SUPPORTING INFORMATION

Photochemical Dihydrogen Production using an Analogue of the Active site of [NiFe] Hydrogenase.

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TRIR Data

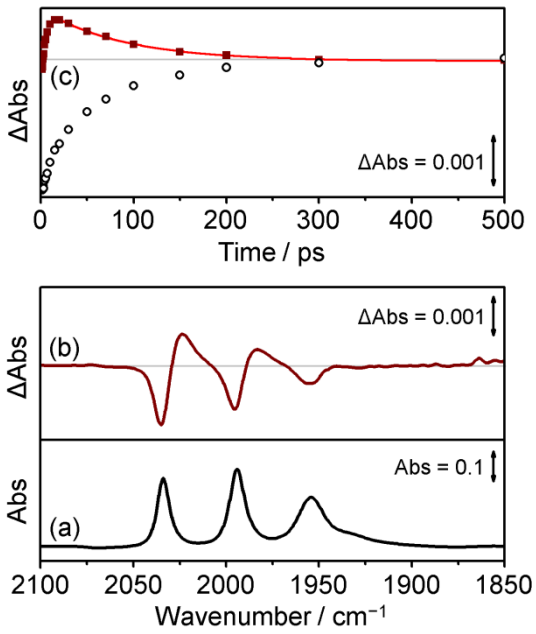

Fig. S1. FTIR and ps-TRIR spectra of **1** (1 mM) in CH_3CN. (a) FTIR ground state spectrum. (b) ps-TRIR difference spectrum taken 20 ps following flash photolysis at 400 nm. (c) Single point TRIR kinetic traces for the transient species formed from **1** (2026 cm^{-1}, brown squares) and the reformation of **1** (2034 cm^{-1}, black circles). The solid red line is a mono-exponential best fit of the decay data (τ = 90 ps).

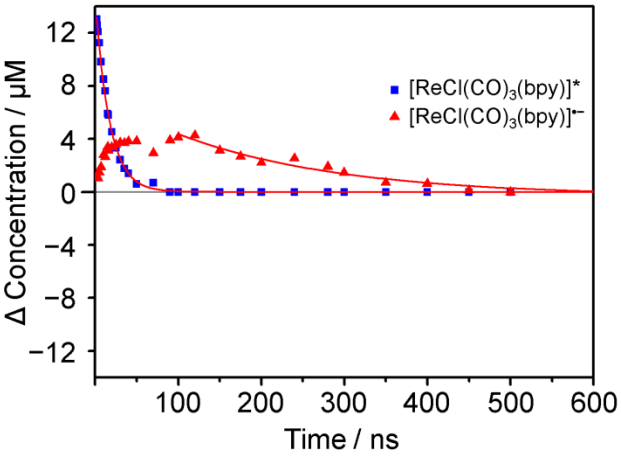

Fig. S2. TRIR kinetic traces for the decay of the ^{3}MLCT excited state [ReCl(CO)$_3$(bpy)]* (blue squares) and the growth and decay of [ReCl(CO)$_3$(bpy)]$^{\bullet-}$ (red triangles), following flash photolysis (355 nm) of **1 (**0.76 mM) and [ReCl(CO)$_3$(bpy)] (0.75 mM) in a solution of NEt_3 (1 M) and CH_3CN. The solid red lines are mono-exponential best fits of the decay data (τ = 17 ns and 195 ns for [ReCl(CO)$_3$(bpy)]* and [ReCl(CO)$_3$(bpy)]$^{\bullet-}$, respectively).

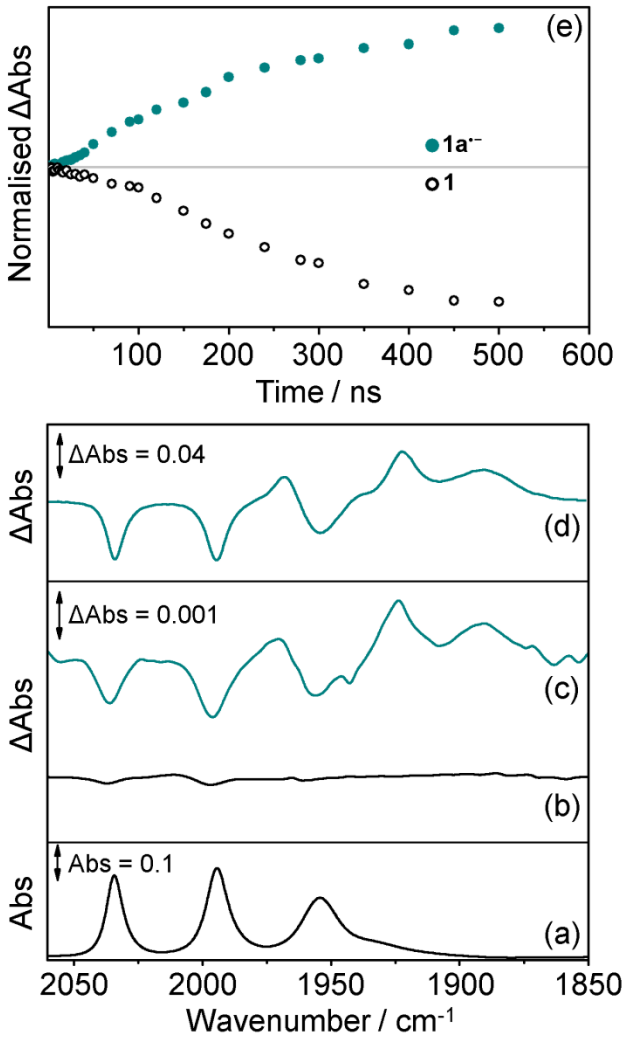

Fig. S3. FTIR and TRIR spectra of **1** (1 mM) and $[Ru(bpy)_3][PF_6]_2$ (1 mM) recorded in a solution of CH_3CN and NEt_3 (1.5 M). (a) FTIR ground state spectrum. TRIR difference spectra at (b) 1.5 ns and (c) 500 ns after flash photolysis at 355 nm. (d) FTIR difference spectrum at 5 seconds after 30 seconds irradiation of an identical solution using a LED white light source and a $\lambda < 420$ nm cut-off filter. (e) TRIR single point kinetic traces for the decay of **1** (black circles, 1955 cm^{-1}) and the growth of $\mathbf{1a}^{\bullet-}$ (green dots, 1926 cm^{-1}).

Electrochemical Data

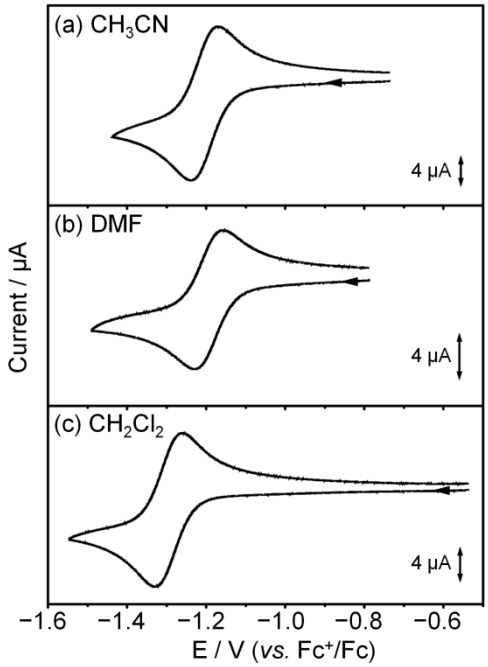

Fig. S4. Cyclic voltammograms of **1** in (a) CH_3CN, (b) DMF and (c) CH_2Cl_2 at 293 K containing [^{n}Bu$_4$N][BF_4] (0.2 M in CH_3CN and DMF, 0.4 M in CH_2Cl_2) as a supporting electrolyte at a scan rate of 100 mV s^{-1}.

Computational and Crystallographic Data

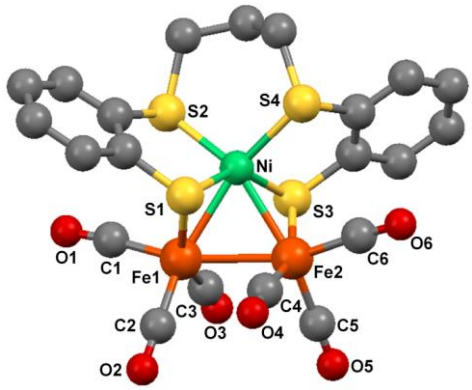

Fig. S5. Crystallographic structure of **1** with atom labelling. H atoms are omitted for clarity (adapted from reference 1).

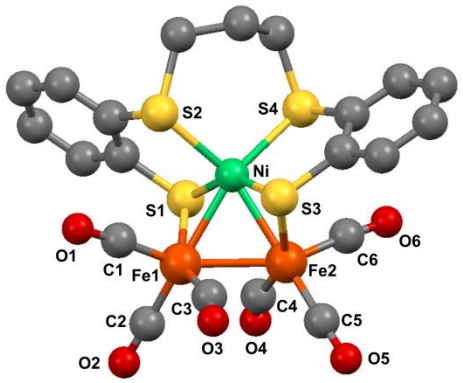

Fig. S6. Calculated structure of **1** with atom labelling. H atoms are omitted for clarity.

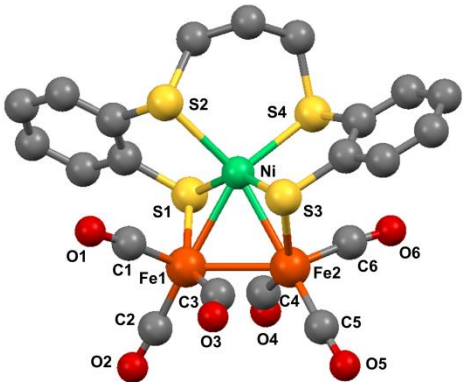

Fig. S7. Calculated structure of **1a**$^{\bullet-}$ with atom labelling. H atoms are omitted for clarity.

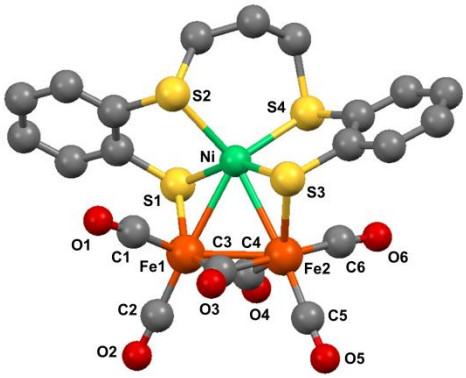

Fig. S8. Calculated structure of **1b**$^{\bullet-}$ with atom labelling. H atoms are omitted for clarity.

Table S1. Selected bond lengths (Å) and angles (°) for the geometry optimised DFT models of **1**, **1a**$^{\bullet-}$, and **1b**$^{\bullet-}$, and the X-ray crystal structure of **1**, adapted from reference 1.

Parameters	**1** XRD	**1**	**1a**$^{\bullet-}$	**1b**$^{\bullet-}$
Ni-S(1)	2.1782(9)	2.23	2.32	2.33
Ni-S(2)	2.2599(8)	2.37	2.52	2.43
Ni-S(3)	2.1865(9)	2.23	2.31	2.32
Ni-S(4)	2.2630(9)	2.37	2.41	2.43
Fe(1)-S(1)	2.2623(8)	2.32	2.39	2.40
Fe(2)-S(3)	2.2672(8)	2.32	2.43	2.39
Fe(1)···S(3)	3.3569(12)	3.43	3.67	3.75
Fe(2)···S(1)	3.2705(12)	3.43	3.69	3.89
Ni-Fe(1)	2.4936(8)	2.43	2.63	2.67
Ni-Fe(2)	2.4855(6)	2.43	2.63	2.73
Fe(1)-Fe(2)	2.6279(7)	2.51	2.58	2.54
Fe(1)-C(1)	1.806(3)	1.76	1.76	1.77
Fe(1)-C(2)	1.790(3)	1.77	1.79	1.78
Fe(1)-C(3)	1.770(3)	1.77	1.83	1.91
Fe(2)-C(4)	1.786(3)	1.77	1.80	1.91
Fe(2)-C(5)	1.789(3)	1.77	1.78	1.78
Fe(2)-C(6)	1.817(3)	1.76	1.77	1.77
Fe(1)···C(4)	2.720(3)	2.34	2.25	1.97
Fe(2)···C(3)	2.780(3)	2.34	2.14	1.98
S(1)-Ni-S(2)	92.92(3)	93	88	89
S(1)-Ni-S(4)	109.16(3)	106	108	107
S(2)-Ni-S(4)	103.77(3)	100	101	106
S(1)-Ni-S(3)	143.22(3)	151	151	153
S(2)-Ni-S(3)	110.53(3)	105	110	106
S(3)-Ni-S(4)	92.81(3)	93	91	90
Fe(1)-Ni-Fe(2)	63.71(2)	62	59	56
Ni-Fe(2)-Fe(1)	58.30(2)	59	61	61
Ni-Fe(1)-Fe(2)	57.993(14)	59	61	63

Table S2. Cartesian coordinates for the calculated structure of **1**.

Ni	0.00331	-0.360114	-0.030972
Fe	-1.172834	1.745829	-0.289246
Fe	1.260998	1.688329	0.323557
O	0.367329	3.132613	-2.344002
O	-2.987783	0.912707	-2.422381
C	-0.052082	2.542997	-1.410222
C	4.246527	-0.849281	-1.562768
C	5.30771	-1.678116	-1.215066
C	-2.280296	1.195474	-1.540093
S	1.671911	0.190792	-1.401517
S	-1.369033	-1.854214	-1.256928
C	-0.969939	-3.662154	-0.851796
C	3.037775	-0.915804	-0.864498
C	-4.061493	-2.428932	-0.751044
O	2.982583	3.980756	-0.274087
C	5.17612	-2.57883	-0.158986

C	-2.953185	-1.699452	-0.320434
C	2.283567	3.082779	-0.032897
C	-5.271166	-2.319742	-0.073619
C	2.910389	-1.826275	0.184267
C	-2.148343	3.157274	0.125598
C	-0.589837	-3.948648	0.589808
C	3.97952	-2.645557	0.547584
O	-2.816488	4.067093	0.40718
C	0.876627	-3.737956	0.9226
C	-3.054051	-0.830126	0.765331
C	-5.374241	-1.466863	1.025176
S	1.345547	-1.907793	1.154589
S	-1.645307	0.186377	1.367115
C	2.365955	1.060299	1.543219
C	-4.274588	-0.723396	1.438939
C	0.173598	2.470127	1.487386
O	3.08141	0.740422	2.405772
O	-0.227736	3.027524	2.448004
H	4.341705	-0.147024	-2.379631
H	6.237776	-1.615525	-1.76408
H	-0.173633	-3.921287	-1.550224
H	-1.867077	-4.208317	-1.138048
H	-3.982073	-3.061261	-1.625797
H	6.003639	-3.215251	0.124008
H	-6.129878	-2.884297	-0.410851
H	-0.80942	-5.006122	0.782886
H	-1.231688	-3.38461	1.273565
H	3.881333	-3.317522	1.389877
H	1.528464	-4.12291	0.138904
H	1.129116	-4.214786	1.867118
H	-6.313458	-1.372312	1.553768
H	-4.349794	-0.053904	2.284862

Table S3. Cartesian coordinates for the calculated structure of **1a**$^{\bullet-}$.

Ni	-0.025378	-0.527346	0.020339
Fe	-1.17803	1.822687	-0.234125
Fe	1.369304	1.702664	0.164882
O	0.339223	2.823967	-2.532262
O	-3.06546	1.01149	-2.335711
C	-0.006207	2.38318	-1.48069
C	4.435715	-0.823452	-1.203396
C	5.541752	-1.502133	-0.705545
C	-2.299662	1.26567	-1.478647
S	1.766603	-0.077556	-1.381088
S	-1.580643	-1.89672	-1.206961

C	-1.359351	-3.767136	-0.958295
C	3.156155	-1.036115	-0.672378
C	-4.287445	-2.304314	-0.648612
O	3.065151	4.070229	-0.372696
C	5.397066	-2.409832	0.343755
C	-3.127615	-1.652871	-0.227259
C	2.360259	3.15411	-0.167068
C	-5.477637	-2.138537	0.050313
C	3.024531	-1.955198	0.374545
C	-2.065523	3.323141	0.136026
C	-0.540061	-4.171593	0.252225
C	4.134367	-2.629054	0.884365
O	-2.696412	4.297856	0.315865
C	0.943634	-3.830801	0.12232
C	-3.145254	-0.783877	0.867159
C	-5.505475	-1.294327	1.161672
S	1.382403	-2.293933	1.140757
S	-1.699948	0.156392	1.453698
C	2.340432	1.090014	1.503608
C	-4.356741	-0.621491	1.556317
C	0.161748	2.453095	1.316818
O	2.988445	0.77168	2.433253
O	-0.070431	2.995377	2.357053
H	4.54641	-0.105263	-2.004484
H	6.520516	-1.310512	-1.127986
H	-0.897464	-4.11005	-1.884597
H	-2.371903	-4.16354	-0.906627
H	-4.261025	-2.920627	-1.538716
H	6.257574	-2.9278	0.747428
H	-6.375422	-2.64407	-0.281517
H	-0.644327	-5.25693	0.371604
H	-0.96837	-3.726344	1.155383
H	4.001541	-3.307778	1.716723
H	1.215837	-3.596831	-0.906748
H	1.5851	-4.631496	0.485289
H	-6.427688	-1.146626	1.71004
H	-4.375684	0.050165	2.403806

Table S4. Cartesian coordinates for the calculated structure of **1b**$^{\bullet-}$.

Ni	0.00028	-0.61947	-0.020171
Fe	-1.19926	1.832888	-0.01577
Fe	1.332995	1.69451	-0.044829
O	0.058171	2.397307	-2.625863
O	-3.211688	1.250999	-2.077068
C	0.022851	2.126255	-1.455944

C	4.481396	-0.856778	-1.121403
C	5.577876	-1.485359	-0.542909
C	-2.403348	1.414867	-1.242834
S	1.79964	-0.195307	-1.443174
S	-1.631762	-1.884519	-1.308383
C	-1.372536	-3.749711	-1.056929
C	3.184803	-1.07596	-0.636537
C	-4.329985	-2.281081	-0.705118
O	2.787209	4.170649	-0.719632
C	5.405428	-2.34873	0.53949
C	-3.15047	-1.668128	-0.279167
C	2.191102	3.195251	-0.450948
C	-5.504192	-2.13173	0.024386
C	3.025595	-1.951517	0.443091
C	-1.862135	3.45614	0.258627
C	-0.565456	-4.130898	0.170869
C	4.124342	-2.576226	1.031825
O	-2.324058	4.522482	0.428887
C	0.918785	-3.778358	0.063677
C	-3.136203	-0.857017	0.859369
C	-5.498334	-1.340984	1.174431
S	1.352059	-2.276054	1.143292
S	-1.656104	0.018721	1.474397
C	2.412022	1.199919	1.270457
C	-4.330439	-0.707781	1.579554
C	0.167651	2.284994	1.341954
O	3.132863	0.965927	2.165308
O	0.164189	2.695877	2.470381
H	4.61264	-0.173109	-1.949333
H	6.570757	-1.289599	-0.929069
H	-0.884078	-4.079515	-1.974576
H	-2.37514	-4.174153	-1.023767
H	-4.327609	-2.856126	-1.622672
H	6.258235	-2.827789	1.003247
H	-6.415686	-2.608818	-0.312478
H	-0.661734	-5.215437	0.303692
H	-1.013552	-3.678185	1.060866
H	3.967181	-3.224148	1.884267
H	1.197388	-3.500432	-0.952537
H	1.562126	-4.58928	0.400574
H	-6.407528	-1.205961	1.747356
H	-4.321512	-0.081234	2.461219

H_2 Production Data

Using [ReCl(CO)$_3$(bpy)] as a photosensitiser in CH_3CN

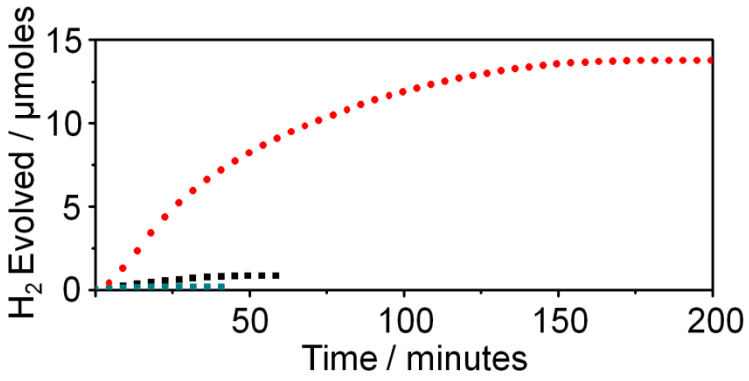

Fig. S9. Time-dependent photo-induced H_2 evolution from a 5 mL degassed solution containing **1** (0.05 mM), [ReCl(CO)$_3$(bpy)] (0.25 mM), TEOA (1 M) and [HTEOA][BF_4] (0.1 M) in CH_3CN at 293 K (red dots). Control experiment in the absence of [HTEOA][BF_4] (black squares) and in the absence of **1** (green squares) from the reaction mixture. Irradiation was performed using a Xe lamp (250 W) and a $\lambda < 420$ nm cut-off filter.

Using [ReCl(CO)$_3$(bpy)] as a photosensitiser in CH_2Cl_2

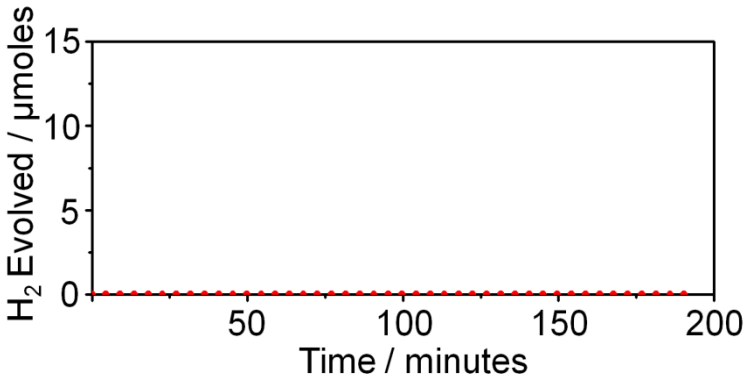

Fig. S10. Time dependent photo-induced H_2 evolution from a 5 mL degassed solution containing **1** (0.05 mM), [ReCl(CO)$_3$(bpy)] (0.25 mM), TEOA (1 M) and [HTEOA][BF_4] (0.1 M) in CH_2Cl_2 at 293 K (red dots, no dihydrogen detected). Control experiment in the absence of [HTEOA][BF_4] or **1** from the reaction mixture produced no detectable dihydrogen. Irradiation was performed using a Xe lamp (250 W) and $\lambda < 420$ nm cut-off filter.

Using [ReCl(CO)$_3$(bpy)] as a photosensitiser in DMF

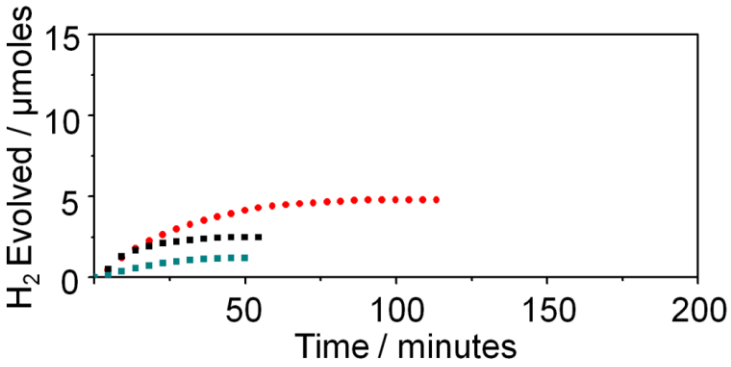

Fig. S11. Time dependent photo-induced H_2 evolution from a 5 mL degassed solution containing **1** (0.05 mM), [ReCl(CO)$_3$(bpy)] (0.25 mM), TEOA (1 M) and [HTEOA][BF_4] (0.1 M) in DMF at 293 K (red dots). Control experiment in the absence of [HTEOA][BF_4] (black squares) and in the absence of **1** (green squares) from the reaction mixture. Irradiation was performed using a Xe lamp (250 W) and a $\lambda < 420$ nm cut-off filter.

Using [Ru(bpy)$_3$][PF$_6$]$_2$ as a photosensitiser in CH$_3$CN

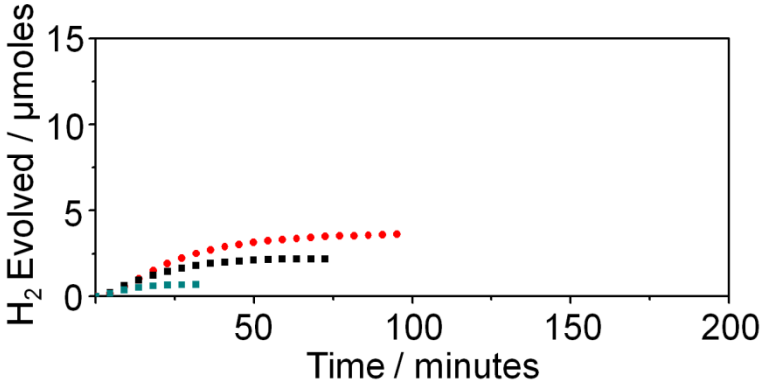

Fig. S12. Time dependent photo-induced H_2 evolution from a 5 mL degassed solution containing **1** (0.05 mM), [Ru(bpy)$_3$][PF_6]$_2$ (0.25 mM), TEOA (1 M) and [HTEOA][BF_4] (0.1 M) in CH_3CN at 293 K (red dots). Control experiment in the absence of [HTEOA][BF_4] (black squares) and in the absence of **1** (green squares) from the reaction mixture. Irradiation was performed using a Xe lamp (250 W) and a $\lambda < 420$ nm cut-off filter.

References

(1) Wang, Q.; Barclay, J. E.; Blake, A. J.; Davies, E. S.; Evans, D. J.; Marr, A. C.; McInnes, E. J. L.; McMaster, J.; Wilson, C.; Schröder, M. *Chem. Eur. J.* **2004**, *10*, 3384-3396.