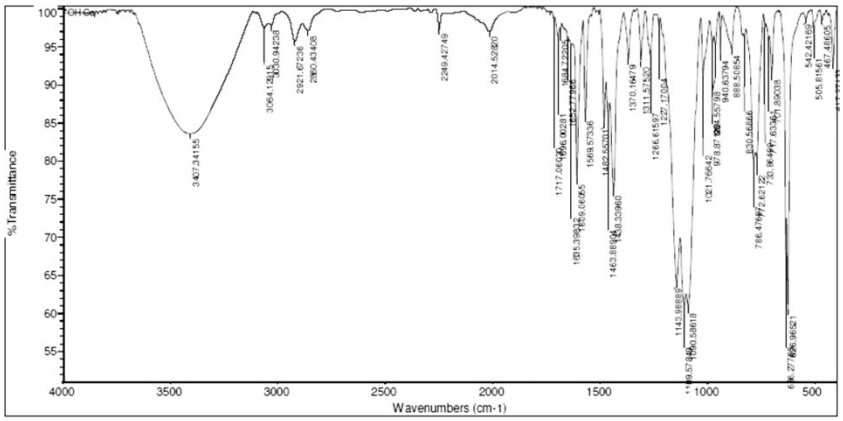
The product is a red-brownish solid and the final yield was 87%.

IR (KBr, cm^{-1}): 3407, 2922, 1609, 1570, 1483, 1438, 1144, 1189, 1091.

ESI+ MS(m/z): Calc. $C_{25}H_{24}N_4OCo$ 455.13, Found 227.5 ($M^{2+}/2$).

Anal. Calcd. ($C_{25}H_{24}Cl_2N_4O_9Co$): C, 45.09; H, 3.63; N, 10.95. **Found:** C, 44.79; H, 3.48; N, 10.84.

IR (KBr, cm^{-1})



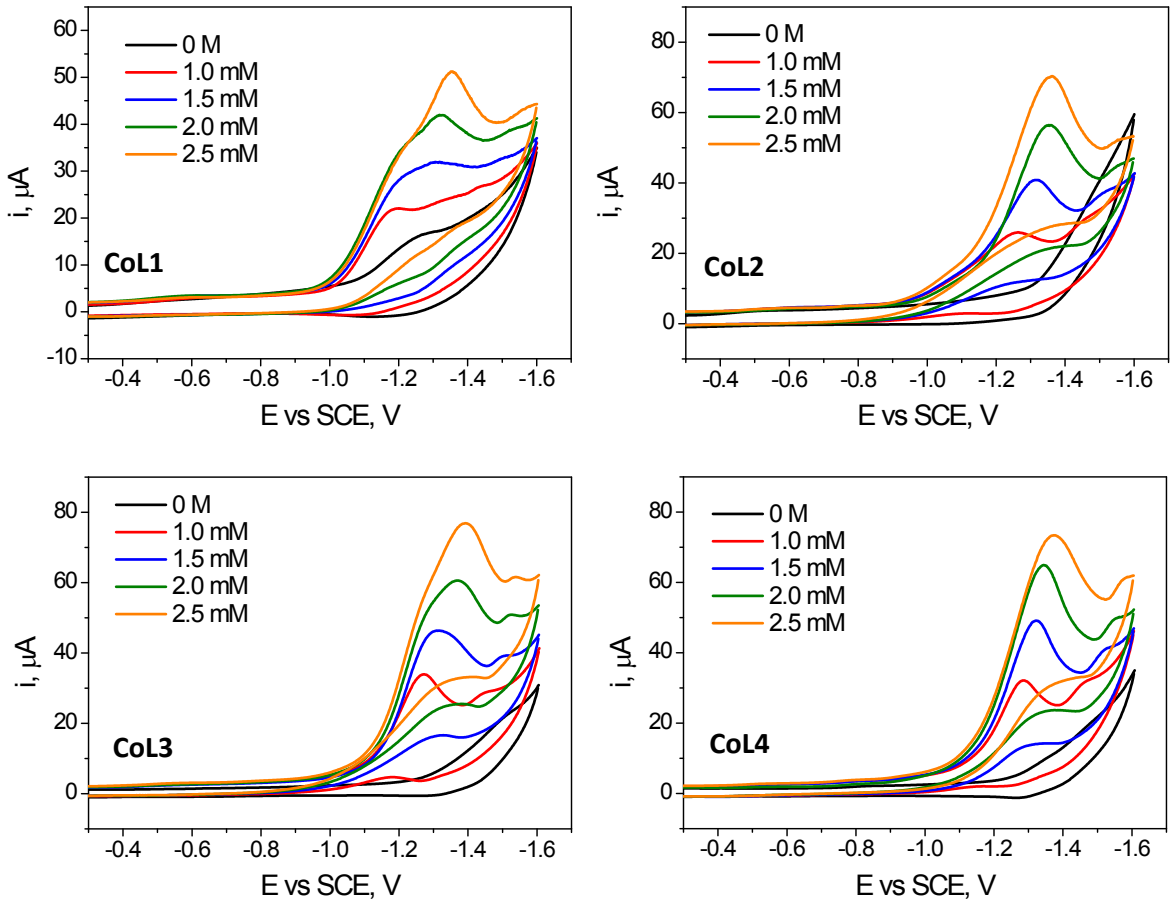


Figure S1. Cyclic voltammetry (CV) of 1 mM **CoL1** (top left panel), 1 mM **CoL2** (top right panel), 1 mM **CoL3** (bottom left panel), and 1 mM **CoL4** (bottom left panel) in argon-purged 50/50 acetonitrile/water (0.1 M $LiClO_4$) upon addition of 0-2.5 mM TFA. Experimental conditions: GC as working electrode, Pt as counter electrode, SCE as reference electrode, room temperature, scan rate v = 100 mV/s.

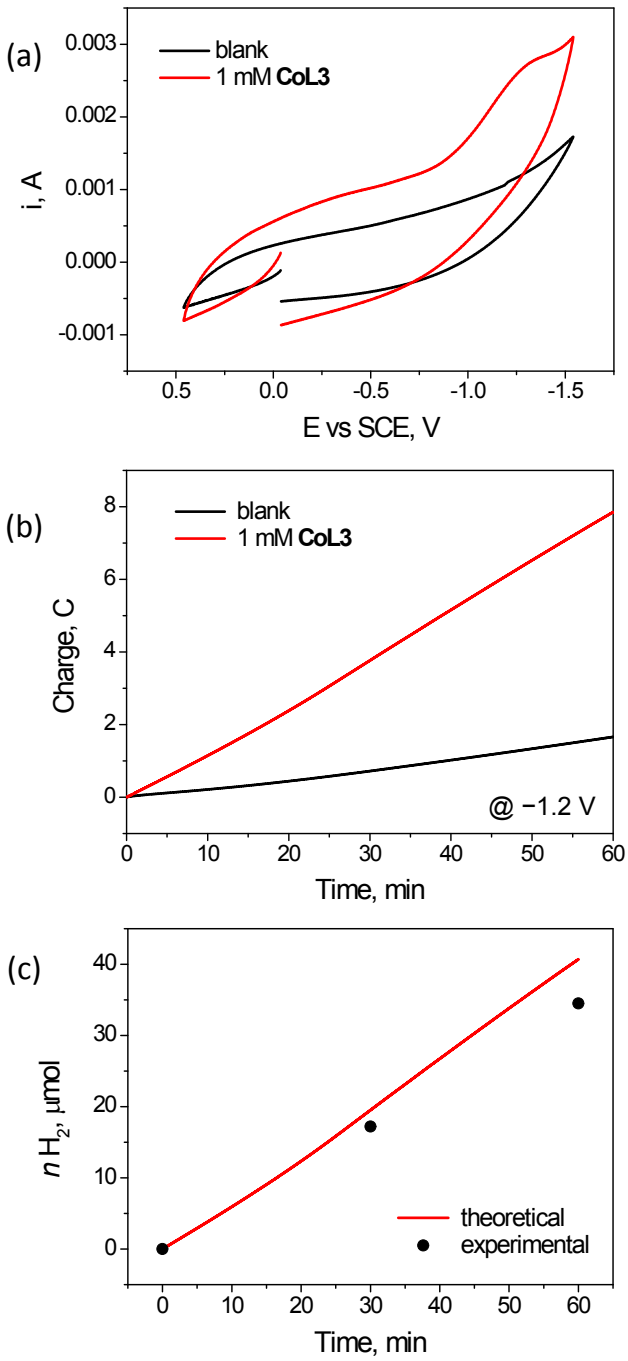


Figure S2. (a) Cyclic voltammetry (CV) of the blank and 1 mM **CoL3** solutions (50/50 acetonitrile/water, 0.1 M $LiClO_4$, 2.5 mM TFA) before bulk electrolysis, scan rate of v = 100 mV/s; (b) charge build-up upon one-hour controlled potential electrolysis at −1.2 V vs. SCE; (c) comparison of the experimental amount of hydrogen produced with the theoretical value assuming 100% Faradaic Efficiency. Experimental conditions: carbon foil (1 cm^2 geometrical area, 0.5 mm thickness) as working electrode, Pt wire as counter electrode, Ag/AgCl as reference electrode, room temperature.

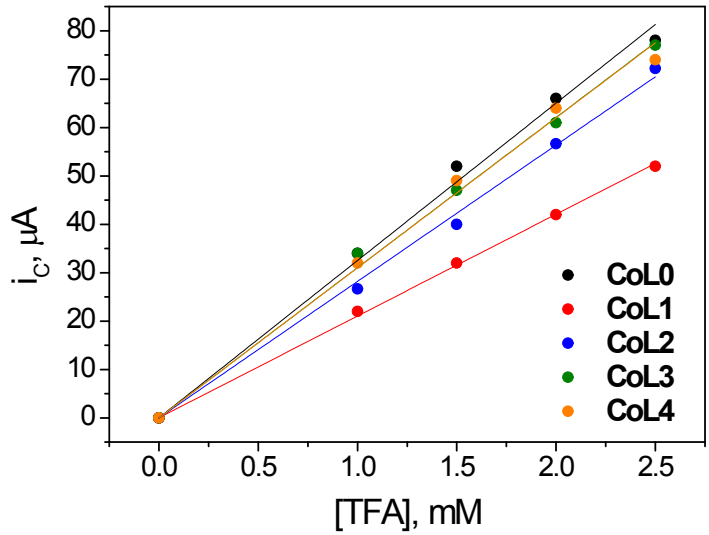


Figure S3. Plot of the catalytic peak current vs. TFA concentration obtained from the electrochemical data reported in Figure 1b (main text) and Figure S1.

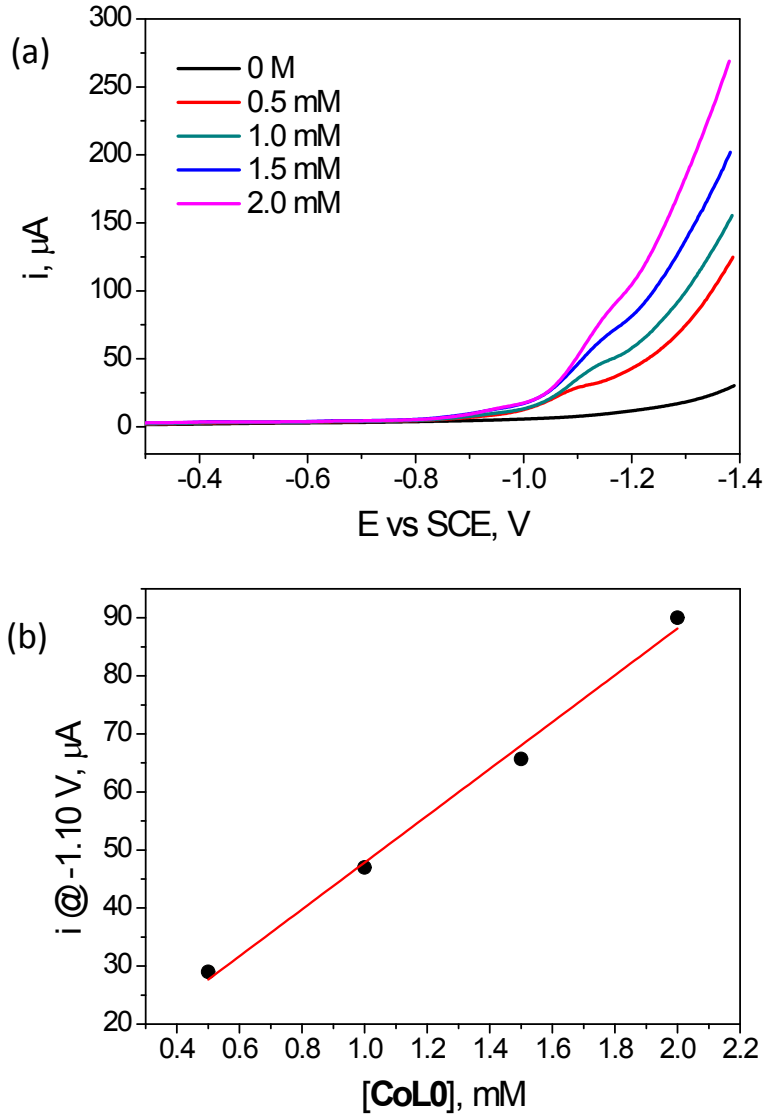


Figure S4. (a) Cyclic voltammetry (CV) of 50 mM TFA in argon-purged 50/50 acetonitrile/water (0.1 M $LiClO_4$) upon addition of 0-2 mM **CoL0** (return scans have been omitted for clarity); (b) plot of the catalytic current at −1.10 V vs. the **CoL0** concentration. Experimental conditions: GC as working electrode, Pt as counter electrode, SCE as reference electrode, room temperature, scan rate v = 100 mV/s.

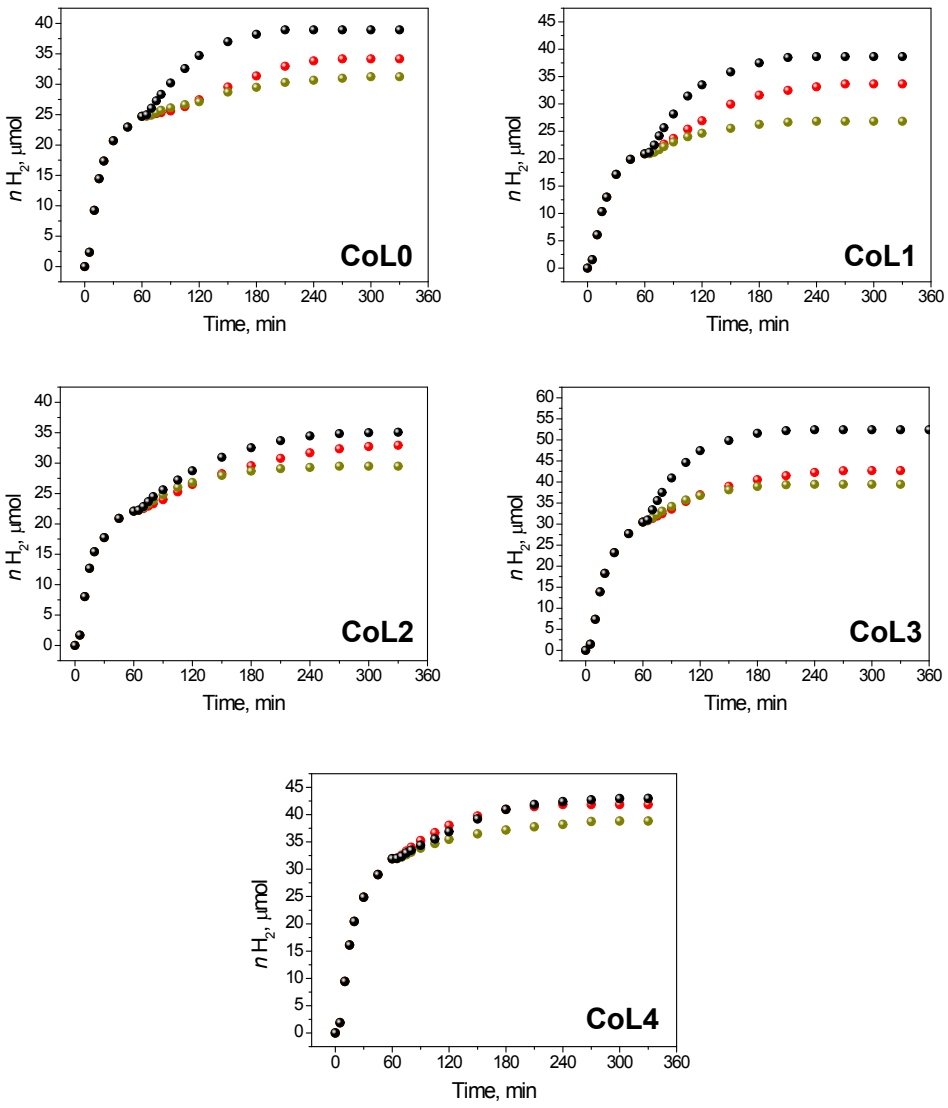


Figure S5. Effect of the addition of different components after 1 h photolysis on the photocatalytic hydrogen evolution activity by **CoL0-4**. Experimental conditions: 1 M acetate buffer solutions (5 mL, pH 5) containing 0.5 mM $Ru(bpy)_3^{2+}$, 0.1 M ascorbic acid, and 75 μM **CoL0-4**, addition of 75 μM **CoL0-4** (dark yellow traces), addition of 0.5 mM $Ru(bpy)_3^{2+}$ (red traces), addition of both 75 μM **CoL0-4** and 0.5 mM $Ru(bpy)_3^{2+}$ (black traces).

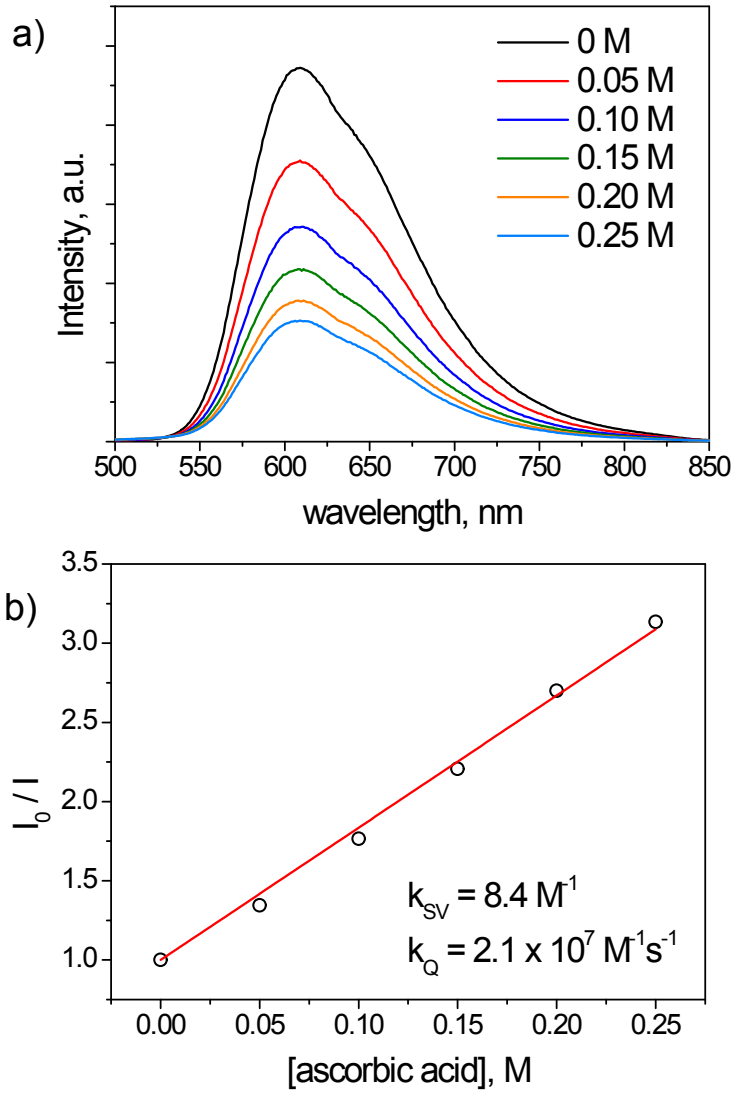


Figure S6. (a) Photoluminescence spectra (excitation at 450 nm) of a 50 μM $Ru(bpy)_3^{2+}$ solution in 1 M acetate buffer (pH 5) in the presence of 0-0.25 M ascorbic acid; (b) Stern-Volmer analysis.

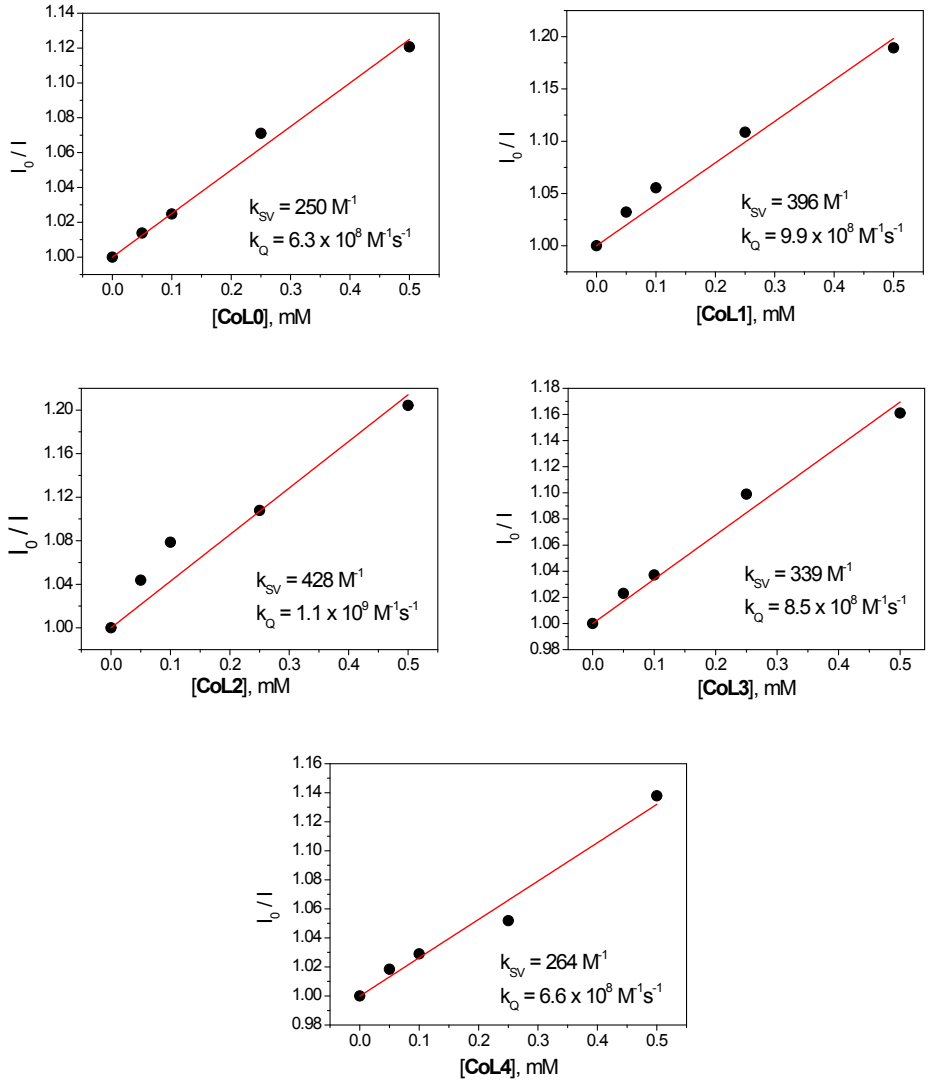


Figure S7. Stern-Volmer analyses of the quenching of the $Ru(bpy)_3^{2+}$ emission by **CoL0-4** obtained from photoluminescence spectra of 50 μM $Ru(bpy)_3^{2+}$ solutions in 1 M acetate buffer (pH 5) (excitation at 450 nm) at different **CoL0-4** concentration.

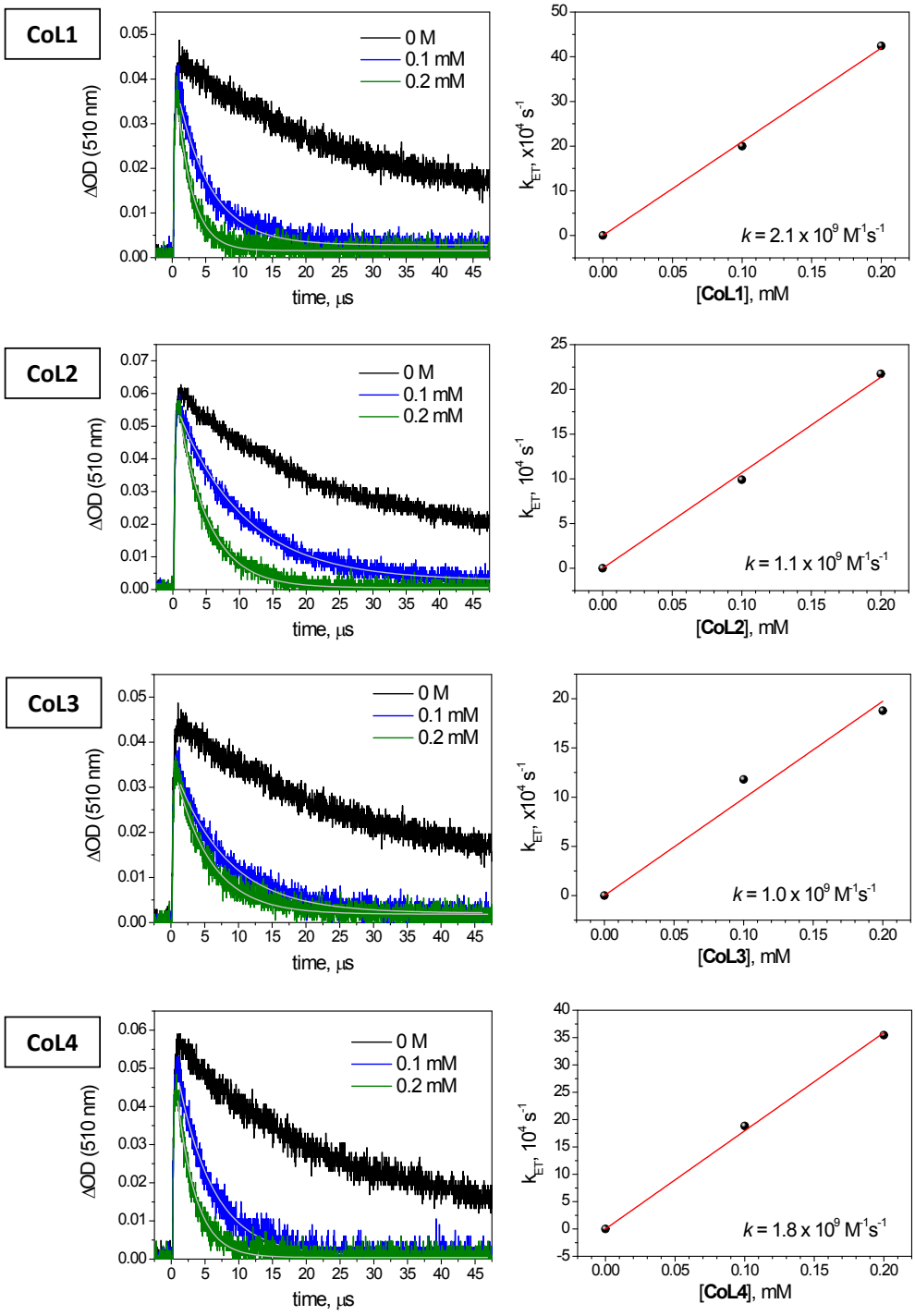


Figure S8. Kinetic traces at 510 nm with related single-exponential fitting (left panels) obtained by laser flash photolysis (excitation at 355 nm) on 0.1 mM $Ru(bpy)_3^{2+}$ solutions in 1 M acetate buffer (pH 5) in the presence of 0.1 M ascorbic acid and 0-0.2 mM **CoL1-4** and plot of the pseudo-first order rate vs. the **CoL1-4** catalyst concentration (right panels) for the estimation of the bimolecular rate constant.

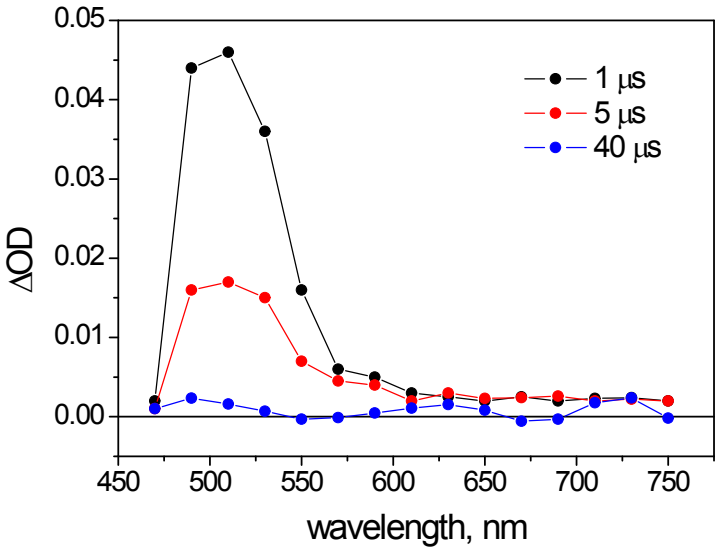


Figure S9. Transient absorption spectra obtained by laser flash photolysis (excitation at 355 nm) of a 1 M acetate buffer (pH 5) solution containing 100 μM $Ru(bpy)_3^{2+}$, 0.1 M ascorbic acid and 0.1 mM **CoL0** at 1, 5, and 40 μs time delays.