Visible Light Promoted Hydration of Alkynes Catalyzed by Rhodium(III) Porphyrins

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1. General considerations

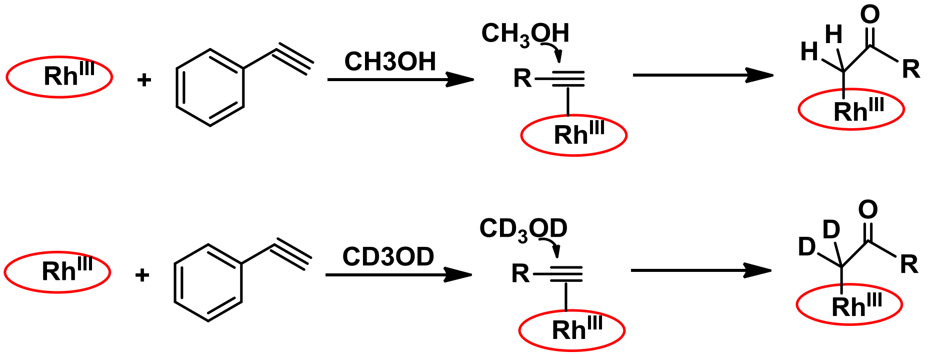
D_2O, CD_3OD and $CDCl_3$ were purchased from Cambridge Isotope Laboratory Inc.; tetra p-sulfonatophenyl porphyrin from Tokyo Chemical Industry (TCI); $(Rh(CO)_2Cl)_2$ from Strem Chemicals Inc.; and all other chemicals were purchased from Alfa Aesar or J&K Scientific Ltd. Unless otherwise noted and used as received. ^1H NMR spectra were recorded on a Bruker AVII-400 spectrometer at ambient temperature. GC-MS results were obtained by the Agilent 7980A/5975C GC/MSD system equipped with the DB-17MS (30m, 0.25mm, 0.25 μ m) column. GC results were obtained by the Agilent 7980A system equipped with the DB-5MS UI (30 m, 0.25 mm, 0.50 μm) column. ESI-MS results were obtained by a Bruker Apex IV FTMS. Visible light in the irradiation experiments was provided by a 500W high-pressure mercury lamp (CHF-XM35-500W, Beijing Trusttech Co., Ltd.,) equipped with a 420-780nm filter and the glass vessel was positioned about 25.0 cm away from the light source.

2. Preparation of $Na_3[(TSPP)Rh^{III}(D_2O)_2]$

$Na_3[(TSPP)Rh^{III}(H_2O)_2]$ was synthesized by following literature methods of Ashley.[1] The equilibrium distribution of $[(TSPP)Rh^{III}(D_2O)_2]^{-3}$, $[(TSPP)Rh^{III}(D_2O)(OD)]^{-4}$ and $[(TSPP)Rh^{III}(OD)_2]^{-5}$ were reported in the previously published paper.[2] ^{1}HNMR (D_2O, 400 MHz) δ(ppm): 9.15 (s, 8H, pyrrole), 8.44 (d, 8H, o-phenyl, $J_{H\text{-}H}$ =8 Hz), 8.25 (d, m-phenyl, $J_{H\text{-}H}$=8 Hz). The stock solution of (TPPS)Rh^{III} was prepared in H_2O solution.

3. Synthesize the key intermediate([(TSPP)Rh-CH_2COPh]$^{4-}$) in situ

Phenylacetylene (0.2 mmol), hydrochloric acid (6 µl, 0.12M) and (TSPP)$Rh^{III}(H_2O)_2$ (2 µmol) were mixed in 0.4 ml CD_3OD in a J. Young Valve NMR tube. The sample was degassed by three freeze-pump-thaw cycles. No ketones or [(TSPP)Rh-CH_2COPh]$^{4-}$ was formed at room temperature (Figure 1S-A). The reaction solution was heated at 60°C in an oil bath over 12 hours, ^{1}H NMR spectra was showed that a new signal formed at 8.70 ppm indicating [(TSPP)Rh-CH_2COPh]$^{4-}$ was formed(Figure 1S-B). After removal the solvent by rot-vap, 0.4 ml CD_3OD was added. From the ^{1}HNMR spectroscopy(Figure 1S-C), the resonances at 8.70 ppm (s, 8H); 8.30-8.10 ppm (m, 16H), 7.16 ppm (m, 1H), 6.67 ppm (m, 2H), 4.67 ppm (m, 2H), which are the same as those of independently synthesized [(TSPP)Rh-CH_2COPh]$^{4-}$. After heated the CD_3OD solution of [(TSPP)Rh-CH_2COPh]$^{4-}$ for 3 days, the resonance at 8.70 ppm was disappeared along with the formation of acetophenone (Figure 1S-D).



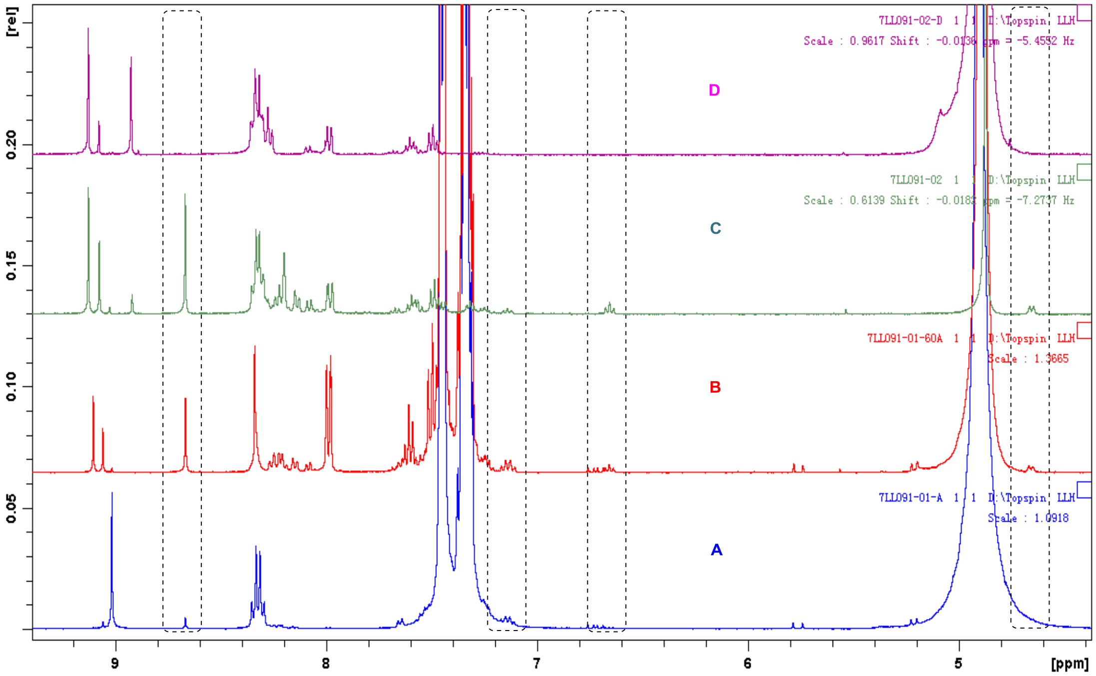
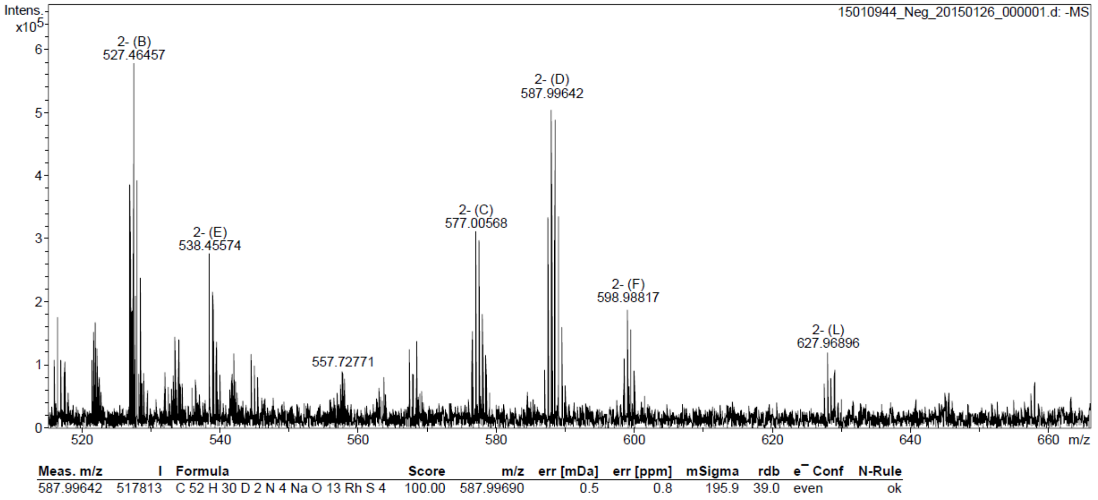


Figure 1S the reaction process of hydration of alkynes recorded by ^{1}H NMR spectra



Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
587.99642	517813	C 52 H 30 D 2 N 4 Na O 13 Rh S 4	100.00	587.99690	0.5	0.8	195.9	39.0	even	ok

Figure 2S ESI-MS of anion [(TSPP)Rh-CD$_2$COPh]$^{4-}$

(ESI-MS : 1175.99284 and Exact Mass: 1175.99489)

4. Independent synthesis of [(TSPP)Rh-CH$_2$COPh]$^{4-}$

Triethylamine(10μl 0.072mmol) and (TSPP)Rh^{III}(H$_2$O)$_2$ (2 μmol) were mixed in 0.4 ml CD$_3$OD in a J. Young Valve NMR tube. The sample was degassed by three freeze-pump-thaw cycles. (TSPP)Rh^I was formed after 1 hour at room temperature.[3] The solvent was removed under vacuum condition, the 2-bronoacetophenone was added, and in glove box the mixture was dissolved in the CD_3OD. The color was turned from brown to dark red indicating (TSPP)Rh-$CH_2COPh]^{4-}$ was formed. The ^1H NMR spectroscopy showed that the resonances at 8.70 (s, 8H); 8.30-8.10 (m, 16H), 7.16 (m, 1H), 6.67 (m, 2H), 4.67 (m, 2H), -4.68 (s, 2H), were the same as that of [(TSPP)Rh-$CH_2COPh]^{4-}$ observed in situ.

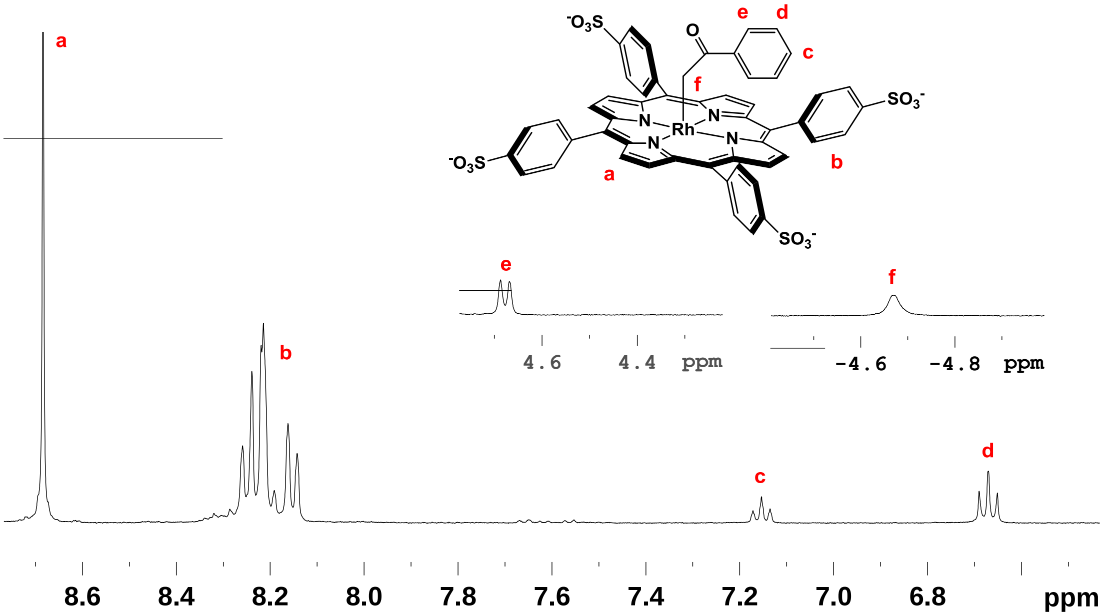
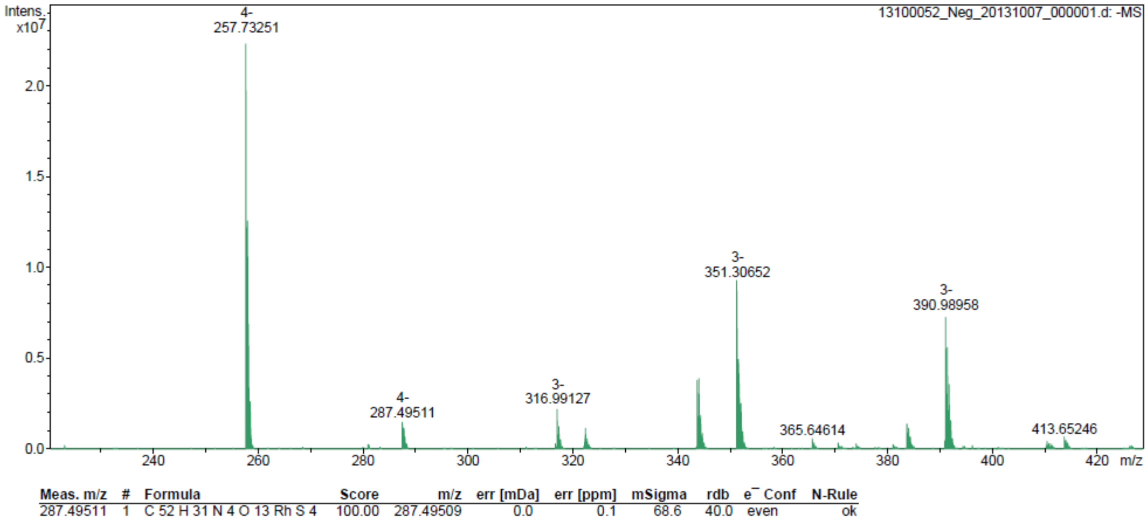


Figure 3S the ^1H NMR spectrum of [(TSPP)Rh-$CH_2COPh]^{4-}$



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e¯ Conf	N-Rule
287.49511	1	C 52 H 31 N 4 O 13 Rh S 4	100.00	287.49509	0.0	0.1	68.6	40.0	even	ok

Figure 4S ESI-MS of anion [(TSPP)Rh-$CH_2COPh]^{4-}$

(ESI-MS: 1149.98044 and Exact Mass: 1149.98255)

5. The dissociation of [(TSPP)Rh-$CH_2COPh]^{4-}$

Table 1S Measurement of the rate constant of the dissociation of $[(TSPP)Rh\text{-}CH_2COPh]^{4-}$ under visible light, pH~1.2, 298 K

entry	t / s	Intergration values of pyrrole ^1H NMR of $(TSPP)RhCH_2COPh$	Intergration values of pyrrole ^1H NMR of (TSPP)Rh-OH	$[(TSPP)RhCH_2\text{-}COPh]^{4-}$ mM	$\ln[(TSPP)RhCH_2\text{-}COPh]^{4-}$	k /s
1	0	8	0	0.0033	-5.71383	0.0497
2	7	8	5.93	0.00189	-6.2690	0.0497
3	14	8	10.81	0.0014	-6.56934	0.0497
4	21	8	17.02	0.00105	-6.85463	0.0497
5	28	8	25.64	0.000783	-7.15067	0.0497
6	35	8	43.84	0.000509	-7.58311	0.0497
7	42	8	57.92	0.000400	-7.82339	0.0497
8	49	8	98.5	0.000248	-8.3031	0.0497

Table 2S Measurement of the rate constant of the dissociation of $[(TSPP)Rh\text{-}CH_2COPh]^{4-}$ under visible light, pH~3.5, 298 K (The external standard was benzaldehyde dissolved in $CDCl_3$)

entry	t / s	Intergration values of aldehyde ^1H NMR of external standard	Intergration values of pyrrole ^1H NMR of $(TSPP)RhCH_2COPh$	$[(TSPP)RhCH_2\text{-}COPh]^{4-}$ mM	$\ln[(TSPP)RhCH_2\text{-}COPh]^{4-}$	k /s
1	0	1	11.63	0.0025	-5.99146	0.00239
2	7	1	11.27	0.00242	-6.02399	0.00239
3	12	1	10.82	0.00233	-6.06189	0.00239
4	17	1	10.63	0.00233	-6.06189	0.00239
5	25	1	10.54	0.00227	-6.08798	0.00239
6	32	1	10.08	0.00217	-6.13303	0.00239
7	92	1	8.93	0.00192	-6.25543	0.00239
8	182	1	7.00	0.0015	-6.50229	0.00239
9	272	1	5.78	0.00124	-6.69264	0.00239
10	392	1	4.41	0.00095	-6.95905	0.00239
11	512	1	3.37	0.00072	-7.23626	0.00239

Table 3S Measurement of the rate constant of the dissociation of $[(TSPP)Rh\text{-}CH_2COPh]^{4-}$ under visible light, pH~4.5, 298 K (The external standard was benzaldehyde dissolved in $CDCl_3$)

entry	t / s	Intergration values of aldehyde ^1H NMR of external standard	Intergration values of pyrrole ^1H NMR of $(TSPP)RhCH_2COPh$	$[(TSPP)RhCH_2\text{-}COPh]^{4-}$ mM	$ln[(TSPP)RhCH_2\text{-}COPh]^{4-}$	k /s
1	0	1	9.52	0.0025	-5.99146	0.00172
2	20	1	9.45	0.00248	-5.9995	0.00172
3	50	1	8.44	0.00222	-6.11025	0.00172
4	80	1	7.78	0.00204	-6.19481	0.00172
5	130	1	6.75	0.00177	-6.33678	0.00172
6	200	1	5.90	0.00155	-6.4695	0.00172
7	320	1	4.99	0.00131	-6.63773	0.00172
8	440	1	3.98	0.00105	-6.85897	0.00172
9	560	1	3.30	0.00087	-7.04702	0.00172
10	780	1	2.59	0.00068	-7.29342	0.00172

Table 4S Measurement of the rate constant of the dissociation of $[(TSPP)Rh\text{-}CH_2COPh]^{4-}$ under visible light, pH~6.5, 298 K (The external standard was benzaldehyde dissolved in $CDCl_3$)

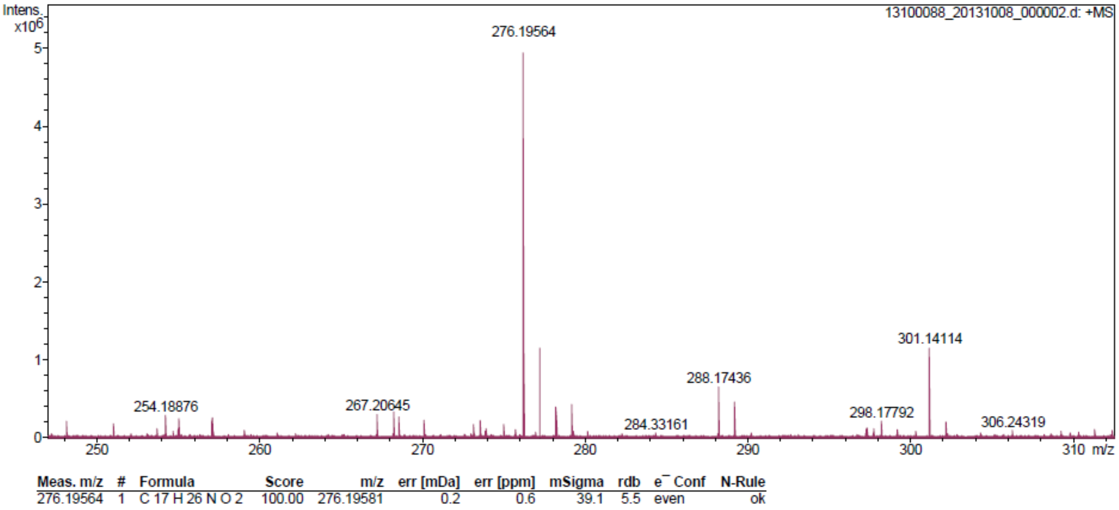
entry	t / s	Intergration values of aldehyde ^1H NMR of external standard	Intergration values of pyrrole ^1H NMR of $(TSPP)RhCH_2COPh$	$[(TSPP)RhCH_2\text{-}COPh]^{4-}$ mM	$ln[(TSPP)RhCH_2\text{-}COPh]^{4-}$	k /s
1	0	1	6.53	0.0025	-5.99146	0.00143
2	120	1	5.6	0.00214	-6.14695	0.00143
3	270	1	4.20	0.00161	-6.43152	0.00143
4	420	1	3.61	0.00138	-6.58567	0.00143
5	520	1	3.13	0.00120	-6.72543	0.00143
6	640	1	2.55	0.00098	-6.92796	0.00143
7	760	1	2.19	0.00084	-7.08211	0.00143
8	966	1	1.65	0.00063	-7.36979	0.00143

Table 5S Measurement of the rate constant of the dissociation of $[(TSPP)Rh\text{-}CH_2COPh]^{4-}$ in dark, pH~1.2, 298 K (The external standard was benzaldehyde dissolved in $CDCl_3$)

entry	t / min	Intergration values of aldehyde ^1H NMR of external standard	Intergration values of pyrrole ^1H NMR of $(TSPP)RhCH_2COPh$	$[(TSPP)RhCH_2\text{-}COPh]^{4-}$ mM	$\ln[(TSPP)RhCH_2\text{-}COPh]^{4-}$	k /h
1	0	1	13.027	0.0033	-5.71383	0.28581
2	32	1	8.856	0.00261	-5.94723	0.28581
3	78	1	6.079	0.00198	-6.22501	0.28581
4	122	1	4.58	0.00158	-6.45312	0.28581
5	205	1	2.859	0.00107	-6.83656	0.28581
6	294	1	1.652	0.000699	-7.26581	0.28581
7	454	1	0.737	0.000359	-7.93089	0.28581
8	478	1	0.665	0.0003143	-8.06503	0.28581

All of these reactions showed first-order kinetics.

The photo-cleavage of Rh-C bonds in $[(TSPP)Rh\text{-}CH_2COPh]^{4-}$ produces $(TSPP)Rh^{II}$ and CH_2COPh radical, which was trapped by TEMPO(TEMPO=2,2,6,6-Tetramethylpiperidine-1-piperidinyloxy) to form TEMPO-CH_2COPh **(Figure 5S). And the** $(TSPP)Rh^{II}$ reacts with $HOCH_3$ to form (TSPP)Rh-H and (TSPP)Rh-OCH_3.[4]



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
276.19564	1	C 17 H 26 N O 2	100.00	276.19581	0.2	0.6	39.1	5.5	even	ok

Figure 5S ESI-MS of TMEPOCH2COPh

(ESI-MS: 275.1877 and Exact Mass: 275.1885)

6. General Procedure for Rh-Catalyzed hydration of alkynes

To a 25 mL Schlenk flask sealed with a Teflon cap, 0.20 mmol alkynes, 2 μmol (TSPP)Rh^{III} and 1.0 ml methanol solution of trifluoromethanesulfonimide (0.06M) was added. After degassed by three freeze-pump-thaw cycles, the solution was stirred at room temperature under visible light irradiation for 12 hours. (500 W Hg lamp, 420-780 nm filter, 25 cm distance, 27 mW/cm^2)

7. The UV-vis absorption of the key intermediate([(TSPP)Rh-CH_2COPh]$^{4-}$)

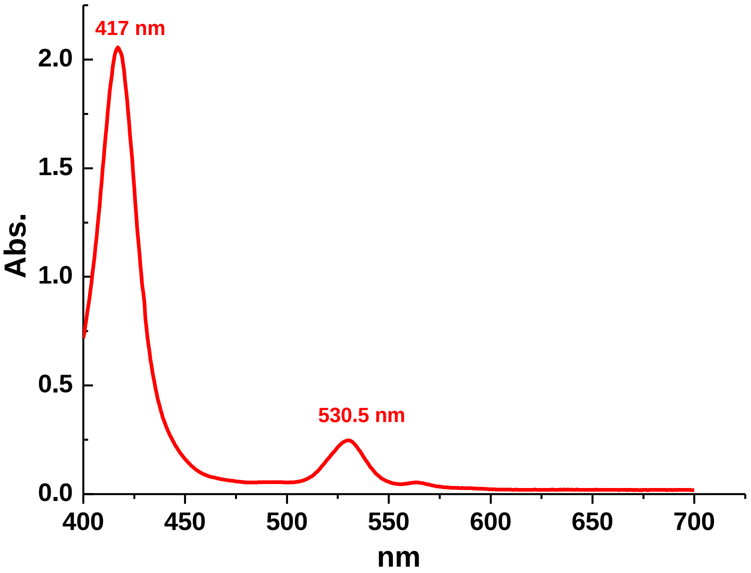


Figure 6S The UV-vis absorption of [(TSPP)Rh-CH_2COPh]$^{4-}$

The UV-vis absorption of [(TSPP)Rh-CH_2COPh]$^{4-}$ shows absorption bands that peak at 417.0 nm (Soret band) and 530.5 nm (Q band), which match well with the emission lines of our Hg lamp in the visible region (420, 430, 500, 520 and 550 nm).

Reference

(1) K. R. Ashley, S. B. Shyu and J. G. Leipoldt, *Inorg. Chem.*, 1980, **19**, 1613;

(2) X. Fu and B. B. Wayland, *J. Am. Chem. Soc.*, 2004, **126**, 2623;

(3) Z. Ling, L. Yun, L. Liu, B and X. Fu, *Chem. Commun.*, 2013, **49,** 4214**;**

(4) S. Li, W. Cui and B. B. Wayland, *Chem. Commun.* 2007, 4024.