Supporting Information

Thiophene-Modified Doubleshell Hollow g-C_3N_4 Nanosphere Boosts NADH Regeneration via Synergistic Enhancement of Charge Excitation and Separation

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Table S1. The calculated BET specific surface areas of different C_3N_4 materials

Material	**Specific surface area ($m^2\ g^{-1}$)**	**Pore size distribution (nm)**
Bulk C_3N_4	10.3	3.9
ATCN-DSCN-0	71.5	3.9
ATCN-DSCN-0.001	74.3	3.9
ATCN-DSCN-0.005	103.69	3.9
ATCN-DSCN-0.010	60.9	3.9

Table S2. Relative ratios of N-C=N and C=C of ATCN-DSCN-0 (undoped) and ATCN-DSCN-0.005 (doped) by C 1s spectral analysis.

	C 1s					
	N-C=N			C-C		
	Position	**Area**	**Area percentage(%)**	**Position**	**Area**	**Area percentage(%)**
undoped	288.0	13625.6	87.69	284.6	1912.6	12.31
doped	287.9	24236.9	77.80	284.6	6917.6	22.20

Table S3. Relative ratios of C-N=C, N-$(C)_3$ and C-N=C of ATCN-DSCN-0 (undoped) and ATCN-DSCN-0.005 (doped) by N 1s spectral analysis.

			undoped	doped
N 1s	C-N=C	Position	398.4	398.4
		Area	22614.6	41053.4
		Area percentage(%)	66.49	67.77
	N-$(C)_3$	Position	399.7	399.7
		Area	7667.9	12911.4
		Area percentage(%)	22.55	21.31
	C-N=C	Position	401.0	400.9
		Area	2116.4	3869.2
		Area percentage(%)	6.22	6.39
	π bonding	Position	404.5	404.4
		Area	1611.3	2746.7
		Area percentage(%)	4.74	4.53

Table S4. Relative ratios of S $2p_{3/2}$ and S $2p_{1/2}$ of ATCN-DSCN-0 (undoped) and ATCN-DSCN-0.005 (doped) by S 2p spectral analysis.

	S 2p					
	S $2p_{3/2}$			S $2p_{1/2}$		
	Position	**Area**	**Area percentage(%)**	**Position**	**Area**	**Area percentage(%)**
undoped	—	—	—	—	—	—
doped	163.9	381.3	66.67	164.9	190.6	33.33

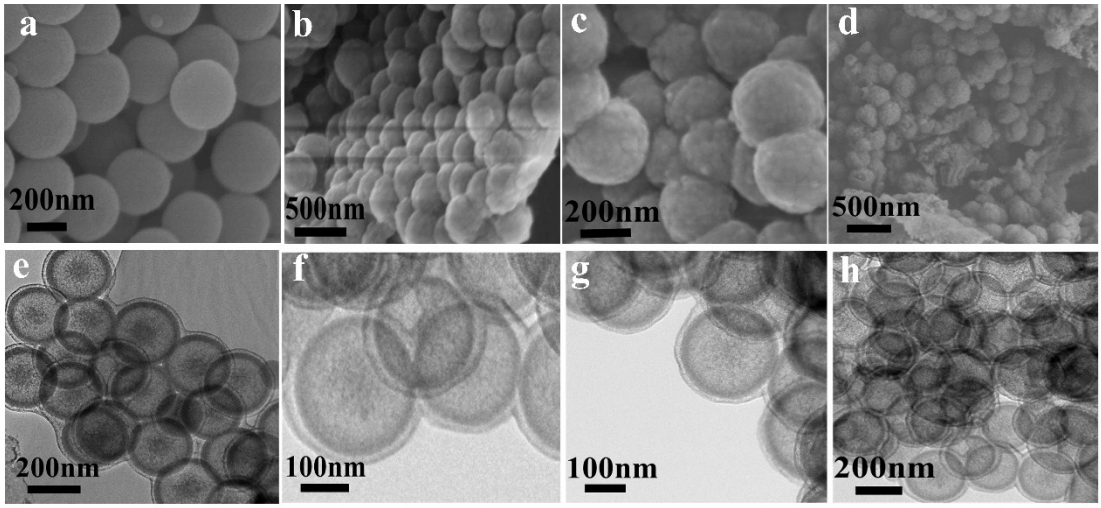

Figure S1. SEM and TEM images of SiO_2 (template), ATCN-DSCN-0 (undoped), ATCN-DSCN-0.001 (the weight ratio of ATCN: SiO_2 is 0.001) and ATCN-DSCN-0.010 (the weight ratio of ATCN: SiO_2 is 0.010). (a) SEM image of SiO_2, which can be seen the slippy surface of SiO_2. (b) TEM image of SiO_2, which can be seen the hollow doubleshell structure of SiO_2. (c) SEM image of ATCN-DSCN-0, which can be seen the uniformity and the rough surface of ATCN-DSCN-0. (d) TEM image of ATCN-DSCN-0, which can be seen the diameter and shell thickness of ATCN-DSCN-0. (e) SEM image of ATCN-DSCN-0.001, which can be seen the uniformity and the rough surface of ATCN-DSCN-0.001. (f) TEM image of ATCN-DSCN-0.001, which can be seen the diameter and shell thickness of ATCN-DSCN-0.001. (g) SEM image of ATCN-DSCN-0.010, which can be seen the uniformity and the rough surface of ATCN-DSCN- 0.010. (h) TEM image of ATCN-DSCN-0.010, which can be seen the diameter and shell thickness of ATCN-DSCN-0.010.

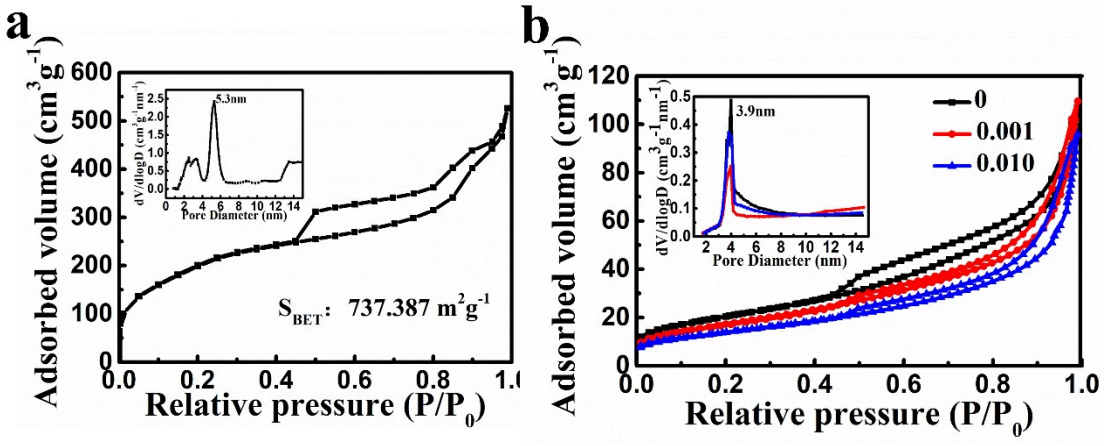

Figure S2. N_2 adsorption-desorption isotherm and Barret-Joyner-Halenda (BJH) pore size distribution plot (inset) of (a) hollow doubleshell SiO_2 and (b) hollow ATCN-DSCN-0, ATCN-DSCN-0.001 and ATCN-DSCN-0.010.

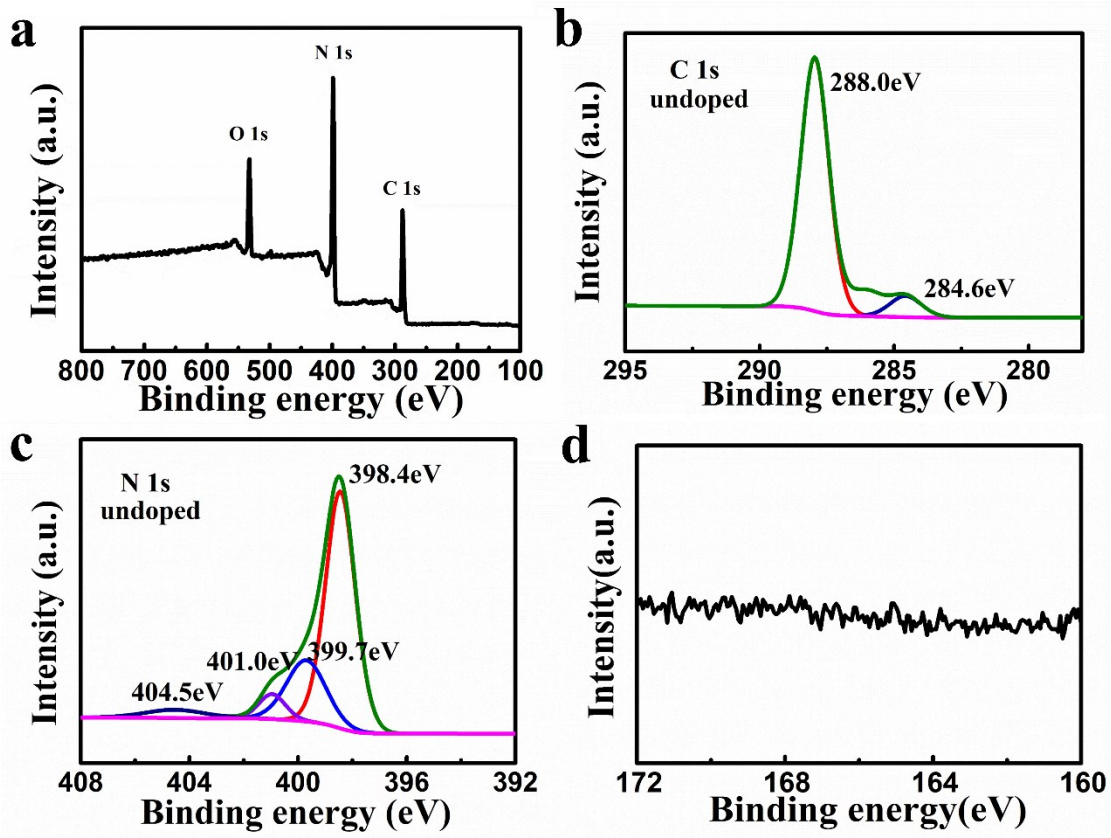

Figure S3. The surface elements analysis of ATCN-DSCN-0 (undoped DSCN). (a) Full scan X-ray photoelectron spectroscopy (XPS) spectra of ATCN-DSCN-0 (undoped). (b) High-resolution C 1s spectra of ATCN-DSCN-0. (c) High-resolution N 1s spectra ofATCN-DSCN-0. (d) High-resolution S 2p spectrum of thiophene undoped DSCN (ATCN-DSCN-0).

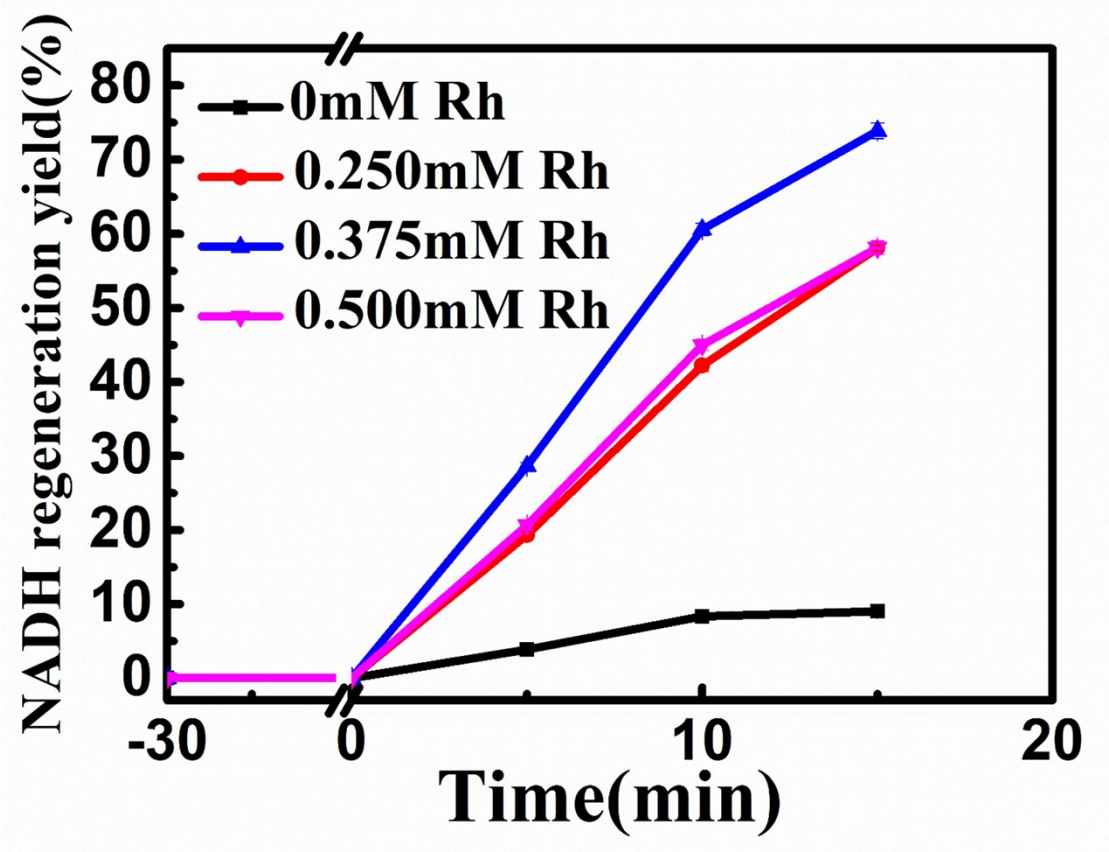

Figure S4. Photo-regenerated NADH yield. The yield of the photo-regenerated NADH with different levels of $[Cp^*Rh(bpy)H_2O]^{2+}$ (pH=7, and ATCN-DSCN-0.005 was used).

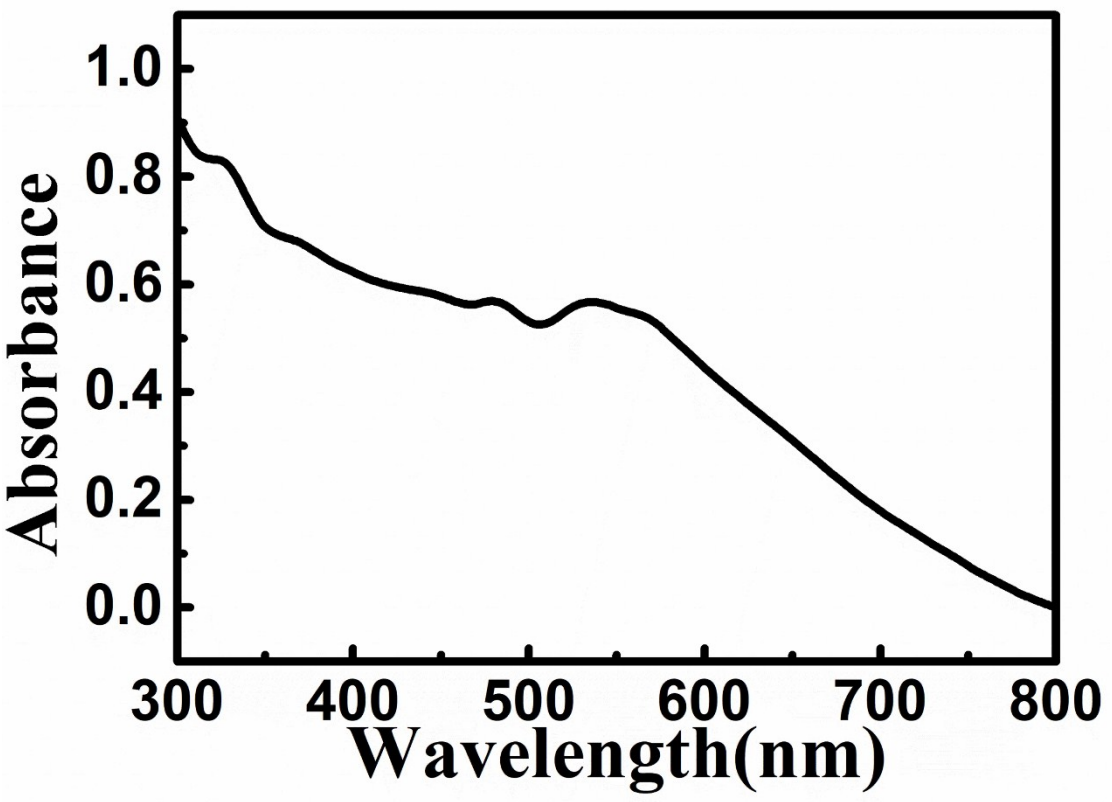

Figure S5. The UV-vis diffuse reflectance spectra (UV-Vis DRS) of thiophene (ATCN).

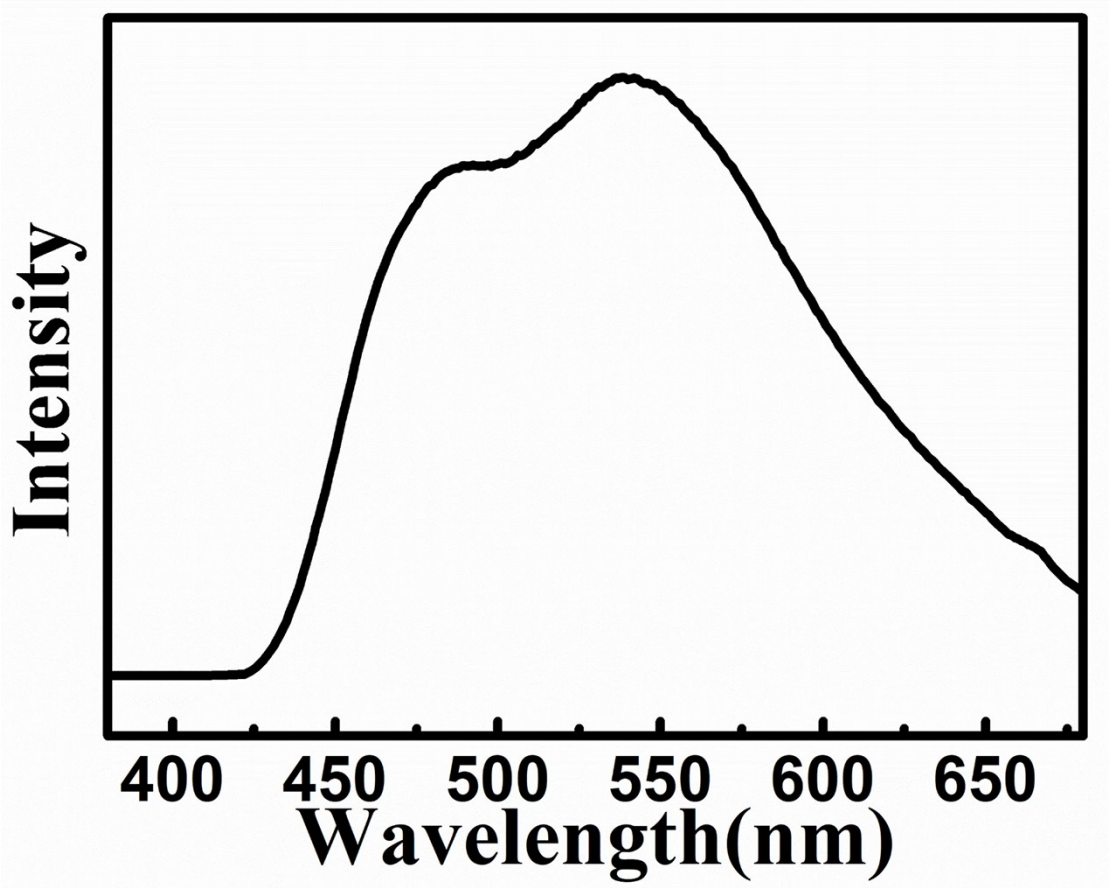

Figure S6. The photoluminescence spectra (PL) of thiophene (ATCN) with an excitation wavelength of 350 nm.

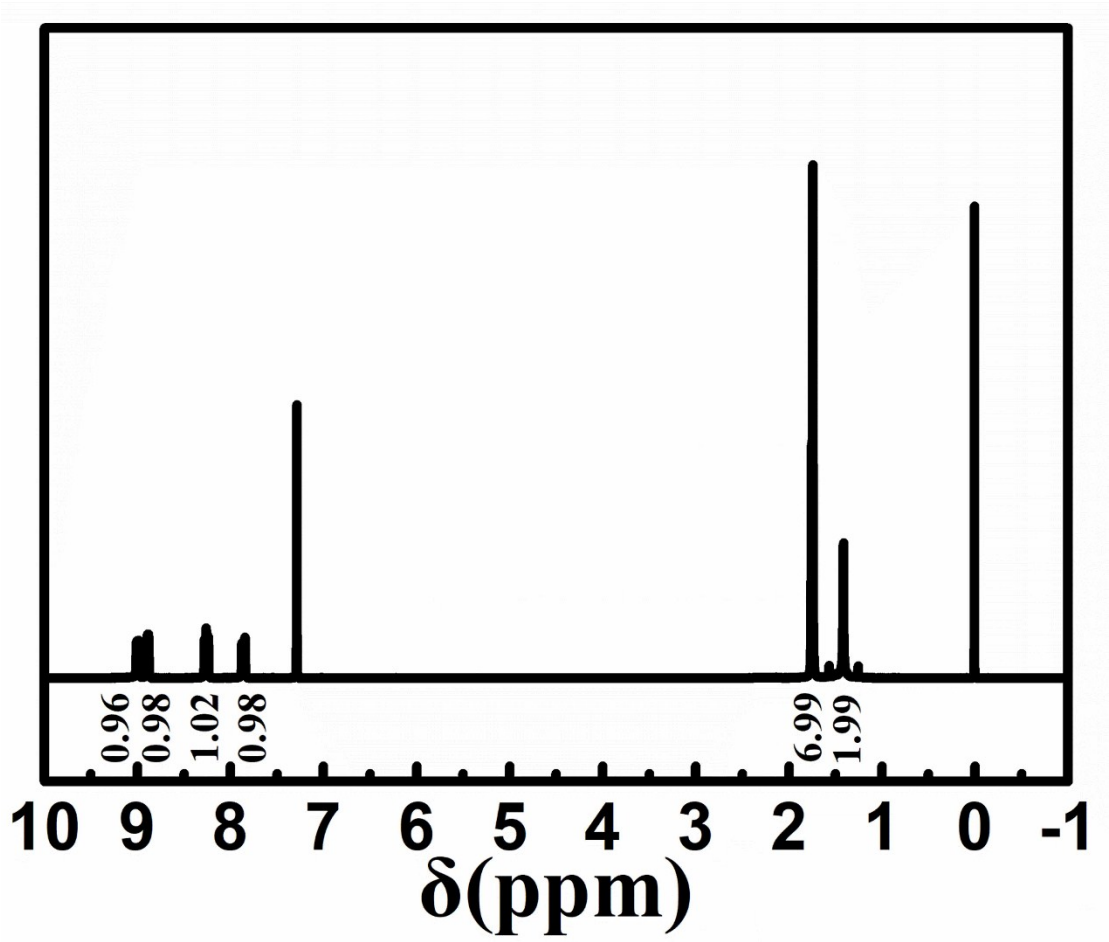

Figure S7. The NMR spectrum of the organometallic compound [Cp*Rh(bpy)Cl]Cl. ^{1}H NMR (300 MHz, CDCl3): Cp*[Rh(2,2'-bpy)] δ (ppm) = 9.08 (d, 2H, H-3,3'), 8.86 (d, 2H, H-6,6'), 8.26 (t, 2H, H-5,5'), 7.84 (t, 2H, H-4,4'), 1.75 (s, 15H, Cp*).

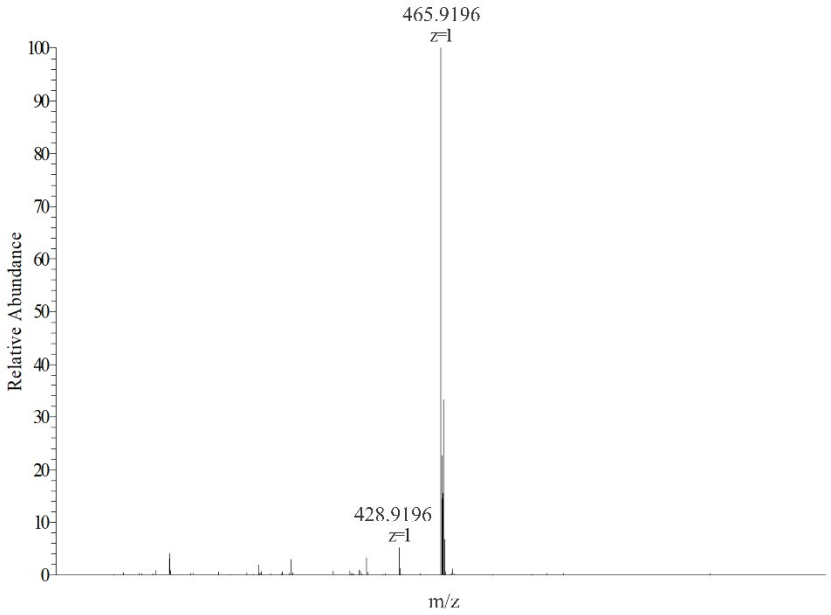

Figure S8. The mass spectra of compound [Cp*Rh(bpy)Cl]Cl dissolved in methanol, which indicates that the gross mass of [Cp*Rh(bpy)Cl]Cl is approximately 465.9196.