Electronic Supplementary Information

A novel supramolecular self-assembling hybrid system for visible-light-driven overall water splitting

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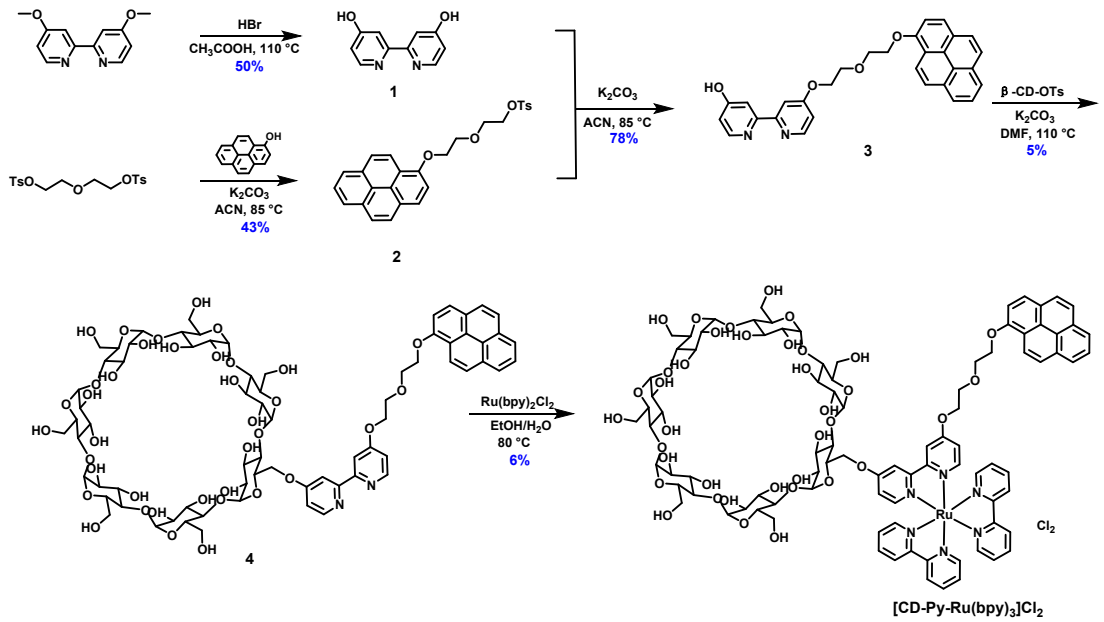
1. General information and materials

All reactions were performed in air atmosphere unless otherwise stated. Reagents were commercially available and used without further purification. All yields were given as isolated yields. Column chromatography was performed with silica gel (200–300 mesh) produced by Qingdao Marine Chemical Factory, Qingdao (China). NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references at 298 K. The chemical shifts (δ) were expressed in ppm and J values were given in Hz. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on Finnigan Mat TSQ 7000 instruments. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent 6540Q-TOF LCMS equipped with an electrospray ionization (ESI) probe. The deionized water was prepared by a Millipore NanoPure purification system. The UV–Vis absorption spectra were measured on a Perkin Elmer Lambda 35 UV–vis Spectrometer. The excitation and emission spectra were recorded on a Hitachi F-7000 Fluorescence Spectrometer. Zeta-potential measurements were performed at 25 °C on a Brookhaven BI-9000AT system (Brookhaven Instruments Corporation, USA), using Smoluchowski model for the calculation of Zeta-potential from the measured electrophoretic mobility. The electrochemical tests are performed by the CHI 630D electrochemical workstation. Transmission electron microscope (TEM) investigations were carried out on a JEM-2100 instrument. The pH of solutions was measured by a Lei Ci PHS-3C pH meter. Powder X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 ADVANCE X. The catalytic products were analyzed by GC9860 equipped with a thermal conductivity detector with a TDX-1 column and a flame ionization detector with an FFAP and PLOT-Q capillary column.

2. Synthesis of host [CD-Py-Ru(bpy)$_3$]Cl$_2$

The synthetic procedures of host **[CD-Py-Ru(bpy)$_3$]Cl$_2$** were shown in **Scheme S1**.



Scheme S1. Synthetic procedures of host **[CD-Py-Ru(bpy)$_3$]Cl$_2$**.

Synthesis of compound 1

4,4'-Dimethoxy-2,2'-bipyridine (3.0 g, 14 mmol) was added to a solution of hydrobromic acid (25 mmol) in acetic acid (150 mL), and the mixture was heated to 110 °C for 12 h. Finally, the solvent was removed, and distilled water (150 mL) was added. The pH of the solution was adjusted to 6.0 and the solution was filtered. Then the filtrate was dried under vacuum to yield compound **1** as a white powder (1.4 g, 7.3 mmol, 50%). M.p. 258−260 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 8.24 (d, J = 6.0 Hz, 2H), 7.50 (d, J = 1.6 Hz, 2H), 6.75 (dd, J_1 = 6.0 Hz, J_2 = 1.6 Hz, 2H), 3.50 (brs, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm): 168.8, 152.4, 147.8, 113.8, 110.1. HR-ESI-MS: m/z calcd $[M + H]^+$ 189.0665, found 189.0659.

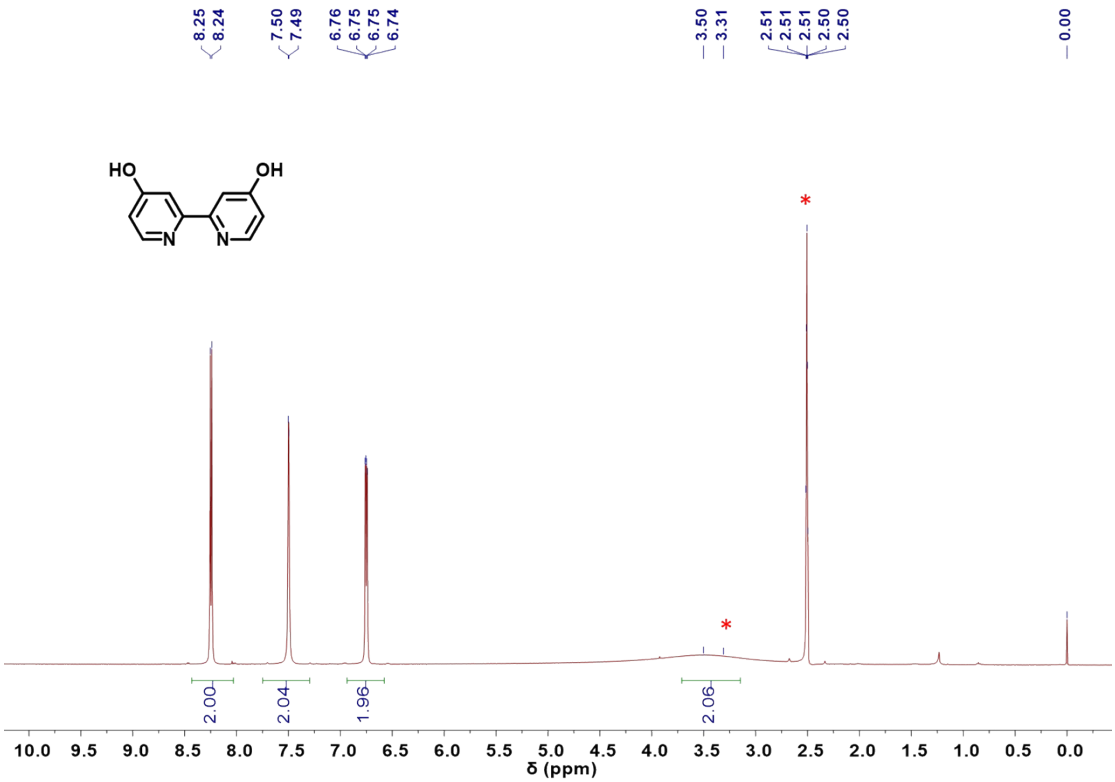


Fig. S1 ^{1}H NMR spectrum (400 MHz, DMSO-*d*6, 298 K) of compound **1** (* refers to solvent peak).

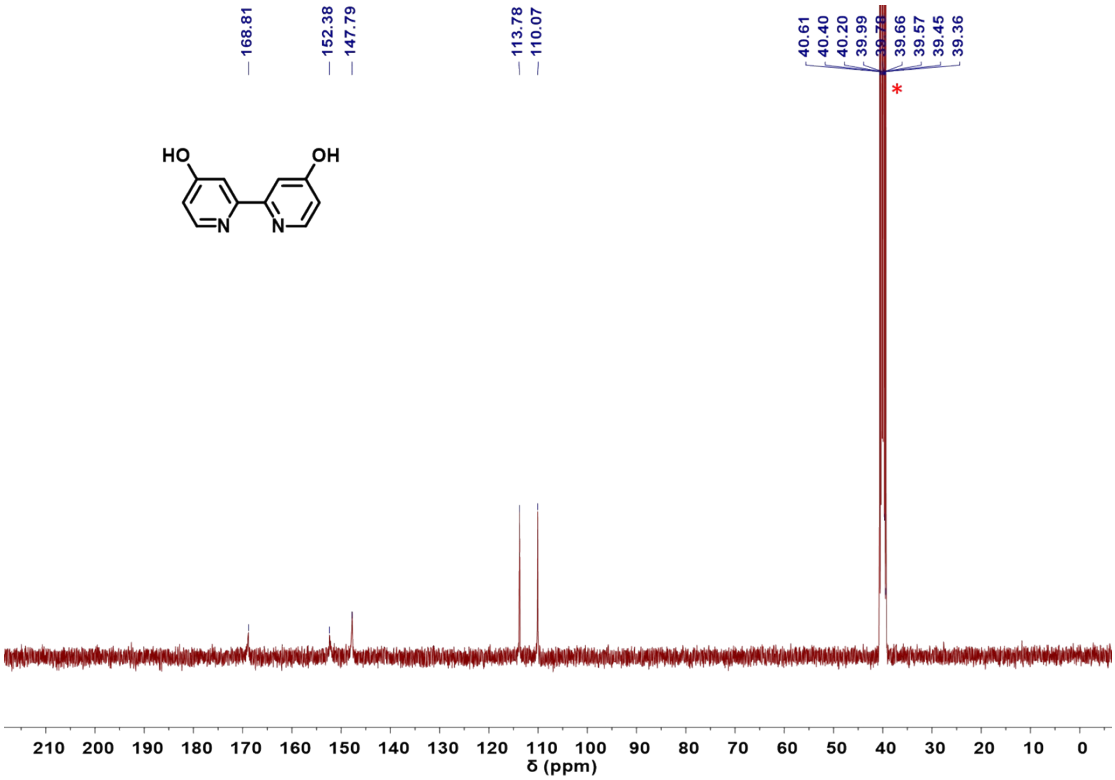


Fig. S2 ^{13}C NMR spectrum (100 MHz, DMSO-*d*6, 298 K) of compound **1** (* refers to solvent peak).

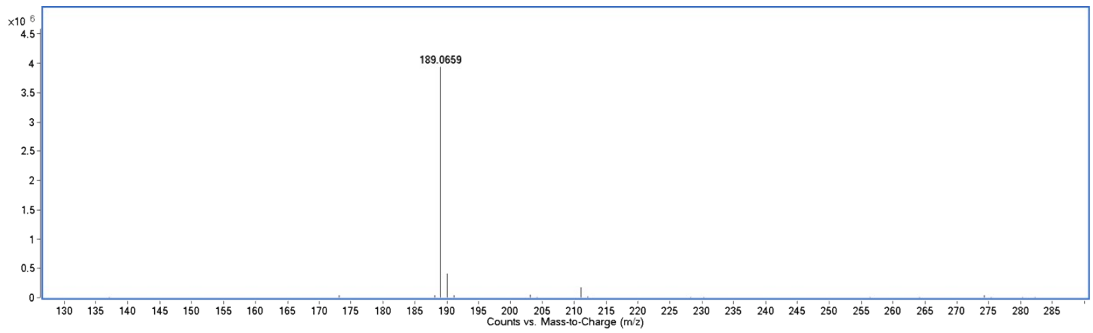


Fig. S3 HR-ESI-MS spectrum of compound **1**.

Synthesis of compound 2

Diethylene glycol di(p-toluenesulfonate) (5.0 g, 12 mmol) was added to a solution of K_2CO_3 (1.7 g, 12 mmol) and 1-pyrenol (0.66 g, 2.8 mmol) in acetonitrile (60 mL), and the mixture was heated to 85 °C for 12 h. After cooling down to room temperature, the solvent was removed and the residual solid was purified by column chromatography (silica, petroleum ether/ethyl acetate= 6/1, *v/v*) to afford compound **2** as a yellow oil (0.59 g, 1.3 mmol, 43%). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ (ppm): 8.32 (d, J = 9.2 Hz, 1H), 7.77−8.01 (m, 7H), 7.67 (dd, J_1 = 6.8 Hz, J_2 = 0.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 4.11 (m, 4H), 3.72−3.74 (m, 2H), 3.65−3.68 (m, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ (ppm): 152.7, 144.8, 132.9, 131.7, 131.6, 129.8, 127.9, 127.3, 126.5, 126.2, 125.8, 125.6, 125.5, 125.2, 124.9, 124.4, 124.3, 121.3, 120.5, 109.5, 70.0, 69.5, 69.0, 68.5, 21.5. HR-ESI-MS: m/z calcd $[M + H]^+$ 461.1423, found 461.1413.

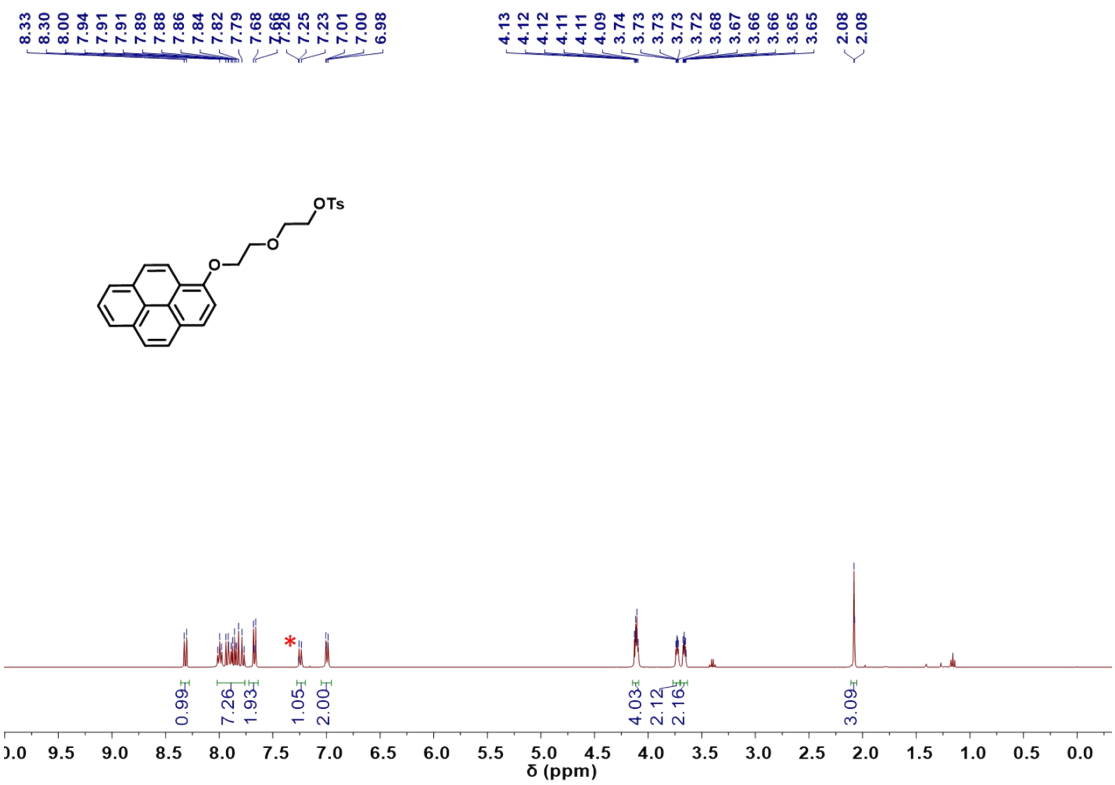


Fig. S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **2** (* refers to solvent peak).

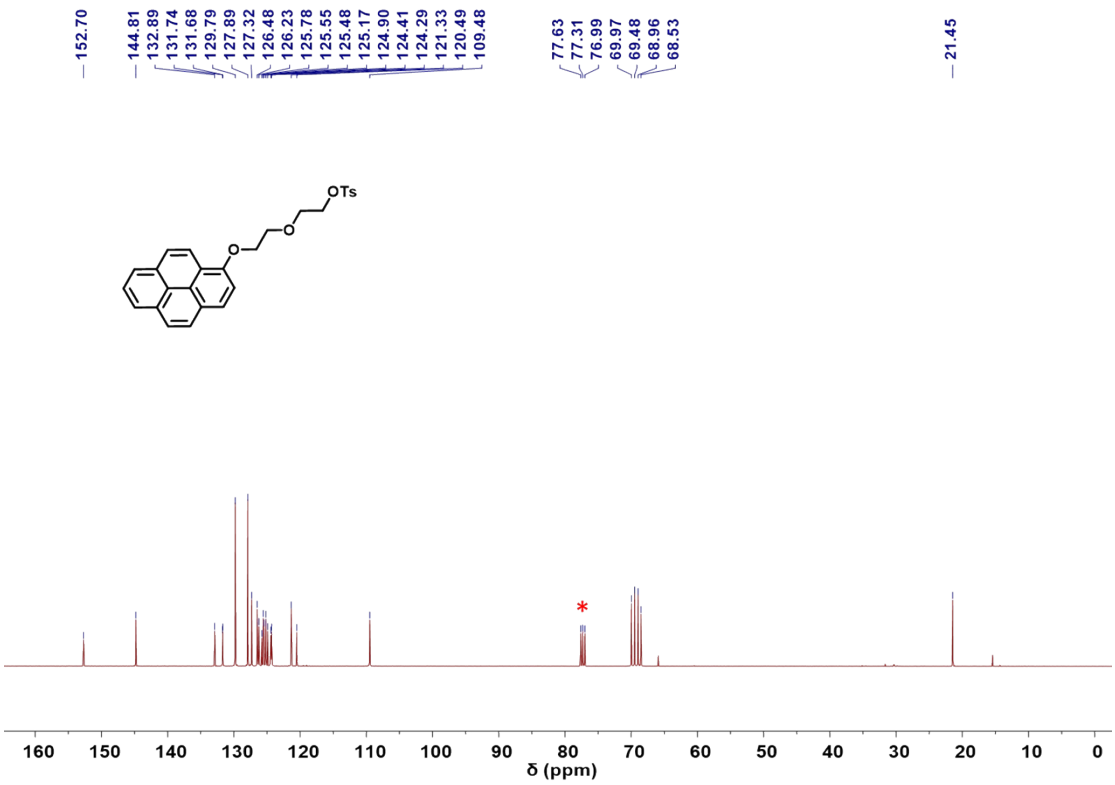


Fig. S5 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **2** (* refers to solvent peak).

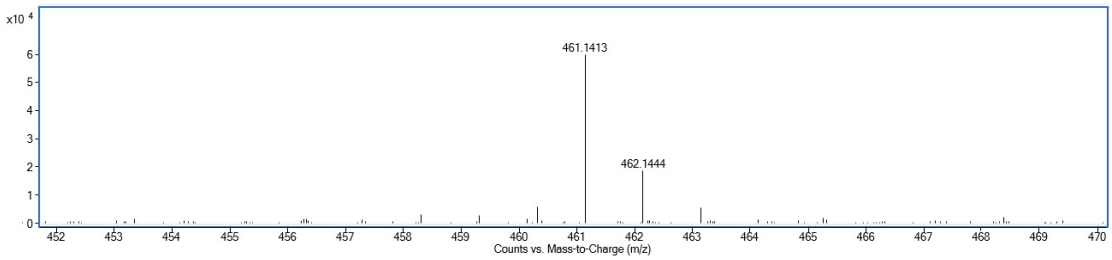


Fig. S6 HR-ESI-MS spectrum of compound **2**.

Synthesis of compound 3

Compound **1** (0.38 g, 2.0 mmol) in DMF (20 mL) was added to a solution of K_2CO_3 (1.7 g, 12 mmol) and compound **2** (0.23 g, 0.48 mmol) in acetonitrile (20 mL). Then the mixture was heated to 85 °C for 12 h. After cooling down to room temperature, the solvent was removed and the residual solid was purified by column chromatography (silica, petroleum ether/ethyl acetate = 5/1, *v/v*) to afford compound **3** as a brown solid (0.18 g, 0.37 mmol, 78%). M.p. 172−175 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 8.46 (d, J = 5.6 Hz, 1H), 8.46 (d, J = 9.2 Hz, 1H), 8.14−8.24 (m, 4H), 7.96−8.08 (m, 4H), 7.89 (d, J = 2.4 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.59−7.60 (m, 1H), 7.03 (dd, J_1 = 4.5 Hz, J_2 = 2.8 Hz, 1H), 6.63−6.65 (m, 1H), 4.50−4.52 (m, 2H), 4.36−4.38 (m, 2H), 4.05−4.07 (m, 2H), 3.98−4.00 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, 298 K) δ (ppm): 173.3, 165.9, 153.0, 150.9, 131.7, 131.5, 127.7, 126.9, 126.8, 126.8, 126.7, 126.4, 125.4, 125.2, 125.2, 124.8, 124.6, 124.5, 121.4, 120.0, 114.0, 111.5, 110.6, 107.0, 69.7, 69.3, 69.0, 68.0, 22.7. HR-ESI-MS: m/z calcd $[M + H]^+$ 477.1815, found 477.1814.

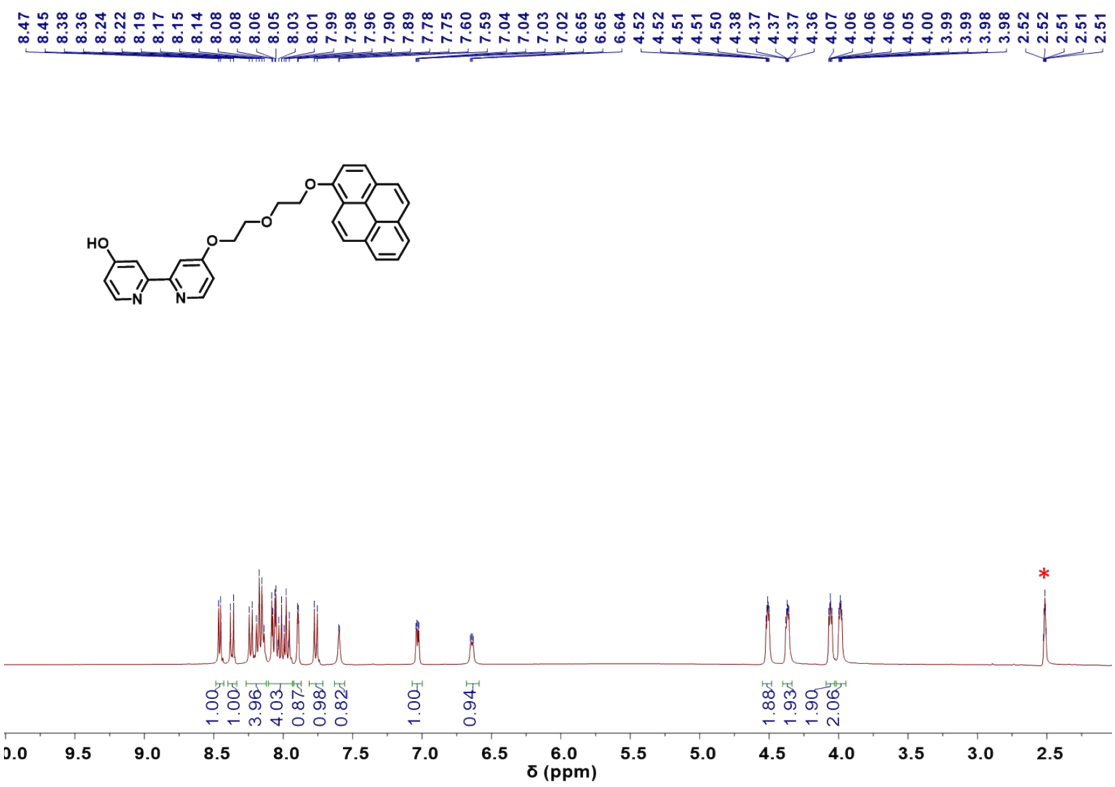


Fig. S7 ^{1}H NMR spectrum (400 MHz, DMSO-*d*6, 298 K) of compound **3** (* refers to solvent peak).

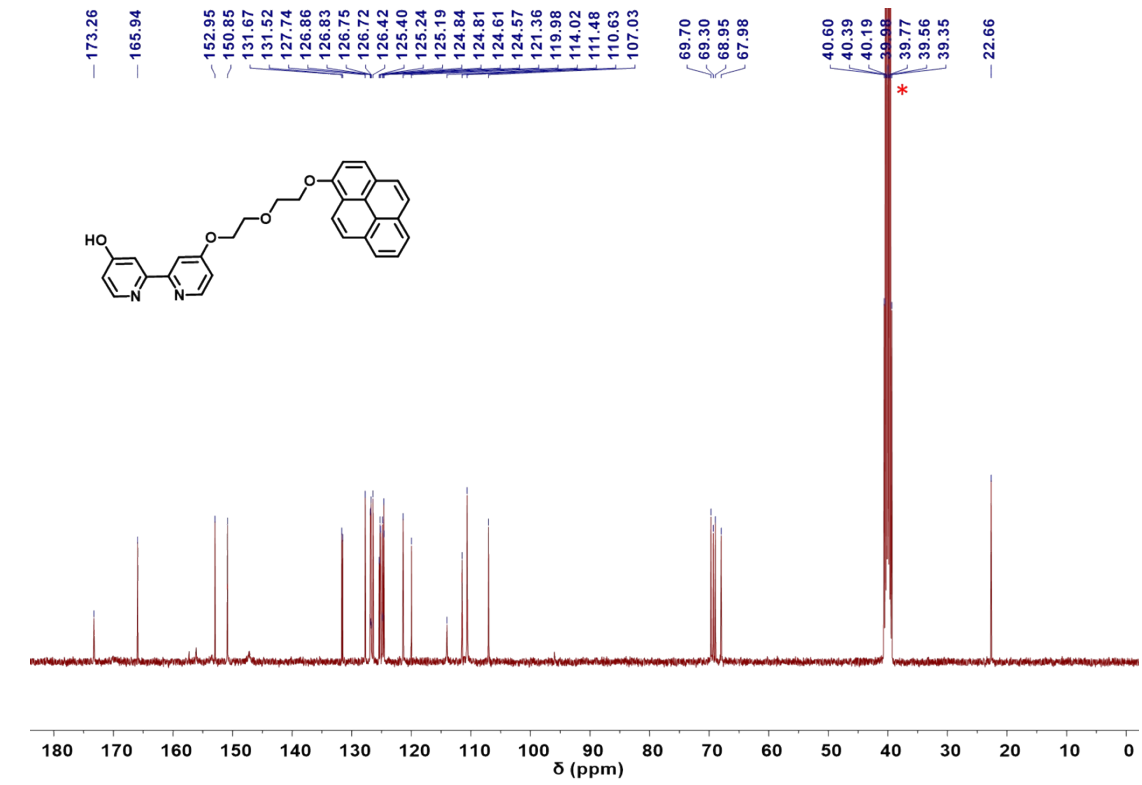


Fig. S8 ^{13}C NMR spectrum (100 MHz, DMSO-*d*6, 298 K) of compound **3** (* refers to solvent peak).

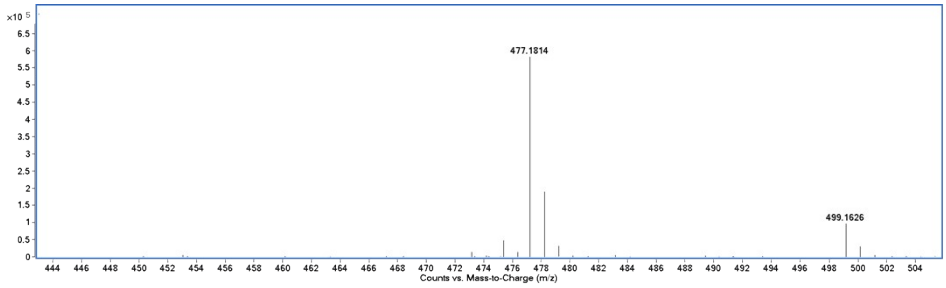


Fig. S9 HR-ESI-MS spectrum of compound **3**.

Synthesis of compound 4

Compound **3** (0.30 g, 0.61 mmol) was added to a solution of β-CD-OTs (0.54 g, 0.42 mmol) and K_2CO_3 (0.12 g, 0.82 mmol) in DMF (50 mL). Then the mixture was heated to 115 °C for 36 h. After cooling down to room temperature, the solvent was removed and the residual solid was purified by column chromatography (silica, dichloromethane/methanol = 1/10, *v/v*) to afford compound **4** as a brown solid (0.04 g, 0.02 mmol, 5%). M.p. 257−262 °C. ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 8.45−8.47 (m, 2H), 8.38 (d, J = 9.2 Hz, 1H), 8.24 (d, J = 8.4 Hz, 1H), 8.16−8.20 (m, 2H), 7.93−8.10 (m, 6H), 7.79 (d, J = 8.4 Hz, 1H), 7.04−7.06 (m, 2H), 5.95 (brs, 6H), 4.79−4.91 (m, 10H), 4.36−4.54 (m, 14H), 4.06−4.08 (m, 2H), 3.99−4.01 (m, 2H), 3.25−3.73 (m, 43H). HR-ESI-MS: m/z calcd $[M + H]^+$ 1593.5407, found 1593.5370.

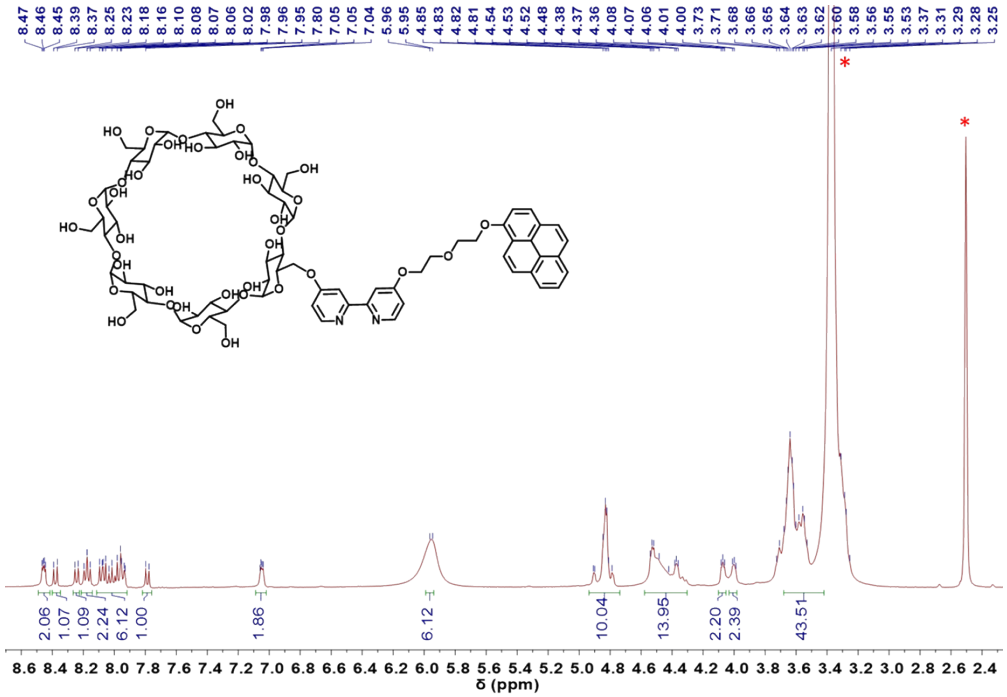


Fig. S10 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **4** (* refers to solvent peak).

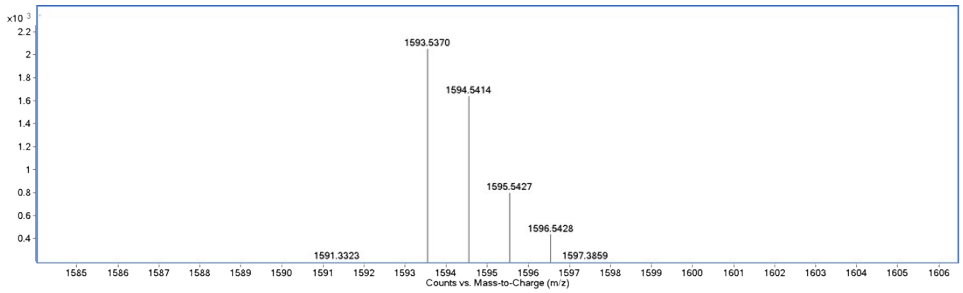


Fig. S11 HR-ESI-MS spectrum of compound **4**.

Synthesis of compound [CD-Py-Ru(bpy)$_3$]Cl$_2$

Compound **4** (0.27 g, 0.17 mmol) and Ru(bpy)$_2$Cl$_2$ (0.08 g, 0.17 mmol) were added to a solution of ethanol/water (50 mL, ethanol/water = 2/1, *v*/*v*). Then the mixture was heated to 115 °C for 36 h. After cooling down to room temperature, the solvent was removed and the residual solid was recrystallized by water to afford compound **[CD-Py-Ru(bpy)$_3$]Cl$_2$** as a red solid (0.02 g, 0.01 mmol, 6%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 8.80−8.82 (m, 4H), 8.48−8.53 (m, 2H), 8.35−8.37 (m, 1H), 8.00−8.26 (m, 11H), 7.66−7.80 (m, 4H), 7.37−7.50 (m, 6H), 7.10−7.18 (m, 2H), 5.74−5.88 (m, 6H), 4.81−4.85 (m, 10H), 4.46−4.52 (m, 14H), 4.01−4.06 (m, 4H), 3.27−3.68 (m, 43H). HR-ESI-MS: m/z calcd [M − 2Cl]$^{2+}$ 1003.2868, found 1003.2870.

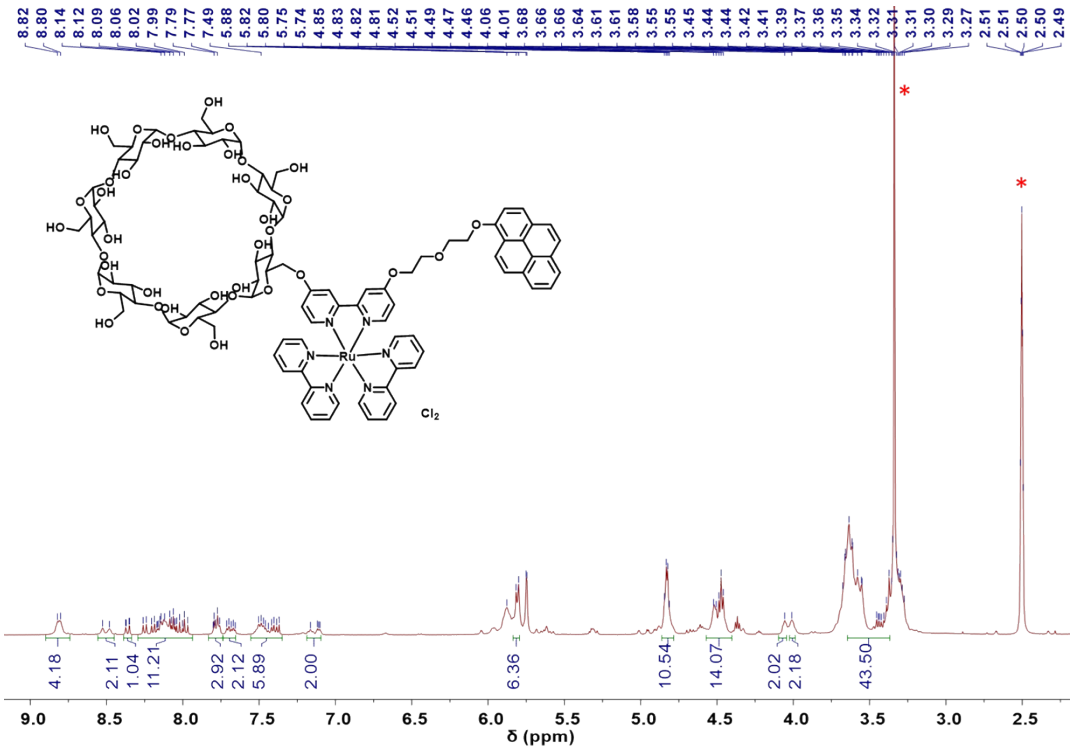


Fig. S12 ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K) of compound **[CD-Py-Ru(bpy)$_3$]Cl$_2$** (* refers to solvent peak).

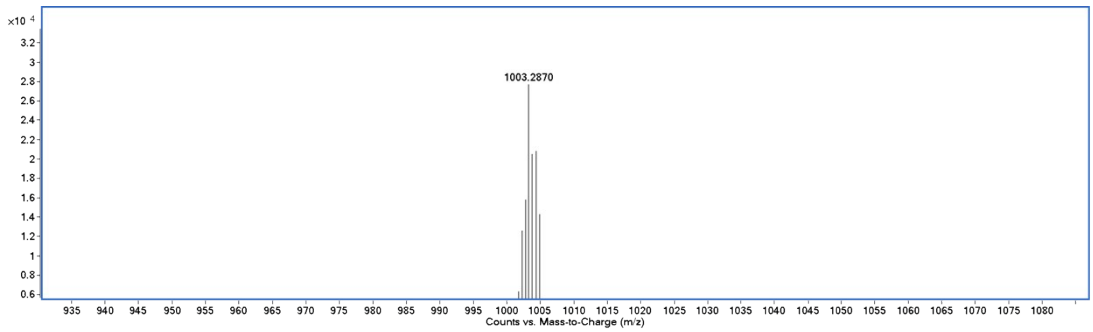
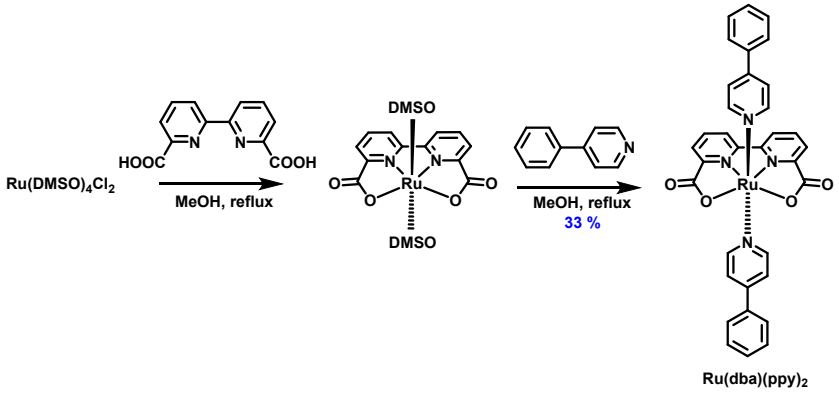


Fig. S13 HR-ESI-MS spectrum of compound **[CD-Py-Ru(bpy)$_3$]Cl$_2$**.

3. Synthesis of guest Ru(dba)(ppy)$_2$

The synthetic procedures of guest **G** were shown in **Scheme S2**.[S1]



Scheme S2. Synthetic procedures of guest **Ru(dba)(ppy)$_2$**.

Synthesis of compound Ru(dba)(ppy)$_2$

2,2′-bipyridine-6,6′-dicarboxylic acid (0.15 g, 0.61 mmol) was added to a solution triethylamine (0.60 mL) and $Ru(DMSO)_4Cl_2$ (0.29 g, 0.61 mmol) in methanol (30 mL), and the mixture was refluxed for 6 h. 4-Phenyl pyridine (0.19 g, 1.2 mmol) was then added to the mixture and the solution was continued to reflux for another 2 h. After cooling down to room temperature, the solvent was removed and the residual solid was purified by column chromatography (silica, dichloromethane/methanol = 5/1, *v/v*) to afford compound **Ru(dba)(ppy)$_2$** as a brown solid (0.13 g, 0.20 mmol, 33%). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ (ppm): 8.74 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 2H), 7.95−7.98 (m, 2H), 7.89−7.92 (m, 2H), 7.76−7.78 (m, 2H), 7.68−7.71 (m, 4H), 7.61−7.62 (m, 4H), 7.46−7.49 (m, 6H).

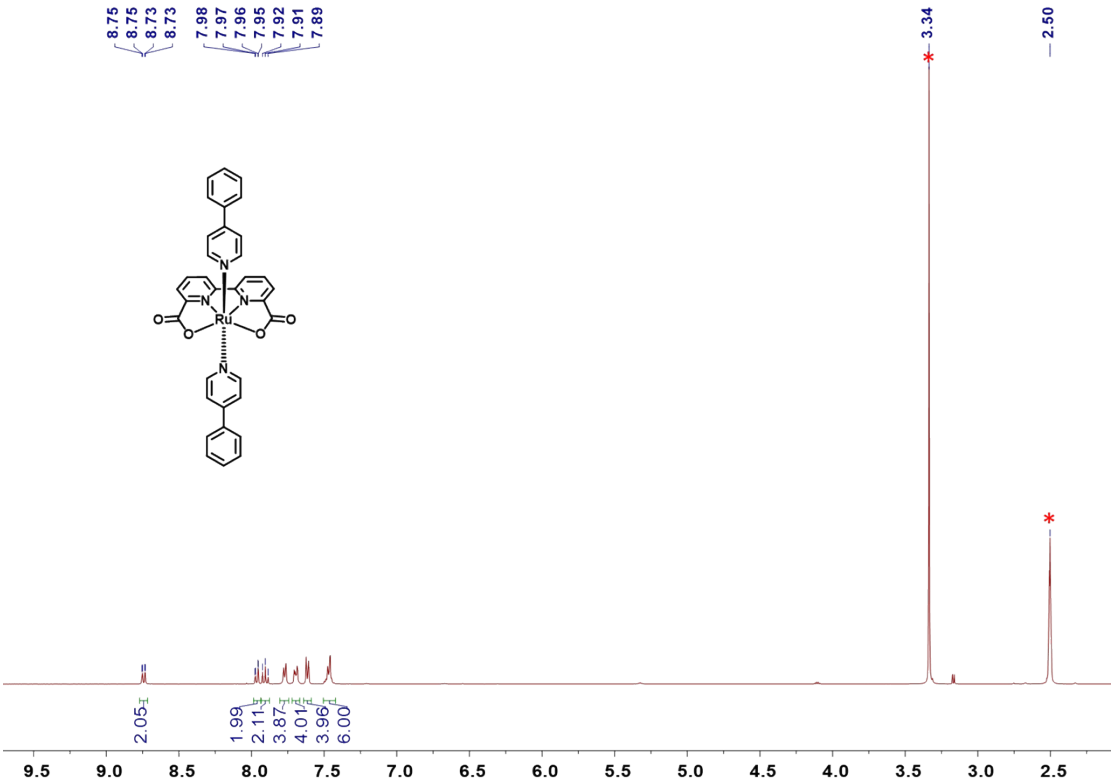


Fig. S14 ^{1}H NMR spectrum (400 MHz, DMSO-*d*6, 298 K) of compound **Ru(dba)(ppy)$_2$** (* refers to solvent peak).

4. Preparation of protonated pC_3N_4

g-C_3N_4 (50 mg) was dissolved in 0.1 M hydrochloric acid aqueous solution (40 mL) and was ultrasound-treated for 1 h. After that, the suspension was vigorously stirred for 2 h at room temperature. Then the mixture was filtered and wash with distilled water. Finally, the protonated pC_3N_4 was dried at 70 °C for 12 h.[S2]

5. Preparation of rGO/pC_3N_4/Pt

GO was dispersed in distilled water and ultrasound-treated for 1 h, followed by dispersing the protonated g-C_3N_4 to the suspension and ultrasound-treated for an additional 2 h. Then sodium borohydride (500 mg) was added and the mixture was refluxed for 3 h. After cooling down to room temperature, solution was filtered and the filtrate was washed several times with distilled water and ethanol. The obtained solid was further dispersed in distilled water, followed by the addition of 2% of chloroplatinic acid and 10% of triethanolamine. After degassed, the suspension was irradiated with Xenon lamp (300 W). Finally, solution was filtered and the filtrate was dried at 70 °C under vacuum to afford rGO/pC_3N_4/Pt as black solid (50 mg).

6. Study of the binding stoichiometry between β-CD and G_M

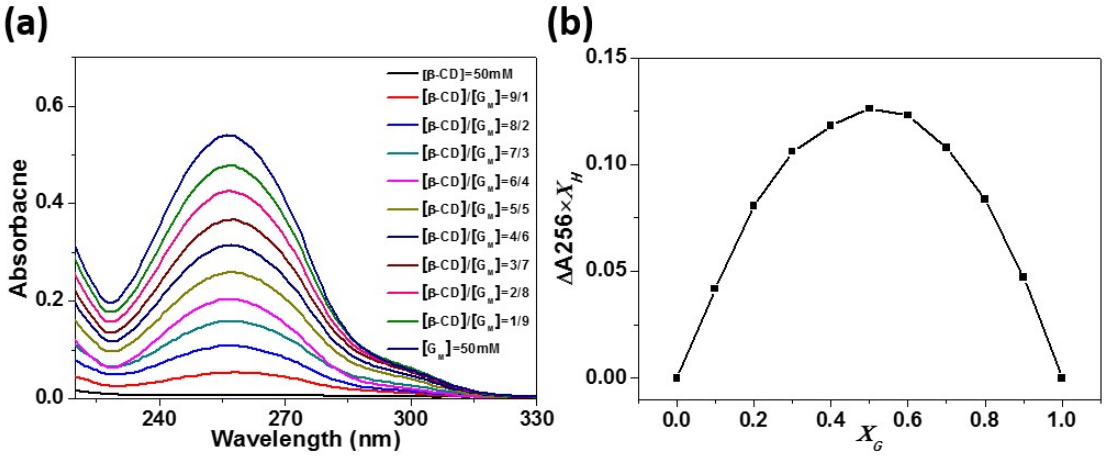


Fig. S15 (a) UV absorption spectra of different molar ratios of β-CD⊃**G**$_M$ solution, maintaining [β-CD] + [**G**$_M$] = 50 μM; (b) Job plot of β-CD⊃**G**$_M$ complex.

7. Investigation of the binding constant between β-CD and G_M

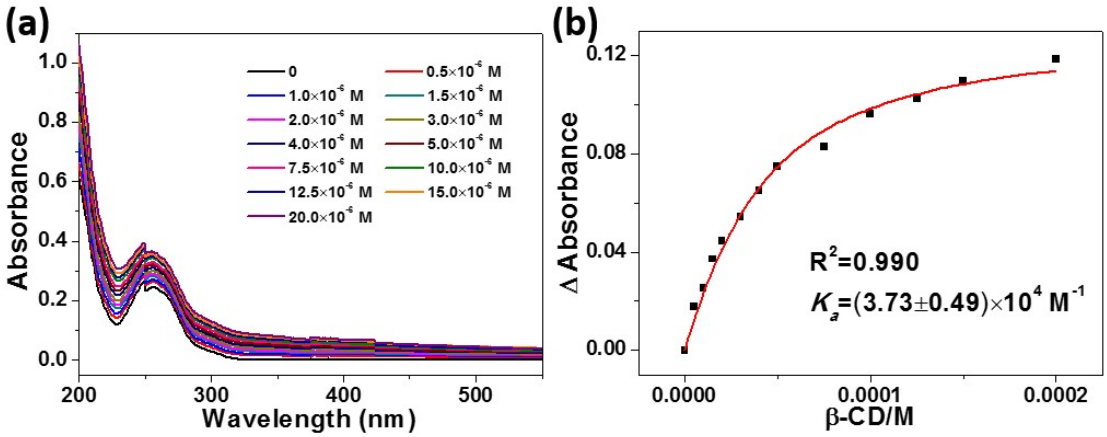


Fig. S16. Determination of the association constants between β-CD and **G**$_M$: UV−vis absorption changes of **G**$_M$ with varied concentrations of β-CD; (b) Dependence of the UV−vis absorption at 256 nm on **G**$_M$ with varied concentrations of β-CD.

To determine the binding affinity between β-CD and **G**$_M$, UV-vis absorption titration experiments were performed. The solution had a constant concentration of **G**$_M$ and varied concentration of β-CD. The binding constant (K_a) between saccharides and **G** was calculated via the non-linear curve-fitting method.

For fitting equation under a 1:1 stoichiometry for **G**$_M$ to β-CD:

$$\Delta A = (\Delta A_\infty/[H]_0)\,(0.5[G]_0 + 0.5([H]_0 + 1/K_a) - (0.5\,([G]_0^2 + (2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \quad (2)$$

Where ΔA is the UV-vis absorption changes at 256 nm at $[H]_0$, ΔA_∞ is the UV-vis absorption

changes at 256 nm when $\mathbf{G_M}$ and β-CD are completely complexed, $[G]_0$ is the initial concentration of $\mathbf{G_M}$, and $[H]_0$ is the fixed initial concentration of β-CD.

8. Zeta potential investigation

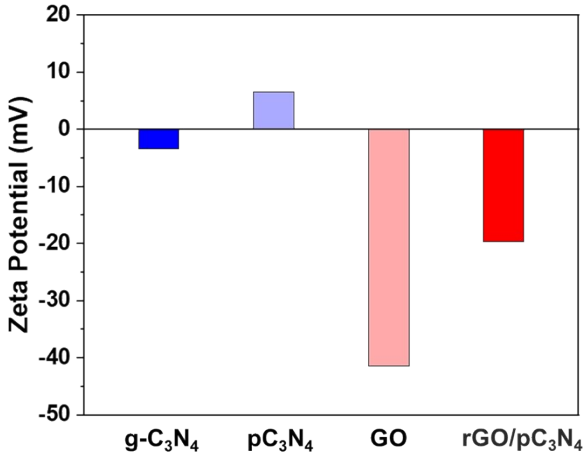


Fig. S17. Zeta potentials of the g-C_3N_4, pC_3N_4, GO and rGO/pC_3N_4.

9. Cyclic voltammograms

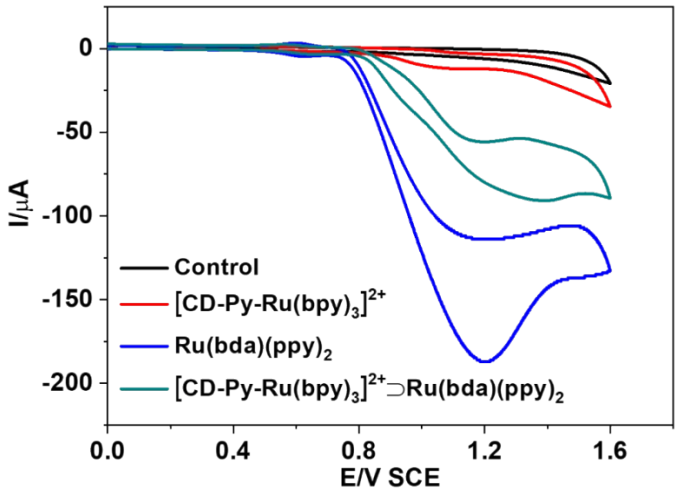


Fig. S18. Cyclic voltammograms of the phosphate buffer solutions (pH = 7.1, 50 mM) containing 10% acetonitrile in the presence of $[CD\text{-}Ru(bpy)_3]^{2+}$, $Ru(bda)(ppy)_2$, and $[CD\text{-}Ru(bpy)_3]^{2+}\supset[Ru(bda)(ppy)_2])^{2+}$, respectively at the scan rate of 100 mV/s. The black curve represents the background.

10. Supplementary table

Table S1. Influence of sacrificial agent against photocatalytic water splitting*.

Sacrificial Agent	Hydrogen (μmol)	Oxygen (μmol)
None	N.D.	N.D.
TEOA	0.07	0.61
$Na_2S_2O_8$	N.D.	1.44
TEOA/$Na_2S_2O_8$	0.10	1.09

* $[CD\text{-}Py\text{-}Ru(bpy)_3]^{2+}$ = 1×10^{-4} M, $Ru(dba)(ppy)_2$ = 1×10^{-4} M, 10% TEOA, $Na_2S_2O_8$ = 6.7×10^{-2} M, C_3N_4/rGO/Pt = 1 mg/mL.

11. References

S1. H. Li, F. Li, B. Zhang, X. Zhou, F. Yu and L. Sun, *J. Am. Chem. Soc.*, 2015, **137**, 4332−4335.

S2. W.-J. Ong, L.-L. Tan, S.-P. Chai, S.-T. Yong and A. R. Mohamed, *Nano Energy*, 2015, **13**, 757–770.