Synthesis of novel heteroleptic oxothiolate Ni(II) complexes and evaluation of their catalytic activity for hydrogen evolution

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Supporting Information

Figures

Tables

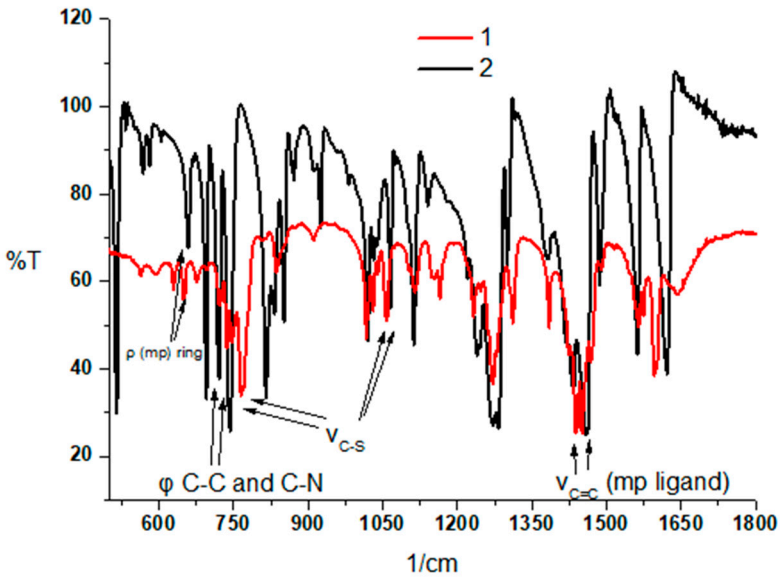
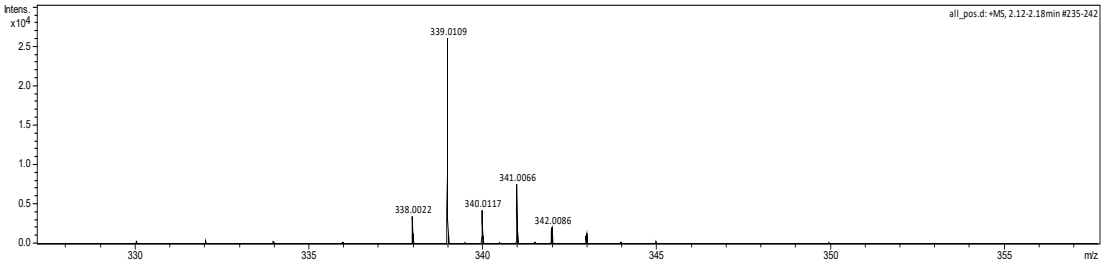
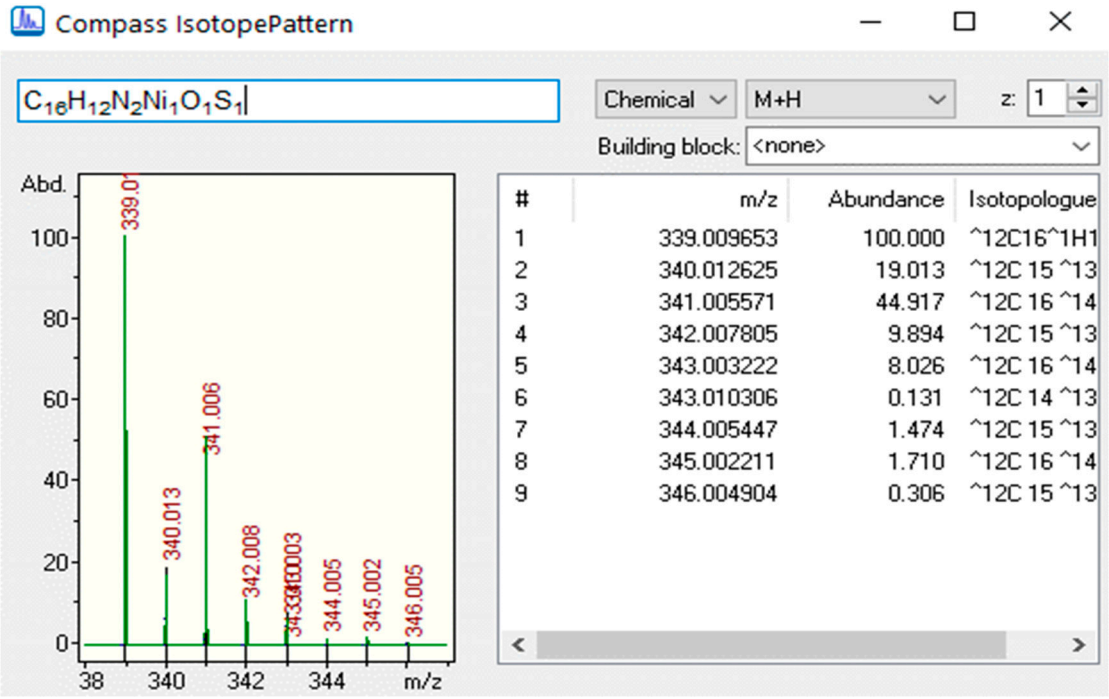


Figure S 1. *IR spectra of complexes* ***1*** *and* ***2****.*



a



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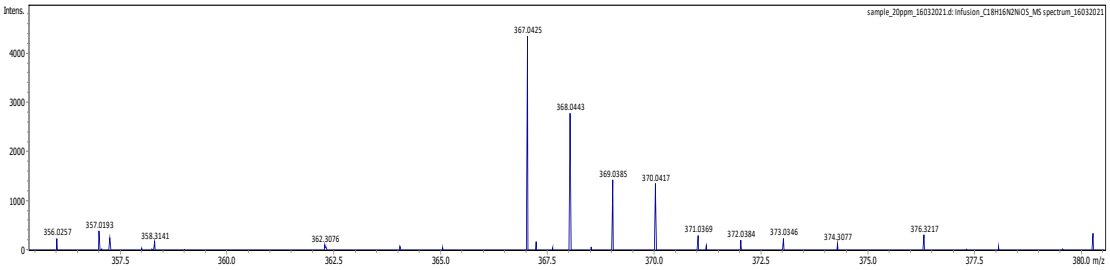

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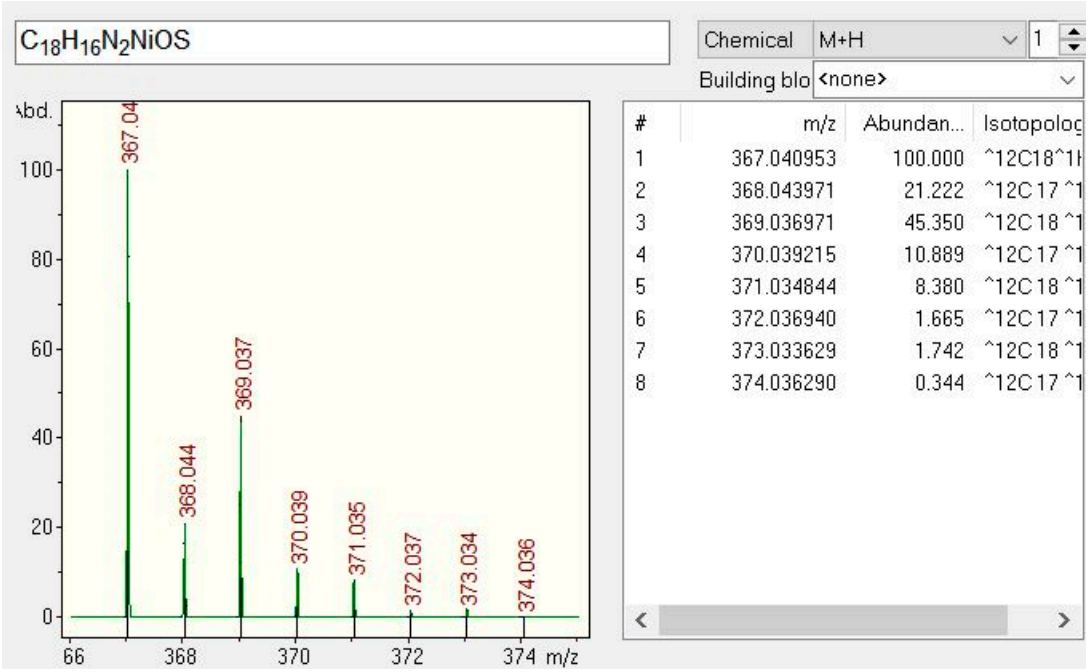


d

Figure S2. a. HRMS of the Complex **1**. b. Compass IsotopePattern window of Complex **1**. Fig. S2a, b display the mass spectrum of the ions on which the identification of **1** was performed. Also, the theoretical mass spectrum (in green color) of the desired m / z and its isotopes were depicted (Figure S2 b). At the Compass Isotope Pattern window, the theoretical mass spectrum and isotope profile of that compound. c. HRMS of the Complex **2**. d. Compass IsotopePattern window of Complex **2**. Fig. S2c, d display the mass spectrum of the ions on which the identification of **2** was performed. Also, the theoretical mass spectrum (in green color) of the desired m / z and its isotopes were depicted (Figure S2 d). At the Compass Isotope Pattern window, the theoretical mass spectrum and isotope profile of that compound.

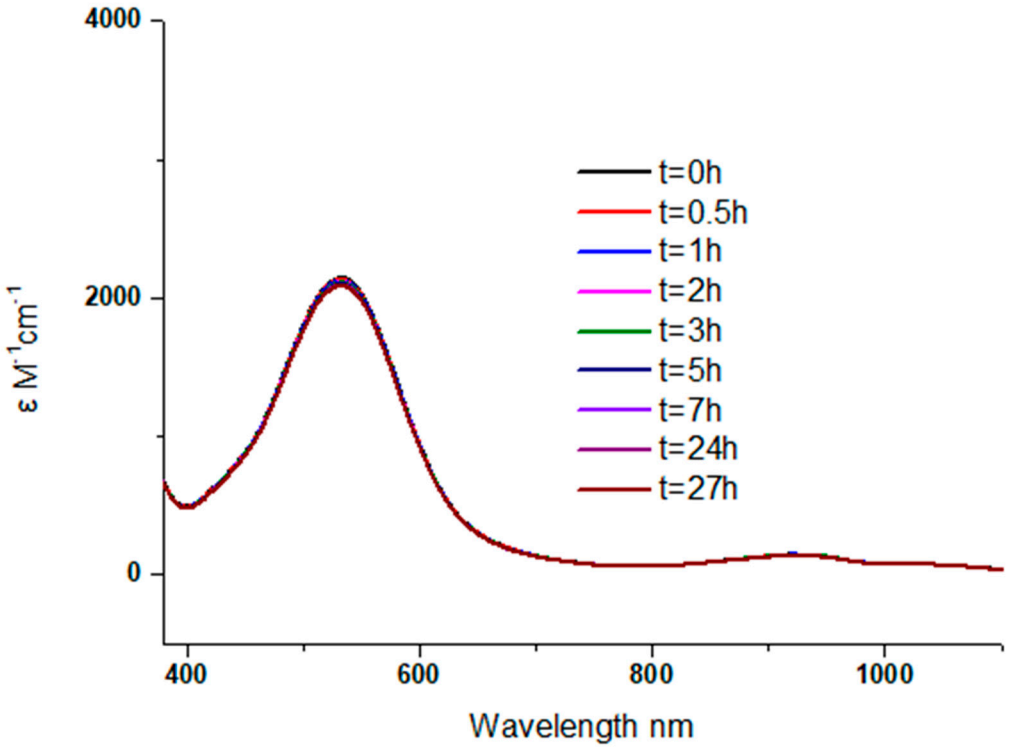


Figure S 3. *Spectroscopical study of complex* ***1*** *in DMF via the use of UV-Vis spectra without irradiation.*

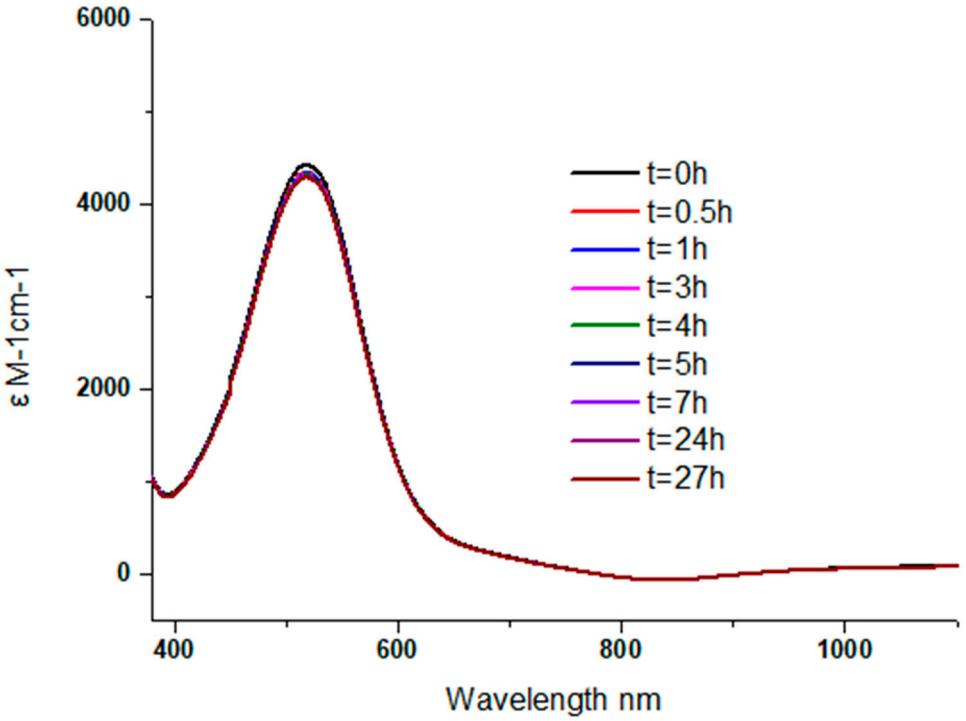


Figure S 4. *Spectroscopical study of complex* ***2*** *in DMF via the use of UV-Vis spectra without irradiation.*

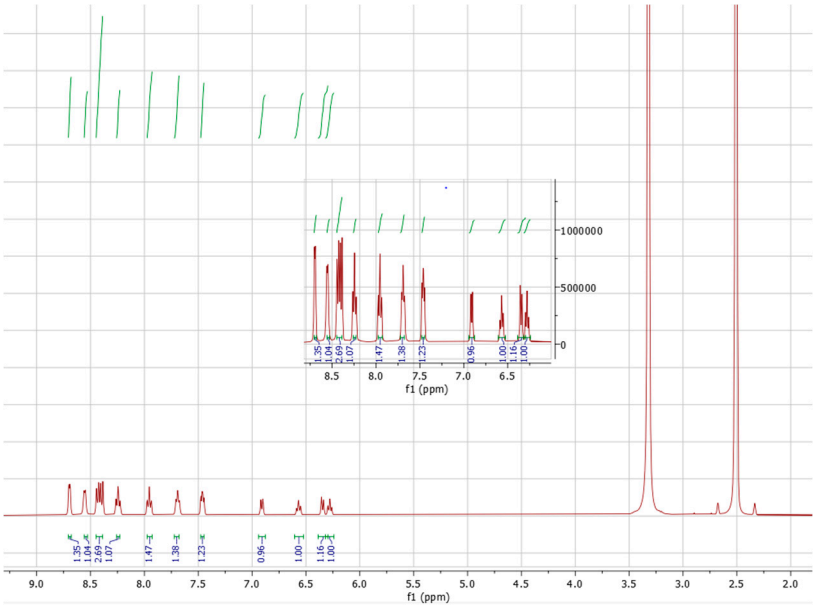


Figure S 5. *^{1}H-NMR spectrum of complex **1** in Dimethyl Sulphoxide-d^{6}.*

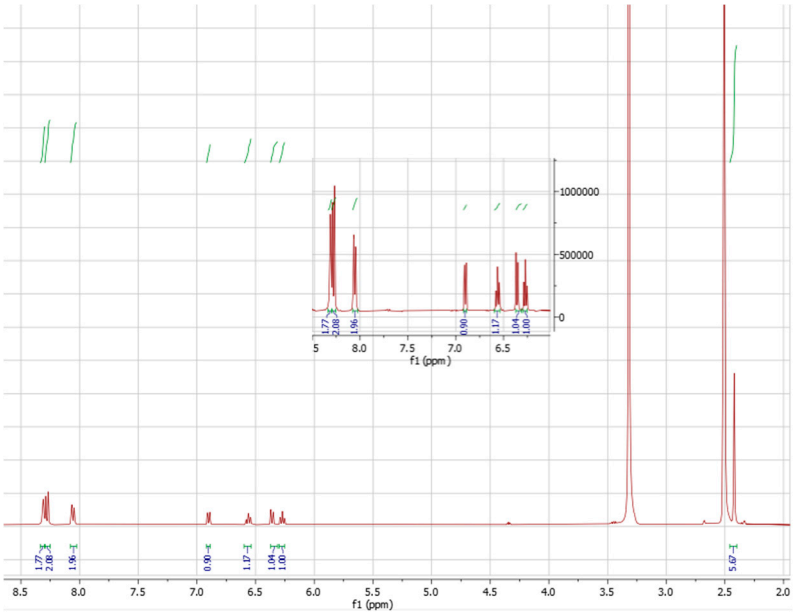
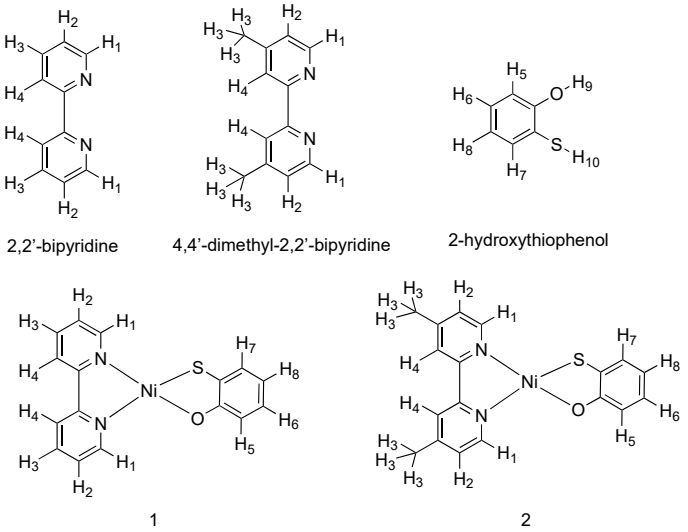


Figure S 6*. ^{1}H- NMR spectrum of complex **2** in Dimethyl Sulphoxide-d^{6}.*

***Table S 1**. [1]H-NMR shift sin ppm for **1, 2** and the free ligands*

Protons	**1 in DMSO-d[6]**	**2 in DMSO-d[6]**	**Bipyridine in DMSO-d[6] [1]**	**4,4-dimethyl-bipyridine in DMSO-d[6] [2]**	**2-hydroxythiophenol in choloroform-d[1] [3]**
H1	8.55 (d, 1H) 8.70 (d, 1H)	7.51 (d, 2H)	8.43 (s, 2H)	7.41 (d, 2H)	
H2	7.95 (t, 1H) 8.24 (t, 1H)	8.26 (d, 2H)	7.99 (s, 2H)	8.12 (d, 2H)	
H3	7.45 (t, 1H) 7.69 (t, 1H)	2.47 (s, 6H)	7.49 (s, 2H)	-	
H4	8.41 (m, 2H)	8.31 (s, 2H)	8.73 (s, 2H)	8.47 (s, 2H)	
H5	6.91 (d, 1H)	6.88 (d, 1H)			7.22 (dd, 1H)
H6	6.56 (t, 1H)	6.54 (t, 1H)			6.85 (t, 1H)
H7	6.35 (d, 1H)	6.31 (d, 1H)			7.06 (dd, 1H)
H8	6.27 (t, 1H)	6.25 (t, 1H)			6.79 (t, 1H)
H9					5.35 (s, 1H)
H10					3.40 (s, 1H)



*For comparison, numbering for ligands is in accordance with **1**.

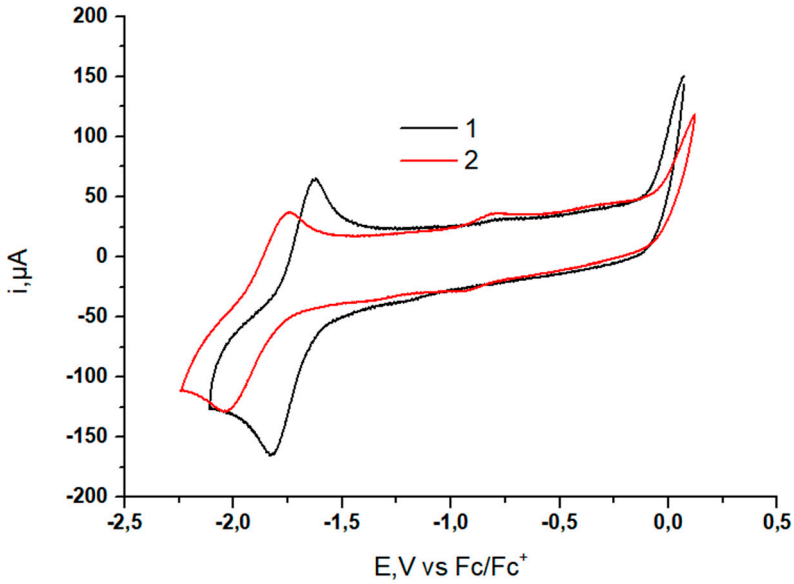


Figure S7. Cyclic voltammograms of a. **1** (10^{-3}M) in DMF (black) and b. **2** (10^{-3}M) in DMF (red), 0,1M n-Bu_4NPF_6, a glassy carbon as a working electrode, an Ag/AgCl as a reference electrode and a Pt wire as a counter electrode. The scan rate was 100mV/s.

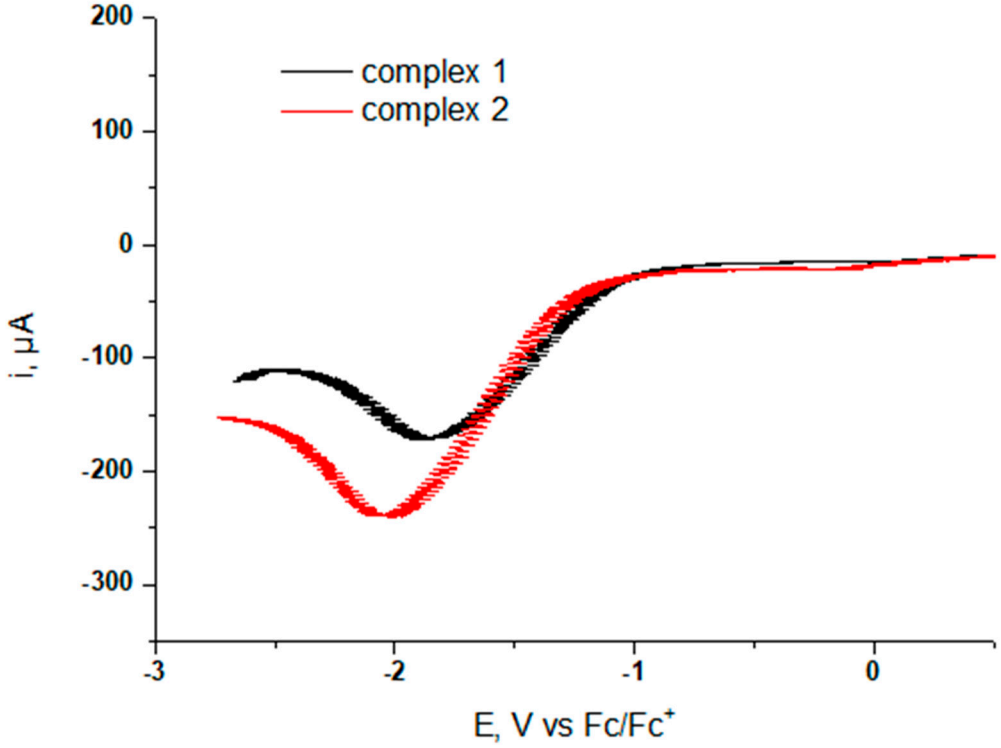


Figure S8. Square wave Voltammetry in DMF of complex **1** (black) and complex **2** (red), with 0,1M n-Bu_4NPF_6, a glassy carbon as a working electrode, an Ag/AgCl as a reference electrode and a Pt wire as a counter electrode. Pulse amplitude 50mV, step potential 20mV.

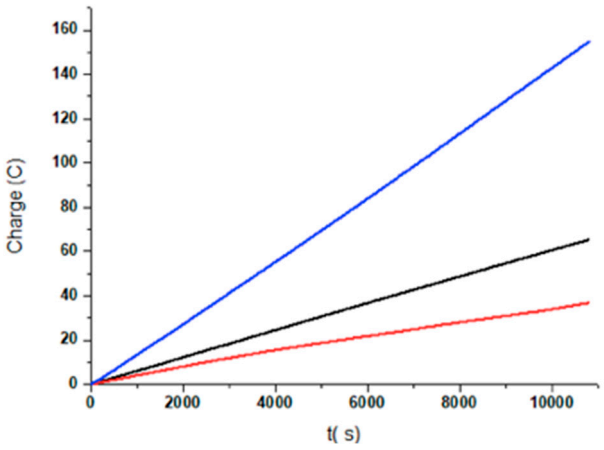


***Figure S 9**. Chronocoulometry for bulk electrolysis vs Fc/Fc^+ of DMF solution with 10mM TFA, with complex **1** at -1.66V (black), with complex **2** at -1.74V (blue) and with the absence of catalysts at -1.74V (red). 0,1M n-Bu_4NPF_6, a graphite rod as a working electrode, an Ag/AgCl as a reference electrode and a Pt wire as a counter electrode was used.*

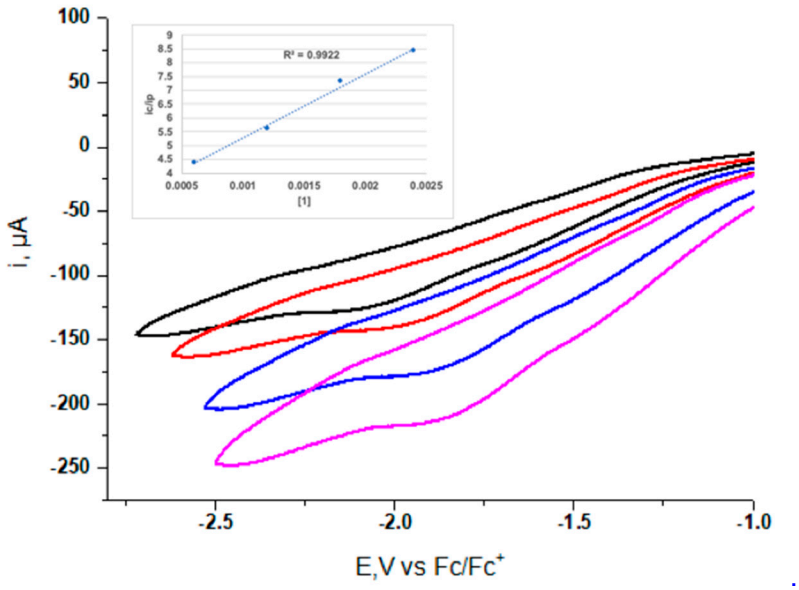


Figure S 10. *CVs in DMF with 0.1 M n-Bu$_4$NPF$_6$ containing 40 mM TFA with 0.6 mM* ***1*** *(black), 1.2 mM* ***1*** *(red), 1.8 mM* ***1*** *(blue), and 2.4 mM* ***1*** *(pink) at u = 100 mV/s. Inset ic/ip= f[1]*

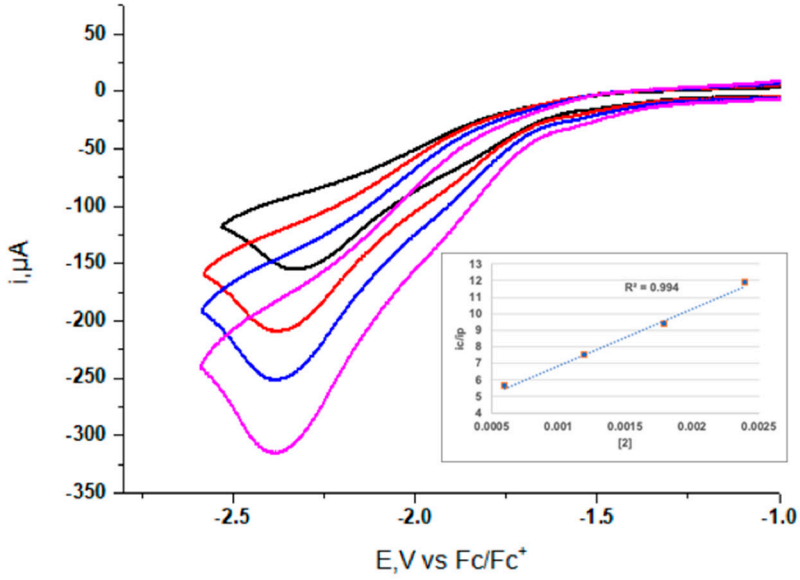


Figure S 11. *CVs in DMF with 0.1 M n-Bu$_4$NPF$_6$ containing 40 mM TFA with 0.6 mM* ***2*** *(black), 1.2 mM* ***2*** *(red), 1.8 mM* ***2*** *(blue), and 2.4 mM* ***2*** *(pink) at u = 100 mV/s. Inset ic/ip= f[2]*

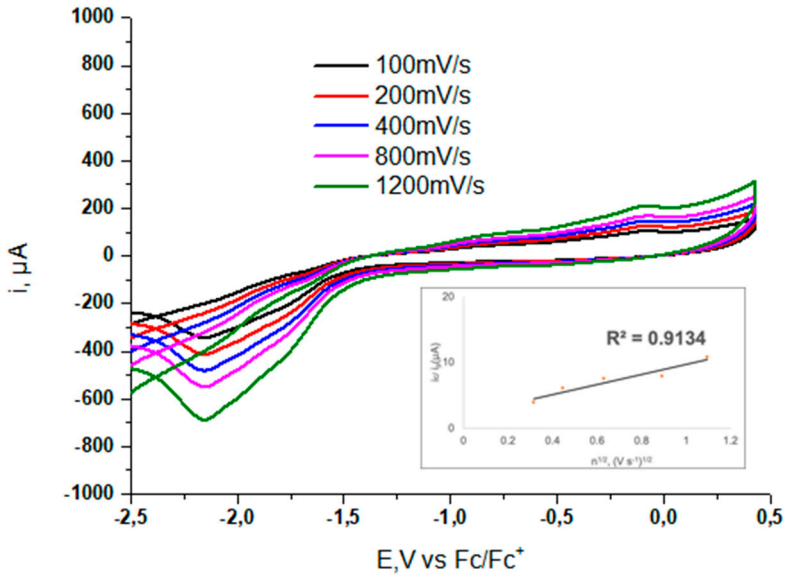


***Figure S 12**. Scan rate dependent cyclic voltammograms of catalyst **1** recorded from 0.1 V/s to 1.2 V/s in DMF and Cottrell plots of peak current versus the square root of scan rate. CVs were collected in DMF with 0.1 M n-Bu$_4$NPF$_6$ as supp. electrolyte using a glassy carbon (work elec.), platinum wire (count elec.) and Ag/Ag$^+$ (ref. elec.). All the potentials were referenced vs Fc/Fc$^+$*

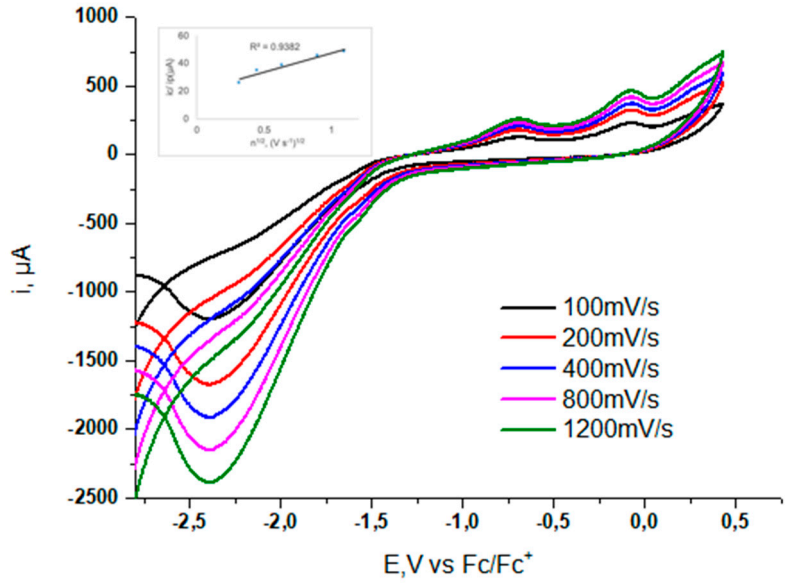


***Figure S 13**. Scan rate dependent cyclic voltammograms of catalyst **2** recorded from 0.1 V/s to 1.2 V/s in DMF and Cottrell plots of peak current versus the square root of scan rate. CVs were collected in DMF with 0.1 M n-Bu$_4$NPF$_6$ as supp. electrolyte using a glassy carbon (work elec.), platinum wire (count elec.) and Ag/Ag$^+$ (ref. elec.). All the potentials were referenced vs Fc/Fc$^+$.*

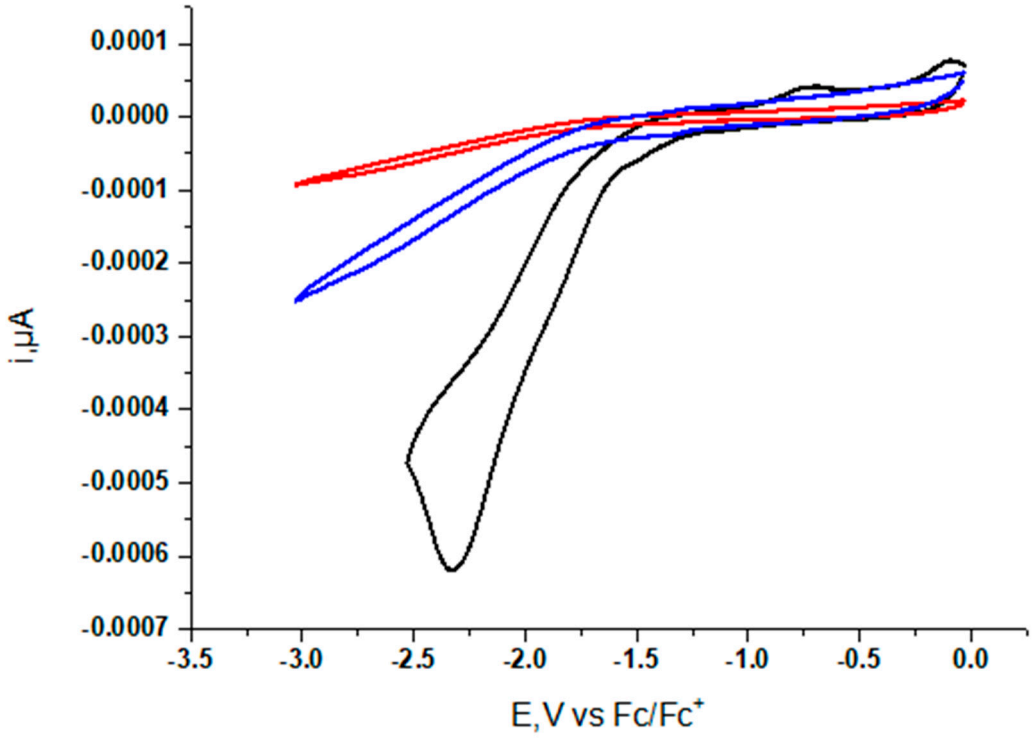


***Figure S 14**. Rinse tests for **2** in the presence of 12mM of TFA: (black) cyclic voltammogram in the presence of catalyst (10^{-3}M) (red) cyclic voltammogram in the absence of catalyst vs Fc/Fc^{+} after linear sweep voltammetry, (blue) cyclic voltammogram in the absence of catalyst vs Fc/Fc^{+} after 3 min potential application (glassy carbon working electrode).*

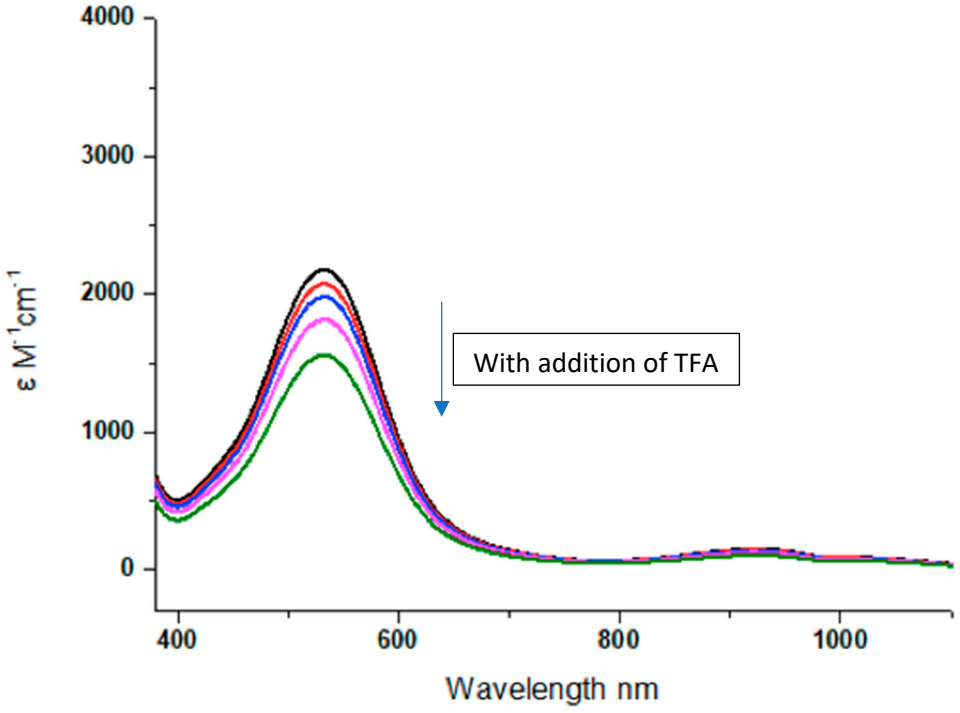


***Figure S 15.** UV-Vis spectrum of the complex **1** (10^{-3}M) in DMF with addition of TFA 0-1eq.*

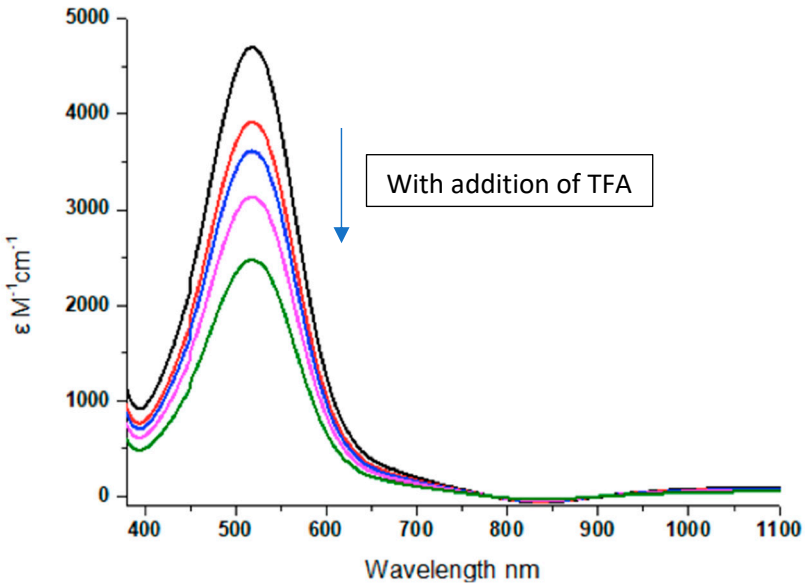


Figure S 16. *UV-Vis spectrum of the complex* ***2*** *(10^{-3}M) in DMF with addition of TFA 0-0.8eq.*

Table S 2. *Absorption maxima of CdTe-QDs TGA coated in DMF: H_2O 1:2.*

CdTe-QD	Absorbance Wavelength in DMF/ H_2O
QD-A	427nm
QD-B	454nm
QD-C	499nm
QD-D	525nm
QD-E	558nm

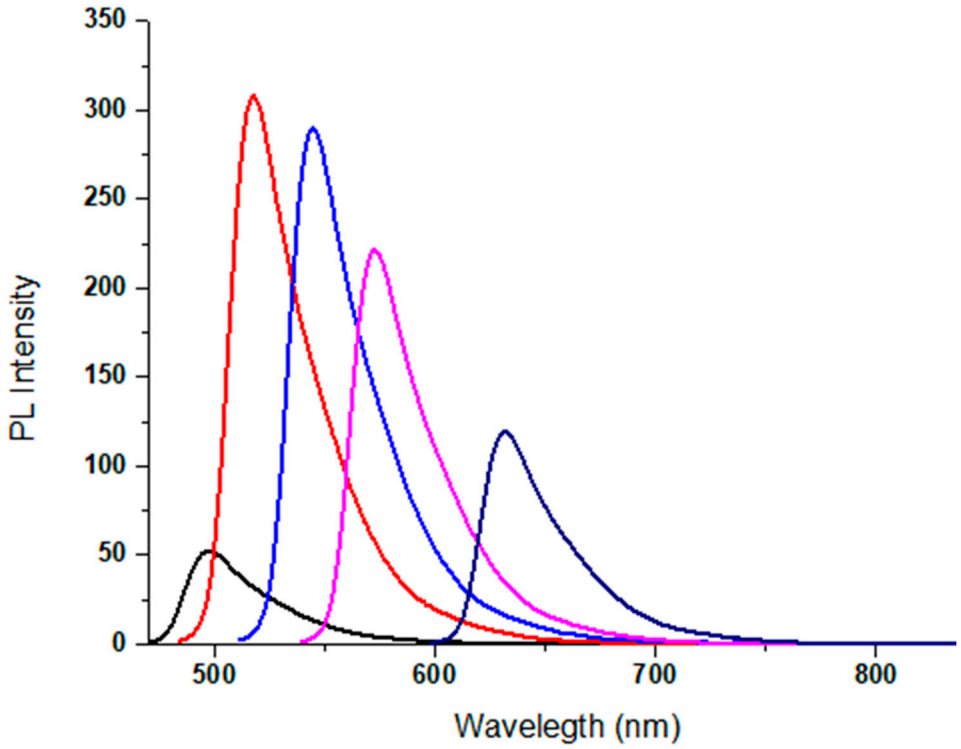


Figure S 17. *Emmision spectra of CdTe-QDs- TGA coated in H_2O. QD-A (black), QD-B (red), QD-C (blue), QD-D (pink), QD-E (deep blue).*

Table S 3*.Study of the photocatalytic hydrogen production via the use of Complex* ***1*** *with CdTe QDs-TGA coated as PS, TEOA and AscOH as electron donor, in a solvent system DMF: H_2O.*

Entry	Complex	PS	Electron Donor	Solvent	pH	TON	TOF	t_{ir}
1	**1** (5* 10^{-6}M)	CdTe-TGA B (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	953.21	7.94	120
2	**1** (5* 10^{-6}M)	CdTe-TGA D (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	763.42	6.36	120
3	**1** (5* 10^{-6}M)	CdTe-TGA C (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	931.97	7.77	120
4	**1** (5* 10^{-6}M)	CdTe-TGA A (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	967.32	8.06	120
5	**1** (5* 10^{-6}M)	CdTe-TGA E(40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	456.78	3.81	120
6	**1** (5* 10^{-6}M)	CdTe-TGA B (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	6243.4	52.03	120
7	**1** (5* 10^{-6}M)	CdTe-TGA C (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	6349.7	52.91	120
8	**1** (5* 10^{-6}M)	CdTe-TGA D (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	6781.2	56.51	120
9	**1** (5* 10^{-6}M)	CdTe-TGA A (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	5032.4	41.94	120

10	**1** ($5^* 10^{-6}$M)	CdTe-TGA E (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	2989.0	24.90	120
11	**1** (10^{-4}M)	CdTe-TGA A (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	155.36	1.29	120
12	**1** (10^{-6}M)	CdTe-TGA A (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	412.78	3.44	120
13	**1** (10^{-5}M)	CdTe-TGA A (40μM)	TEOA (0.1M)	DMF:H_2O (1:2)	10.55	931.50	7.76	120
14	**1** (10^{-5}M)	CdTe-TGA A(40μM)	TEOA (1M)	DMF:H_2O (1:2)	10.55	902.47	7.52	120
15	**1** (10^{-4}M)	CdTe-TGA D (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	856.31	7.14	120
16	**1** (10^{-6}M)	CdTe-TGA D (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	112.80	0.94	120
17	**1** (10^{-5}M)	CdTe-TGA D (40μM)	AscOH (0.5M)	DMF:H_2O (1:2)	4.5	6700.23	55.84	120
18	**1** (10^{-5}M)	CdTe-TGA D (40μM)	AscOH (1M)	DMF:H_2O (1:2)	4.5	6692.76	55.77	120
19	**1** (10^{-5}M)	CdTe-TGA D (40μM)	AscOH (0.1M)	DMF:H_2O (1:30)	4.5	2056.78	17.14	120

Table S 4*.Study of the photocatalytic hydrogen production via the use of Complex* ***2*** *with CdTe QDs-TGA coated as PS, TEOA and AscOH as electron donor, in a solvent system DMF: H_2O*

Entry	Complex	PS	Electron Donor	Solvent	pH	TON	TOF	t_{ir}
1	**2** ($5^* 10^{-6}$M)	CdTe-TGA B (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	85.4	0.71	120
2	**2** ($5^* 10^{-6}$M)	CdTe-TGA D (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	57.2	0.48	120
3	**2** ($5^* 10^{-6}$M)	CdTe-TGA C 40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	46.7	0.39	120
4	**2** ($5^* 10^{-6}$M)	CdTe-TGA A (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	98.6	0.82	120
5	**2** ($5^* 10^{-6}$M)	CdTe-TGA E (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	102.7	0.86	120
6	**2** ($5^* 10^{-6}$M)	CdTe-TGA B (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	4056.9	33.81	120
7	**2** ($5^* 10^{-6}$M)	CdTe-TGA C (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	3112.3	25.94	120
8	**2** ($5^* 10^{-6}$M)	CdTe-TGA D (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	2345.9	19.55	120
9	**2** ($5^* 10^{-6}$M)	CdTe-TGA A (40μM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	3256.7	27.14	120
10	**2** (10^{-4}M)	CdTe-TGA E (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	5.82	0.24	24
11	**2** (10^{-6}M)	CdTe-TGA E (40μM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	67.16	2.80	24

12	**2** (10^{-5}M)	CdTe-TGA E (40µM)	TEOA (0.1M)	DMF:H_2O (1:2)	10.55	97.21	4.05	24
13	**2** (10^{-5}M)	CdTe-TGA E (40µM)	TEOA (1M)	DMF:H_2O (1:2)	10.55	97.60	4.07	24
14	**2** (10^{-4}M)	CdTe-TGA B (40µM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	3978.91	33.16	120
15	**2** (10^{-6}M)	CdTe-TGA B (40µM)	AscOH (0.1M)	DMF:H_2O (1:2)	4.5	3997.55	33.32	120
16	**2** (10^{-5}M)	CdTe-TGA B (C= 40µM)	AscOH (0.5M)	DMF:H_2O (1:2)	4.5	4012.80	33.44	120
17	**2** (10^{-5}M)	CdTe-TGA B (40µM)	AscOH (1M)	DMF:H_2O (1:2)	4.5	4047.69	33.73	120
18	**2** (10^{-5}M)	CdTe-TGA B (40µM)	AscOH (0.1M)	DMF:H_2O (1:30)	4.5	782.40	6.52	120

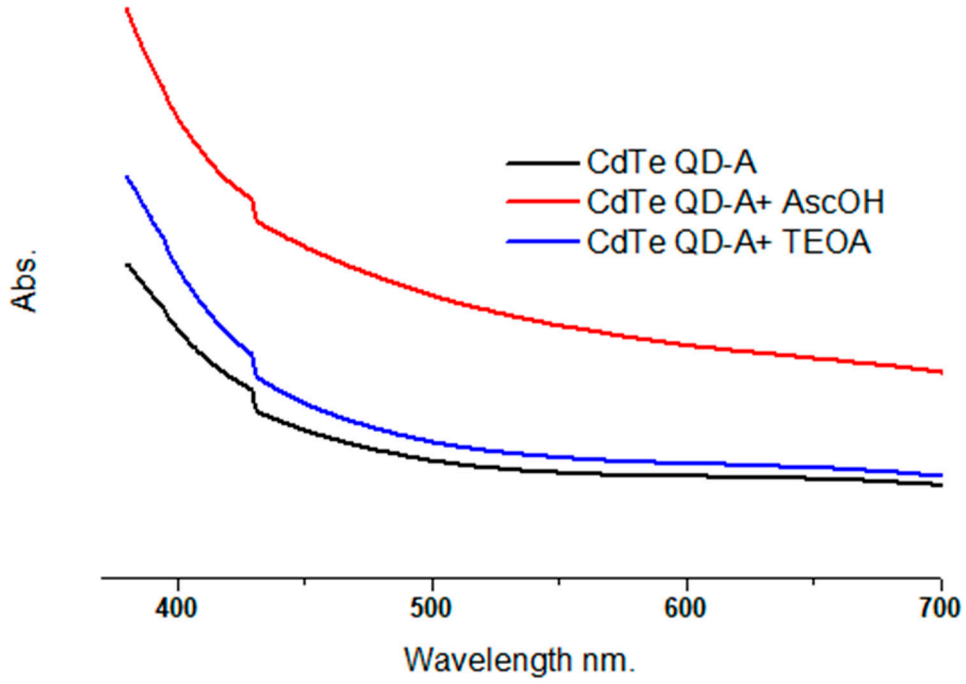


Figure S 18. *UV-Vis spectra of CdTe-QD A in DMF/H_2O 1: 2 without an electron donor (black), with AscOH 0.5M (red), with TEOA 0.5M (blue).*

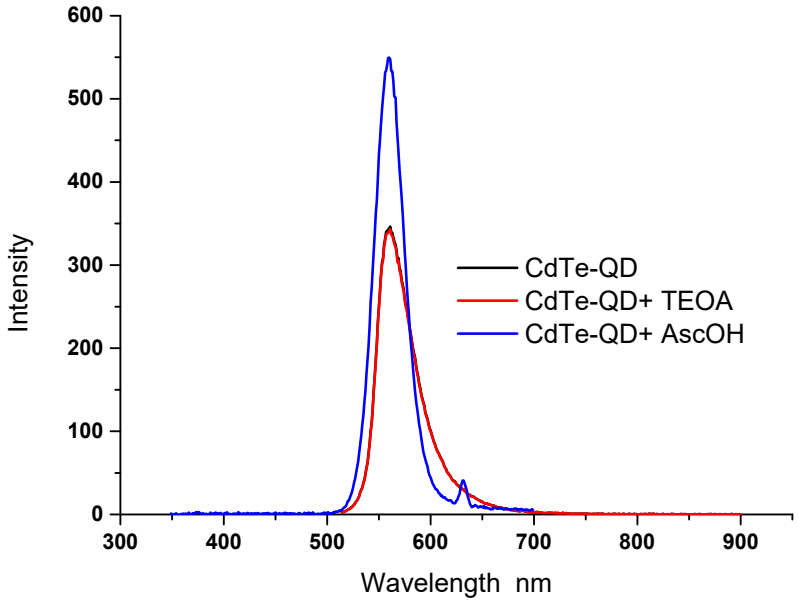


Figure S 19. *Emission spectra of CdTe-QD C in DMF/H_2O 1: 2 without an electron donor (black), with TEOA 0.5M (red), with AscOH 0.5M (blue).*

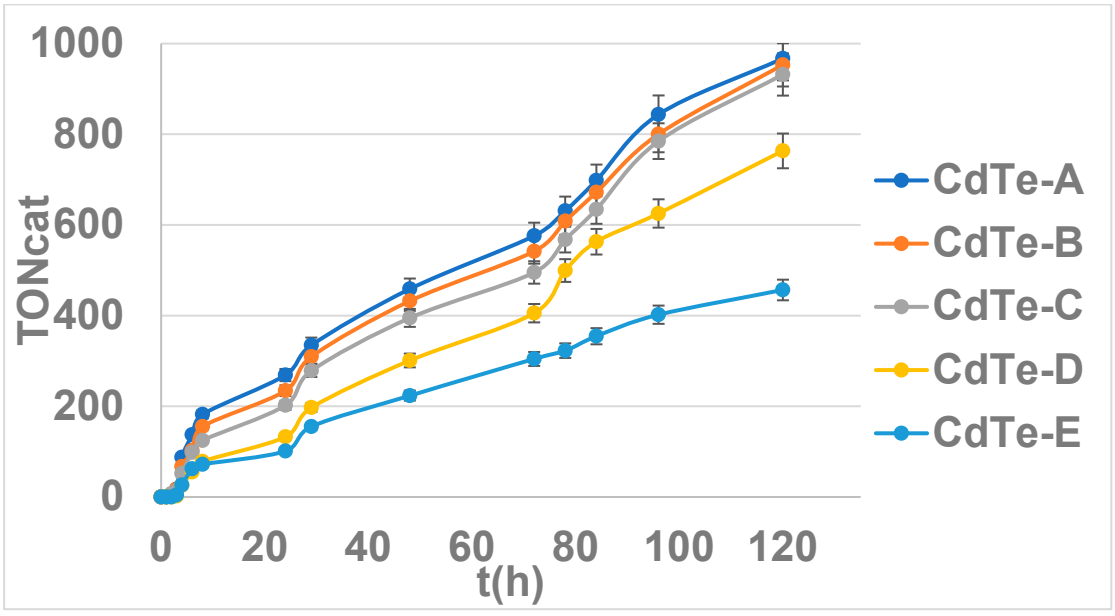


Figure S 20. *Light-driven hydrogen production from a system containing complex **1** at 5*10^{-6}M, TEOA (0.5 M) in DMF: H_2O 1:2 at pH 4.5 with different sized TGA-coated CdTe QDs at 40.0 μM A (blue), B (red), C (green), D (purple), E (light blue) , F (orange) upon irradiation for 120 hours at 25 °C and 1 atm.*

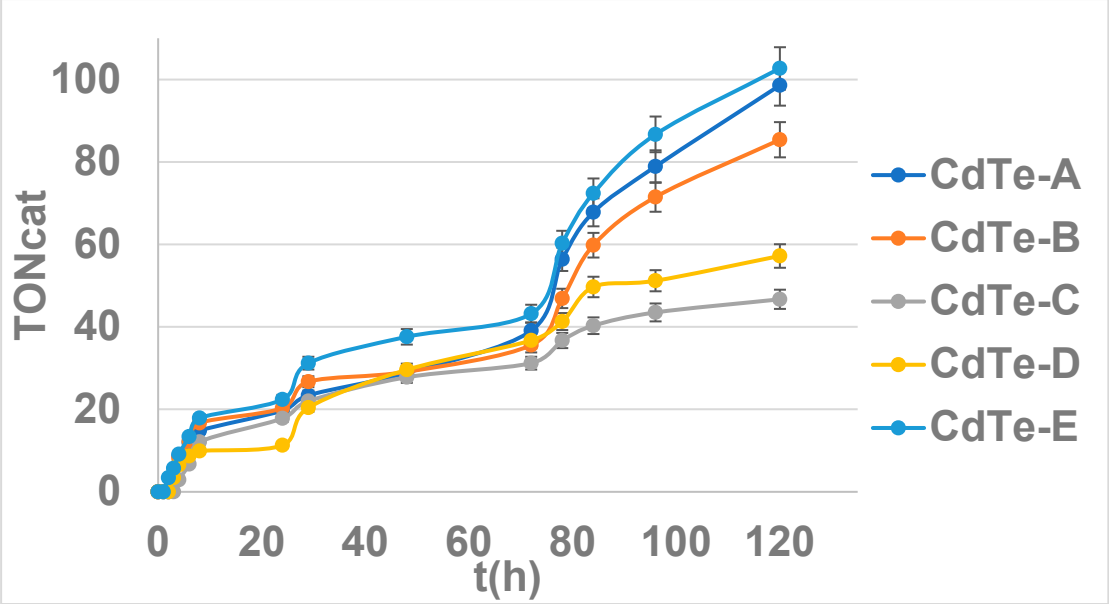


***Figure S 21**. Light-driven hydrogen production from a system containing complex **1** at 5*10-6M, TEOA (0.5 M) in DMF: H_2O 1:2 at pH 4.5 with different sized TGA-coated CdTe QDs at 40.0 μM A (blue), B (red), C (green), D (purple), E (light blue) , F (orange) upon irradiation for 120 hours at 25 °C and 1 atm.*

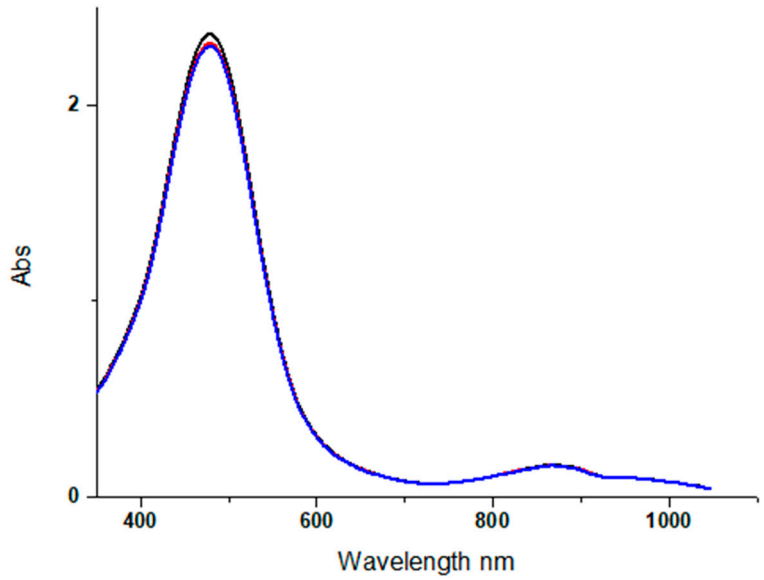


***Figure S 22**. UV-Vis spectra of complex **1** (10^{-4}M) in DMF: H_2O 1:2 with CdTe QDs-C 40μM and AscOH 0.1M, t=0h (black), t=48h (red), t=120h (purple).*

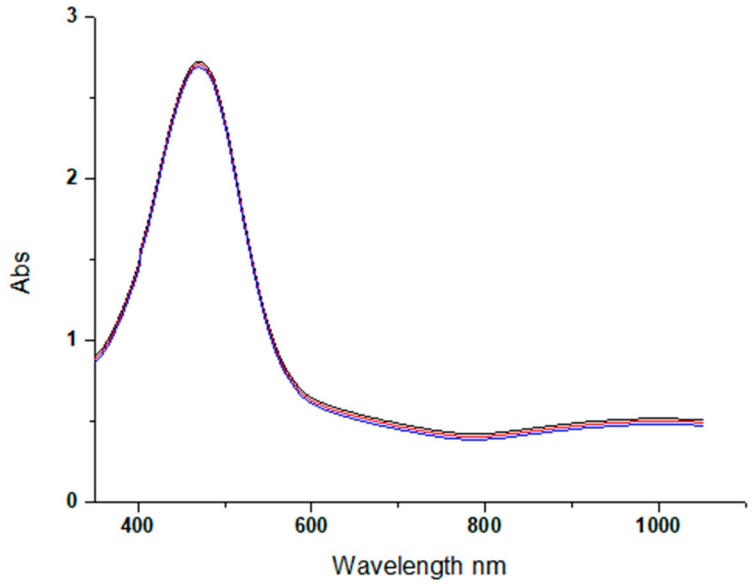


***Figure S 23**. UV-Vis spectra of complex **2** (10^{-4}M) in DMF: H_2O 1:2 with CdTe QDs-C 40μM and AscOH 0.1M, t=0h (black), t=48h (red), t=120h (purple).*

***Table S 5**.Study of the photocatalytic hydrogen production via the use of Complex **1** and **2** with different concentrations of the complexes with fluorescein as PS, TEOA as electron donor in a solvent system DMF: H_2O.*

Entry	Complex	PS	Electron Donor	Solvent	pH	TON	TOF	t_{ir}
1	**1** (5* 10^{-5}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	1045.67	43.57	24
2	**1** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	4697.29	195.72	24
3	**1** (5* 10^{-7}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	2111.29	87.97	24
4	**2** (5* 10^{-5}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	667.29	27.80	24
5	**2** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	390.56	16.27	24
6	**2** (5* 10^{-7}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	253.95	10.58	24

Table S 6*.Study of the photocatalytic hydrogen production via the use of Complex* ***1*** *and* ***2*** *with fluorescein as PS with different concentrations of Fl, TEOA as electron donor in a solvent system DMF: H_2O.*

Entry	Complex	PS	Electron Donor	Solvent	pH	TON	TOF	t_{ir}
1	**1** (5* 10^{-6}M)	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	245.79	10.24	24
2	**1** (5* 10^{-6}M)	Fl (2mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	387.97	16.16	24
3	**1** (5* 10^{-6}M)	Fl (4mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	59.69	2.49	24
4	**1** (5* 10^{-6}M)	Fl (8mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	88.42	3.68	24
5	**1** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	4697.29	195.72	24
6	**2** (5* 10^{-6}M)	Fl (2mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	376.47	15.69	24
7	**2** (5* 10^{-6}M)	Fl (4mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	91.20	3.80	24
8	**2** (5* 10^{-6}M)	F Fl (8mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	25.02	1.04	24
9	**2** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.1M)	DMF:H_2O (1:2)	10.55	372.02	15.50	24
10	**2** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	390.56	16.27	24

Table S 7*.Study of the photocatalytic hydrogen production via the use of Complex* ***1*** *and* ***2*** *with fluorescein as PS, TEOA as electron donor with different concentrations of TEOA, in a solvent system DMF: H_2O.*

Entry	Complex	PS	Electron Donor	Solvent	pH	TON	TOF	t_{ir}
1	**1** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.1M)	DMF:H_2O (1:2)	10.55	294.36	12.27	24
2	**1** (5* 10^{-6}M)	Fl (1mM)	TEOA (1M)	DMF:H_2O (1:2)	10.55	77.30	3.22	24
3	**1** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	4697.29	195.72	24
4	**2** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.1M)	DMF:H_2O (1:2)	10.55	372.02	15.50	24
5	**2** (5* 10^{-6}M)	Fl (1mM)	TEOA (1M)	DMF:H_2O (1:2)	10.55	368.13	15.34	24
6	**2** (5* 10^{-6}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	390.56	16.27	24

Table S 8*.Study of the photocatalytic hydrogen production via the use of Complex* ***1*** *and* ***2*** *with fluorescein as PS, TEOA as electron donor, in a solvent system DMF: H_2O with different solvent ratios and with additions to the photocatalytic system.*

Entry	Complex	PS	Electron Donor	Solvent	pH	TON	TOF	t_{ir}
1	**1** ($5^* 10^{-6}$M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:1)	10.55	599.46	24.98	24
2	**1** ($5^* 10^{-6}$M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:45)	10.55	502.52	20.93	24
3	**1** ($5^* 10^{-6}$M)	Fl (1mM) With addition of Fl 1mM after 24 hours	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	5719.59	119.16	48
4	**1** ($5^* 10^{-6}$M)	Fl (1mM)	TEOA (0.5M) With addition of TEOA 0.5M after 24 hours	DMF:H_2O (1:2)	10.55	5006.47	104.30	48
5	Mercury poisoning test **1** (C= $5^* 10^{-6}$M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	4265.81	177.74	24
6	**1** (C= $5^* 10^{-6}$M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	4697.29	195.72	24
7	**2** ($5^* 10^{-6}$M)	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:1)	10.55	153.30	6.39	24
8	**2** ($5^* 10^{-6}$M)	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:45)	10.55	1705.34	71.06	24
9	**2** ($5^* 10^{-6}$M)	Fl (0.8mM) With the addition of Fl 1mM after 24 hours	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	2234.18	46.55	48
10	**2** ($5^* 10^{-6}$M)	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:2)	10.55	1709.79	35.62	48

			With the addition of TEOA 0.5M after 24 hours					
11	Mercury poisoning test **2** (5* 10^{-6}M)	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:45)	10.55	1453.62	60.57	24
12	**2** (5* 10^{-6}M)	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:45)	10.55	1705.34	71.06	24

***Table S 9**. Study of the photocatalytic hydrogen production via the use of Complex **[Ni(mp$_2$)]$^-$**.*

Entry	Complex	PS	Electron Donor	Solvent	TON	t_{ir}
1	[Ni(mp$_2$)]$^-$ (5* 10^{-6}M)	Fl (1mM)	TEOA (0.5M)	DMF:H_2O (1:2)	1452.45	24
2	[Ni(mp$_2$)]$^-$ (5* 10^{-6}M)	CdTe- QD B 40μM	AscOH (0.1M)	DMF:H_2O (1:2)	3841.69	24

***Table S 10.** Control Experiments*

Entry	Complex	PS	Electron Donor	Solvent	TON	t_{ir}
1	**1** (5* 10^{-6}M)	-	TEOA (0.5M)	DMF:H_2O (1:2)	0	24
2	**2** (5* 10^{-6}M)	-	TEOA (0.5M)	DMF:H_2O (1:2)	0	24
3	-	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:2)	0	24
4	$NiCl_2$*$6H_2O$ (5* 10^{-6}M)	Fl (0.8mM)	TEOA (0.5M)	DMF:H_2O (1:2)	0	24
5	-	CdTe- QD A 40μM	TEOA (0.5M)	DMF:H_2O (1:2)	0	24
6	-	CdTe- QD C 40μM	TEOA (0.5M)	DMF:H_2O (1:2)	0	24
	-	CdTe- QD A 40μM	AscOH (0.1M)	DMF:H_2O (1:2)	0	24

	-	CdTe- QD C 40μM	AscOH (0.1M)	DMF:H_2O (1:2)	0	24

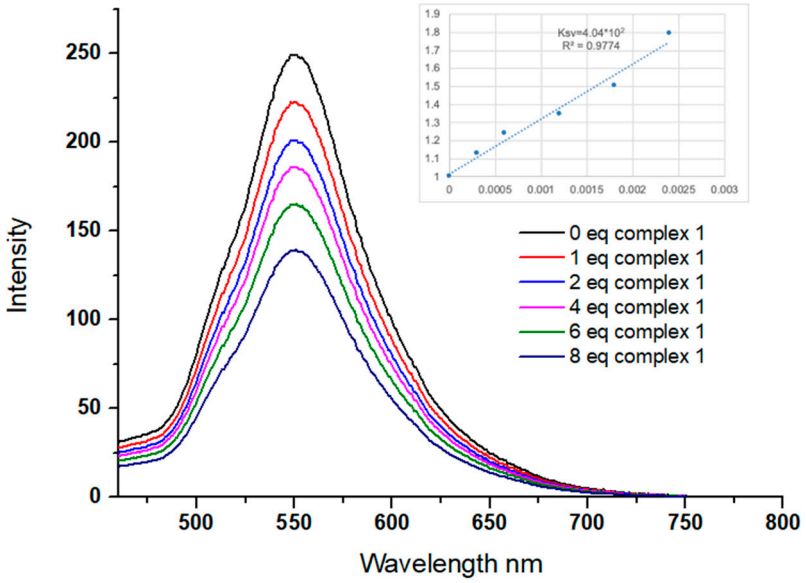


Figure S 24. *Emmision spectra of Fluorescein (0.3mM) in DMF/H_2O 1: 2 (black)and with the addition of 1-8 eq of complex* ***1****.*

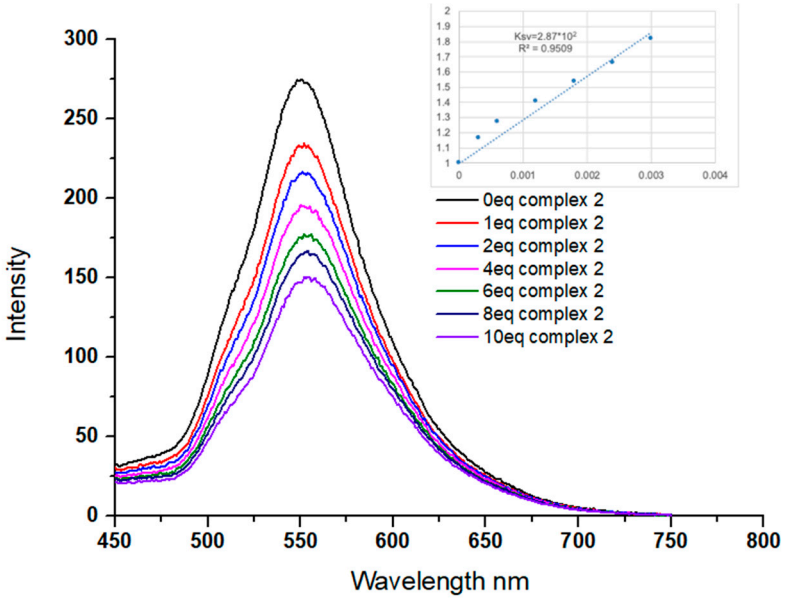


Figure S 25. *Emmision spectra of Fluorescein (0.3mM) in DMF/H_2O 1: 2 (black) and with the addition of 1-10 eq of complex* ***2****.*

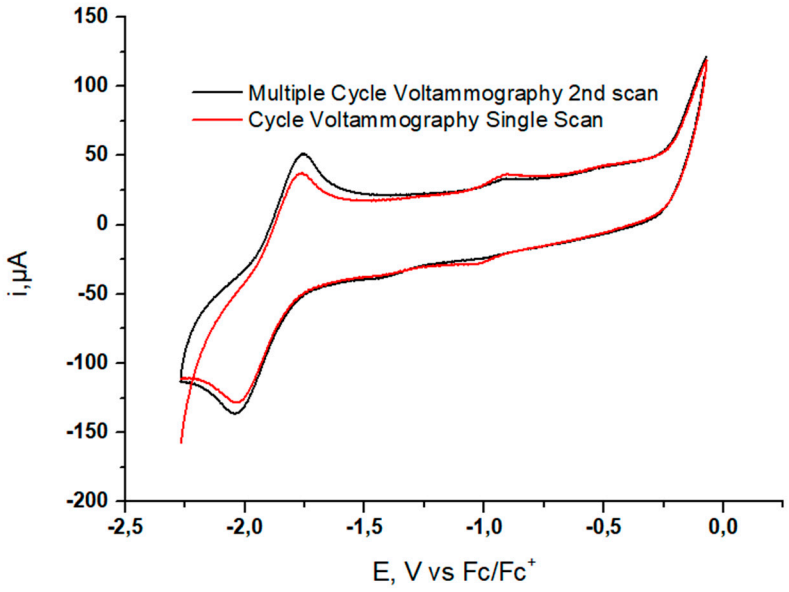


Figure S 26. Cyclic voltammograms of **2** (10^{-3}M) in DMF (black) with the Multiple Cycle scan method and **2** (10^{-3}M) in DMF (red) with the Single Scan method, with 0,1M n-Bu_4NPF_6, a glassy carbon as a working electrode, an Ag/AgCl as a reference electrode and a Pt wire as a counter electrode. The scan rate was 100mV/s.

References

1. Topchiyan, P.; Vasilchenko, D.; Tkachev, S.; Baidina, I.; Korolkov, I.; Sheven, D.; Berdyugin, S.; Korenev, S. New Heteroleptic Iridium(III) Nitro Complexes Derived from Fac-[Ir(NO2)3(H2O)3]. *Journal of Molecular Structure* **2019**, *1182*, 100–108, doi:10.1016/j.molstruc.2019.01.013.
2. Ghiasi, Z.; Amani, V.; Mirzaei, P.; Safari, N.; Abedi, A. Trichloridothallium(III) Complexes with Bipyridine Derivatives: From Structure to Luminescence Properties. *Aust. J. Chem.* **2013**, *66*, 676, doi:10.1071/CH12549.
3. Schaefer, T.; Veregin, R.P.; McKinnon, D.M. The Three Conformations of 3, 5-Dichloro-2-Hydroxythiophenol in Solution. *Canadian Journal of Chemistry* **1981**, *59*, 3204–3207.