Supporting Information

Phosphine Coordination to a Cobalt Diimine-Dioxime Catalyst Increases Stability during Light-Driven H_2 Production

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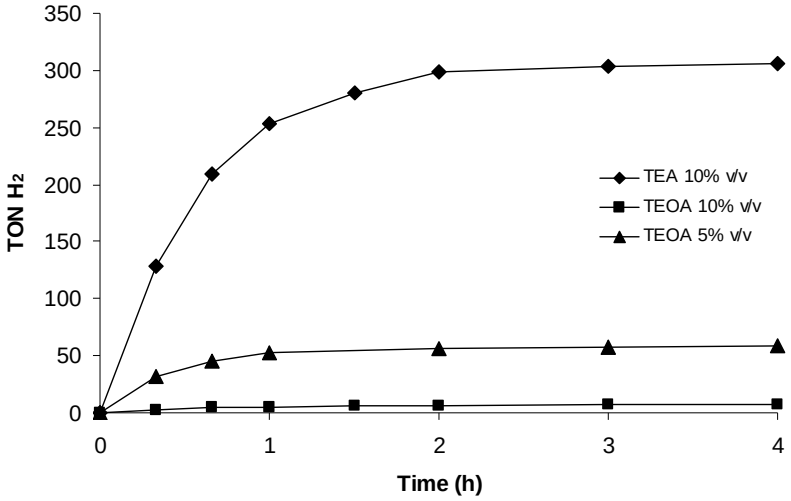

Figure S1. Photocatalytic hydrogen evolution using TEA or TEOA as a sacrificial electron donor ([**1**] = 1×10^{-4} M; [**PS**] = 1×10^{-4} M; pH = 10; CH_3CN/H_2O, 1:1, v/v).

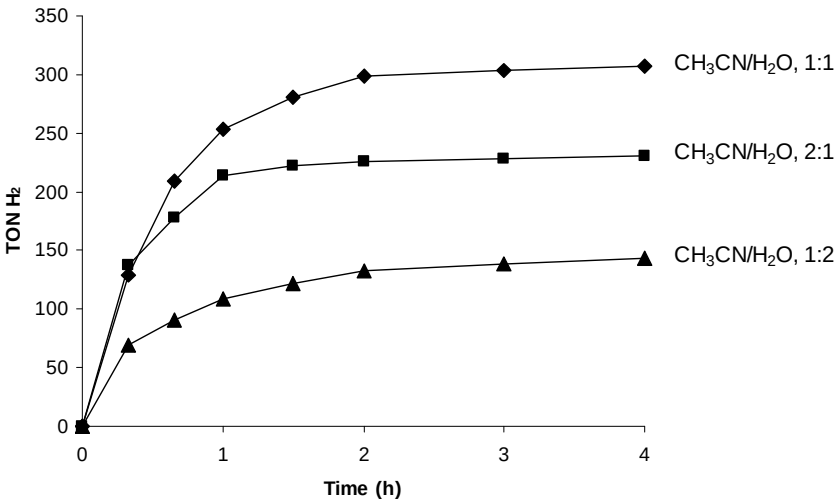

Figure S2. Photocatalytic hydrogen evolution at different CH_3CN/H_2O ratios ([**1**] = 1×10^{-4} M; [**PS**] = 1×10^{-4} M; pH = 10; TEA, 10%).

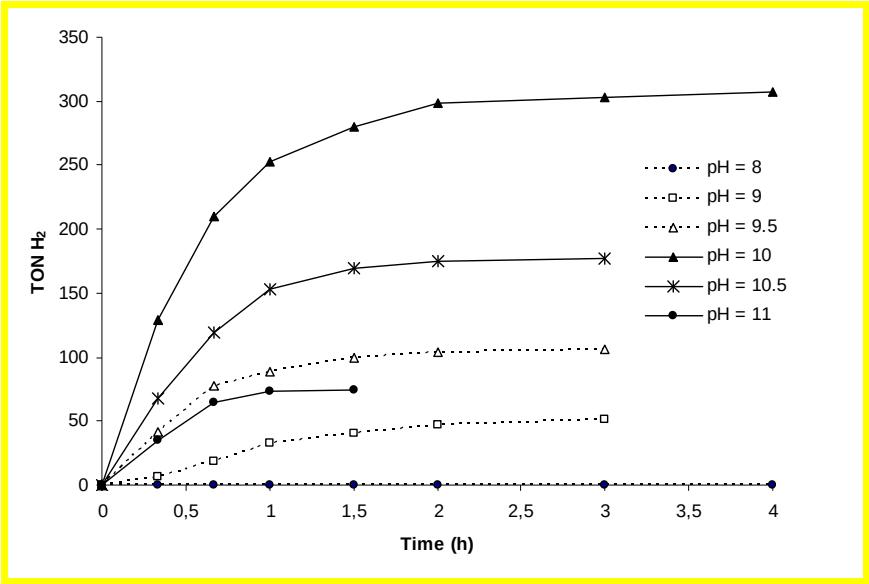

Figure S3. Photocatalytic hydrogen evolution at different pH values ([**1**] = 1×10^{-4} M; [**PS**] = 1×10^{-4} M; CH_3CN/H_2O, 1:1 v/v; TEA, 10%).

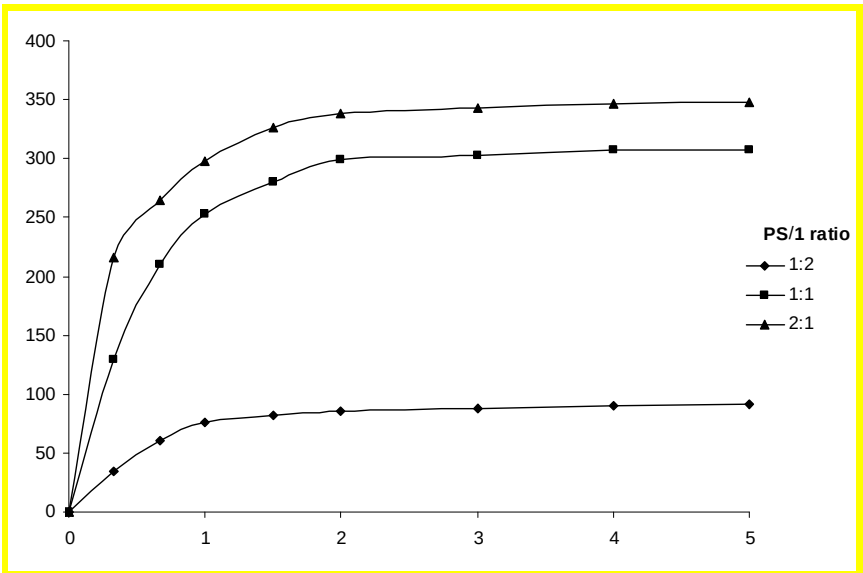

Figure S4. Photocatalytic hydrogen evolution at different **PS**/**1** ratios ([**1**] = 1×10^{-4} M; CH_3CN/H_2O, 1:1 v/v; TEA, 10%).

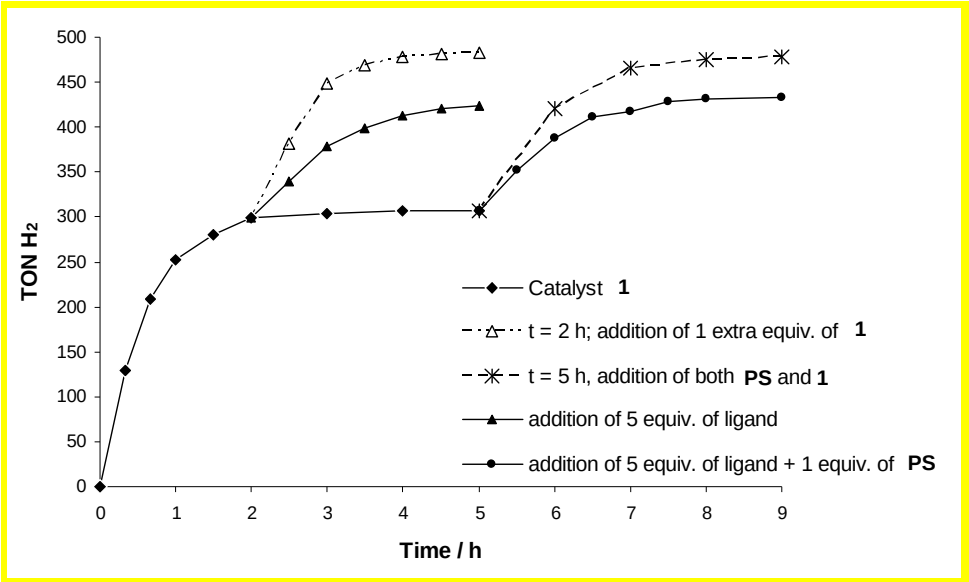

Figure S5. Photocatalytic hydrogen evolution using **1** as catalyst with addition of 5 equiv. of {(DOH)(DOH)pn} ligand after 2h of irradiation and addition of 5 equiv. of {(DOH)(DOH)pn} ligand together with 1 equiv. of PS after 5h of irradiation (initial conditions: [**1**] = 1×10^{-4} M; [**PS**] = 1×10^{-4} M; CH_3CN/H_2O, 1:1 v/v; TEA, 10%).

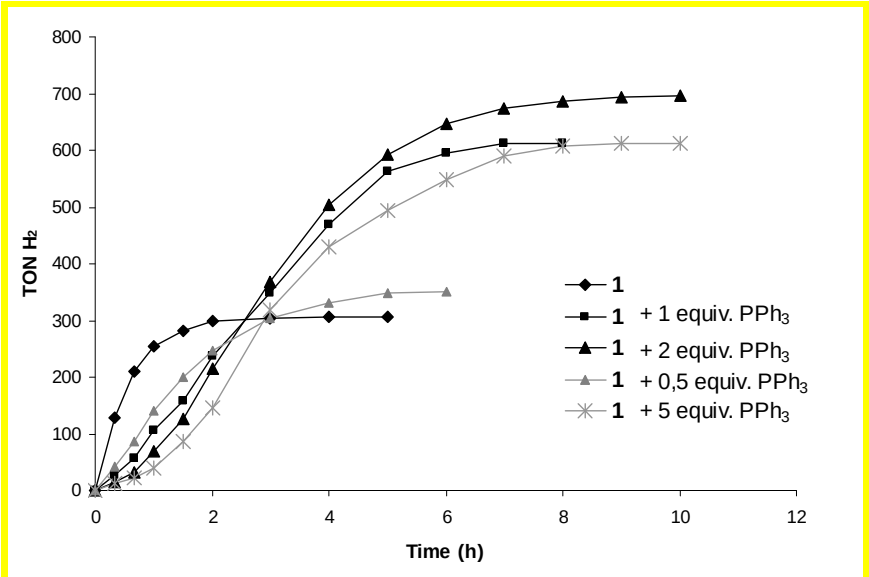

Figure S6. Photocatalytic hydrogen evolution using catalyst **1** in the absence and in the presence of 0.5, 1, 2 and 5 equiv. of PPh_3 ([**1**] = 1×10^{-4} M; [**PS**] = 1×10^{-4} M; CH_3CN/H_2O, 1:1 v/v; TEA, 10%).

Time (h)	**1**	**1** + 0.5 equiv.PPh_3	**1** + 1 equiv.PPh_3	**1** + 2 equiv.PPh_3	**1** + 5 equiv.PPh_3
0	0	0	0	0	0
0.33	129	42	27	14	12
0.66	210	87	56	33	22
1	253	140	107	68	39
1.5	280	199	158	127	86
2	299	247	236	215	145
3	303	303	348	368	319
4	307	331	469	504	430
5	307	347	563	592	495
6		350	596	648	547
7			612	675	590
8			613	686	608
9				695	612
10				696	612

Table S1. TON measured after different irradiation times, corresponding to Figure 3.

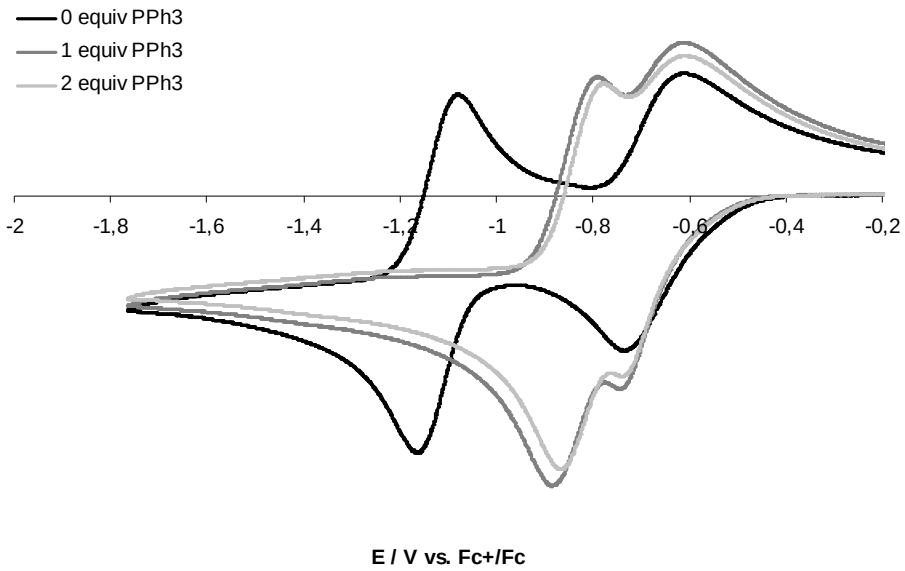

Figure S7. Cyclic voltammograms of [Co(DO)(DOH)pnBr$_2$] (**1**; 2.10^{-3} mol.L^{-1}) recorded in a CH_3CN solution of *n*-Bu_4NBF_4 (0.1 mol.L^{-1}) on a glassy carbon electrode at 100 mV.s^{-1} in the presence of 0, 1, and 2 equiv of PPh_3.

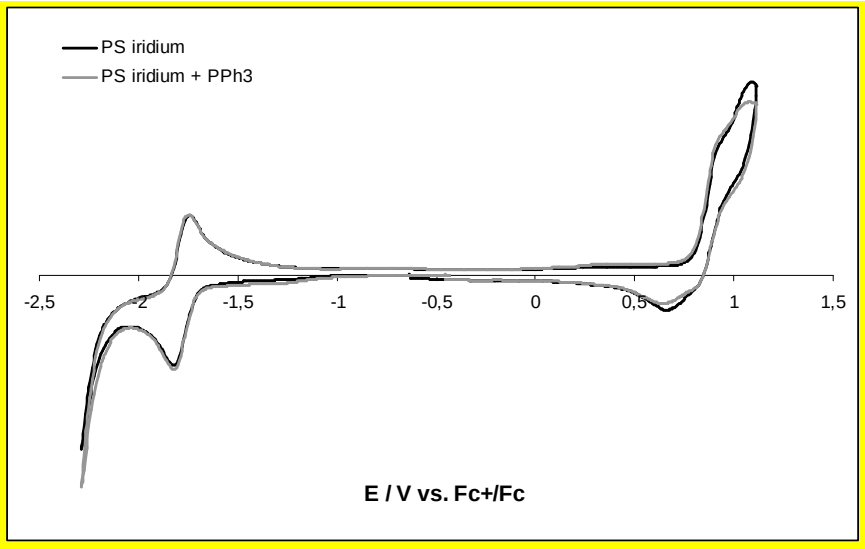

Figure S8. Cyclic voltammograms of $[Ir(ppy)_2(bpy)][PF_6]$ (**PS**; 2.10^{-3} mol.L^{-1}) recorded in a CH_3CN solution of *n*-Bu_4NBF_4 (0.1 mol.L^{-1}) on a gold electrode at 100 mV.s^{-1} in the presence of 0 and 2 equiv of PPh_3.
These voltammograms show that the iridium photosensitizer is not affected by addition of PPh_3 to the photocatalytic medium.

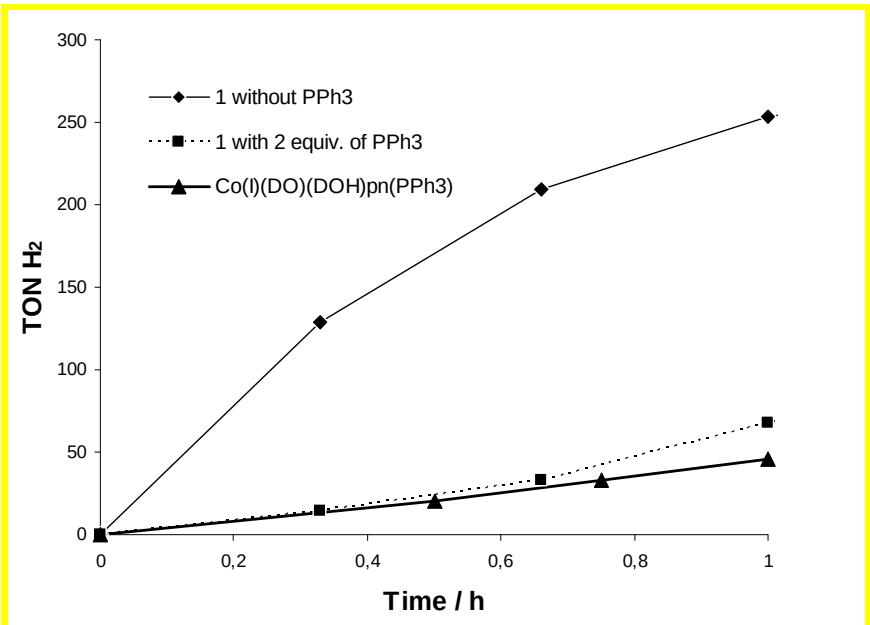

Figure S9. Photocatalytic evolution of H_2 during the first hour of irradiation, using $[Co^{I}(DO)(DOH)pn(PPh_3)]$ as the catalyst ([**PS**] = 1×10^{-4}M; pH = 10; CH_3CN/H_2O, 1:1, v/v), compared with the photocatalytic evolution of H_2 using catalyst **1** in absence and in presence of 2 equiv. of PPh_3.