Supplementary Materials for

Bimolecular Proximity of Ruthenium Complex and Methylene Blue within an Anionic Porous Coordination Cage for Enhancing Photocatalytic Activity

Yu Fang, Zhifeng Xiao, Angelo Kirchon, Jialuo Li, Fangying Jin, Tatsuo Togo, Liangliang Zhang, Hong-Cai Zhou*

Correspondence to: zhou@chem.tamu.edu

This PDF file includes:

Contents

Section 1. Materials and instrumentation

1, 3, 5-Tris(4-Carboxyphenyl)Benzene (H_3L), $CoCl_2$, N, N-dimethylformamide (DMF), Acetonitrile, $CHCl_3$ were purchased from TCI USA and Sigma Aldrich. Na_4H_4V was synthesized from *p*-tert-butylsulfonylcalix[4]arene (H_4TBSC) according to reported literature procedures.[1] All commercial chemicals were used without further purification unless otherwise mentioned. Single crystal X-ray diffraction was carried out Bruker Quest diffractometer equipped with a MoKα sealed-tube X-ray source (graphite radiation monochromator, $\lambda = 0.71073$) and a low temperature device (110 K). SEM was performed on a FEI Quanta 600 FE-SEM. TEM was performed on a FEI Tecnai G2 F20 ST microscope at 200 kV equipped with a field emission gun. ESI Mass and MALDI-TOF-MS was conduct by Applied Biosystems PE SCIEX QSTAR system. The electronic absorption spectra were measured on a Hitachi U-4100 UV-Vis-NIR spectrophotometer. The excitation and emission spectra have been corrected for the wavelength-dependent lamp intensity and detector response, respectively.

Section 2. Guest encapsulation of PCCs

Methylene Blue working Curve

Methylene Blue (MB) was dissolved into acetonitrile to prepare solution with concentration of 0.1 mg/100mL, 0.2 mg/100mL, 0.3 mg/100mL, 0.4 mg/100mL, 0.5 mg/100mL, 0.6 mg/100mL, and 0.7 mg/100mL. The absorbance was recorded (Table S1) and fitted by a linear equation (Fig. S1).

Table S1. MB working curve.

Concentration (mg/100 mL)	Absorbance of 653 nm
0.1	0.214
0.2	0.440
0.3	0.637
0.4	0.866
0.5	1.057
0.6	1.278
0.7	1.490

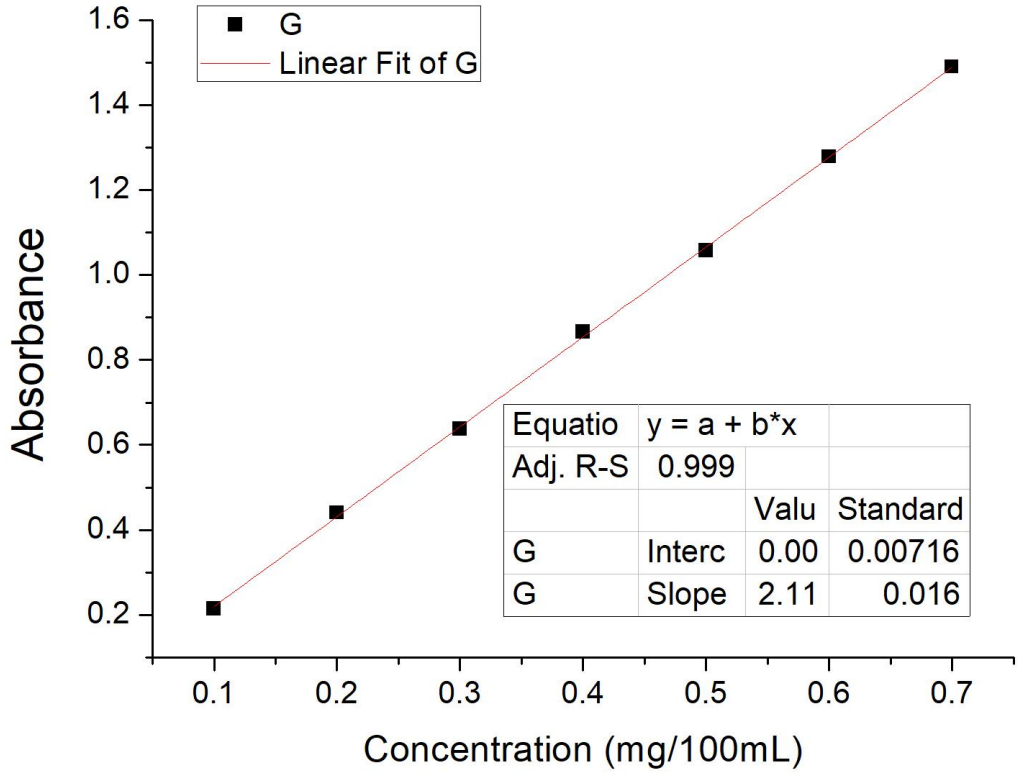

Fig. S1 Linear fitting of MB working curve.

Solid-Liquid MB Encapsulation by PCC-2

Typical dye encapsulation procedure for PCC-2 is: 10.0 mg of activated single crystal of PCC-2 was soaked in a solution of 5 mg of Methylene Blue (MB) in 10 mL Acetonitrile, and stirred at room temperature for 40 mins. Then the supernatant was separated by centrifugation and analyzed by UV-Vis spectrum (diluted with the range of 0.1-0.7 mg/100 mL). By comparing the initial and final concentration, the encapsulated drug amount is 1.9 mg for 10 mg PCC-2. The loading ratio is 0.19 mg/mg and it's about 7 MB molecule per one PCC-2 cage. After encapsulation of MB dye, MB@PCC-2 was fully dissolved in DMF and the solution was shown in Fig. S2. Comparing to free dye, the peak of MB@PCC-2 blue shifted for 5.0 nm. The MB@PCC-2 solid was further characterized by Elemental analysis. Elemental analysis: calculated (%) for $Na_{24}(Et_3NH)_6$ $[C_{360}H_{222}S_{48}O_{198}Co_{24}]\cdot 7$ $[C_{16}H_{18}ClN_3S]\cdot 4$ MeOH · 12 H_2O, Calc: C 42.73, H 3.22, N 2.63, S 13.74; found (%):C 42.71, H 3.12, N 2.59 S 13.55.

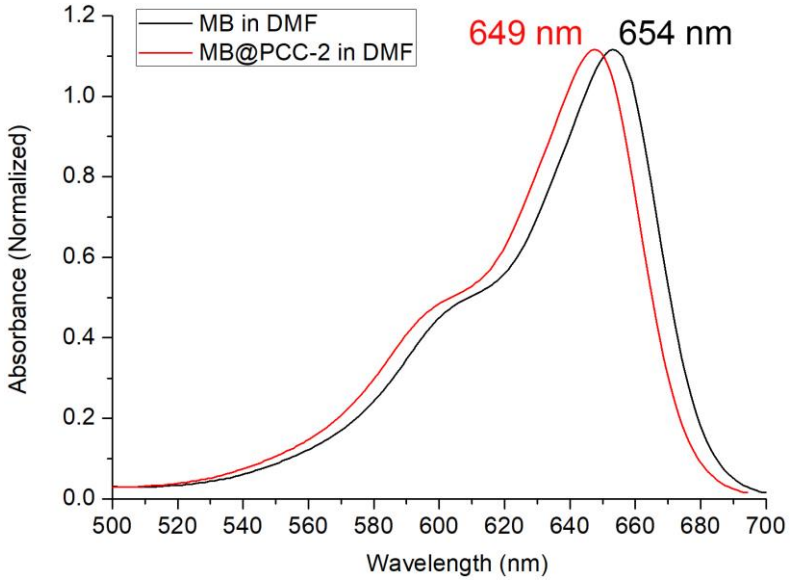

Fig. S2 UV-Vis spectrum of MB and MB@PCC-2 in DMF solution.

$Ru(bpy)_3Cl_2$ complex working Curve

$Ru(bpy)_3Cl_2$ (Ru) was dissolved into acetonitrile to prepare solution with concentration of 0.3 mg/100mL, 0.4 mg/100mL, 0.5 mg/100mL, 0.6 mg/100mL, 0.7 mg/100mL, 0.8 mg/100mL, 0.8 mg/100mL, and 0.9 mg/100mL. The absorbance was recorded (Table S2) and fitted by a linear equation (Fig. S3).

Table S2. Ru working curve.

Concentration (mg/100 mL)	Absorbance of 285 nm
0.3	0.336
0.4	0.464
0.5	0.561
0.6	0.672
0.7	0.797
0.8	0.918
0.9	1.019

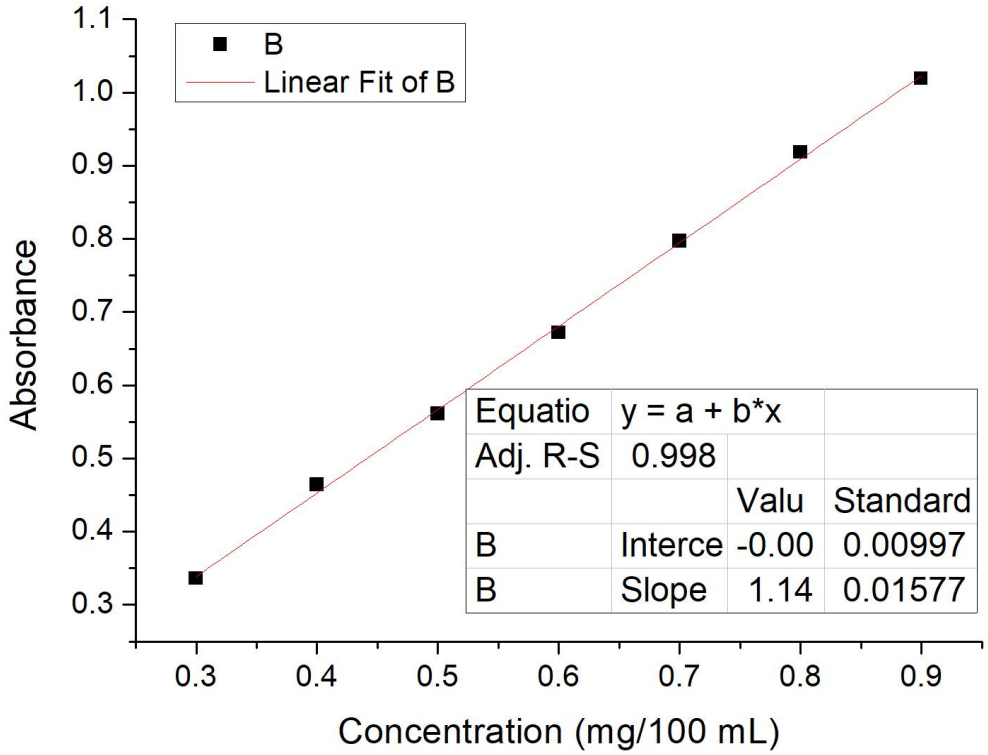

Fig. S3 Linear fitting of Ru working curve.

Solid-Liquid Ru Encapsulation by PCC-2

Typical Ru encapsulation procedure for PCC-2 is: 10.0 mg of activated single crystal of PCC-2 was soaked in a solution of 5 mg of Methylene Blue (MB) in 10 mL Acetonitrile, and stirred at room temperature for 40 mins. Then the supernatant was separated by centrifugation and analyzed by UV-Vis spectrum (diluted with the range of 0.1-0.7 mg/100 mL). By comparing the initial and final concentration, the encapsulated drug amount is 1.9 mg for 10 mg PCC-2. The loading ratio is 0.19 mg/mg and it's about 7 MB molecule per one PCC-2 cage. After encapsulation of MB dye, MB@PCC-2 was fully dissolved in DMF and the solution was shown in Fig. S2. Comparing to free dye, the peak of MB@PCC-2 blue shifted for 6.0 nm. The MB@PCC-2 solid was further characterized by Elemental analysis. Elemental analysis: calculated (%) for $Na_{24}(Et_3NH)_6$ $[C_{360}H_{222}S_{48}O_{198}Co_{24}]\cdot 3$ $[RuC_{30}H_{24}N_6Cl_2]\cdot 5$ MeOH · 18 H_2O, Calc: C 41.70, H 2.95, N 2.38, S 10.88; found (%):C 41.75, H 3.02, N 2.39 S 10.85.

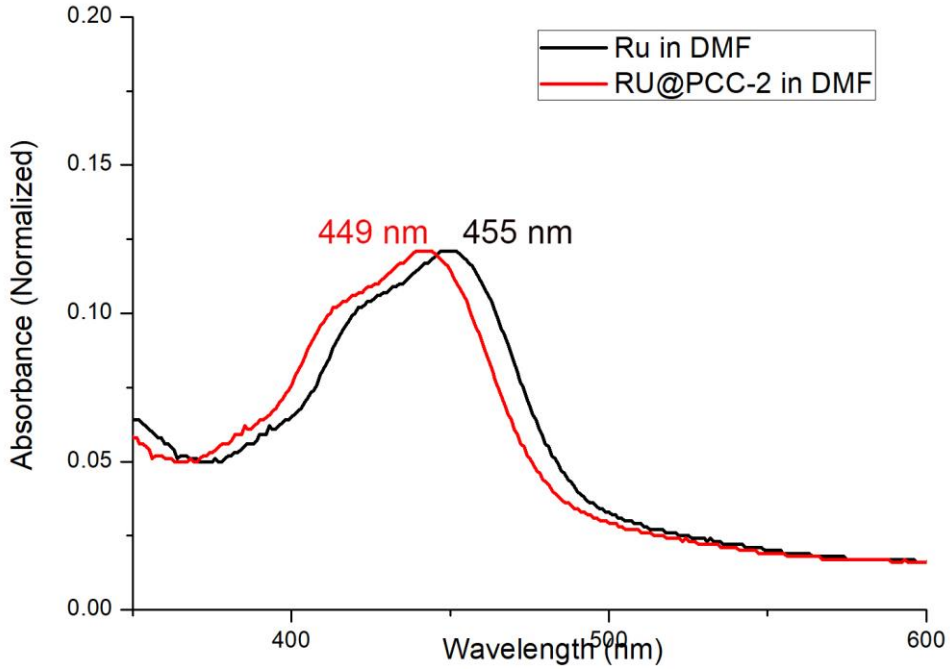

Fig. S4 UV-Vis spectrum of Ru and Ru@PCC-2 in DMF solution.

Simulation of Ru@PCC-2

For investigating the size between the Ru and the cavity of PCC-2, we run a molecular modeling. And we found that three molecules of Ru can be encapsulated within the cavity of PCC-2 (Fig. S5).

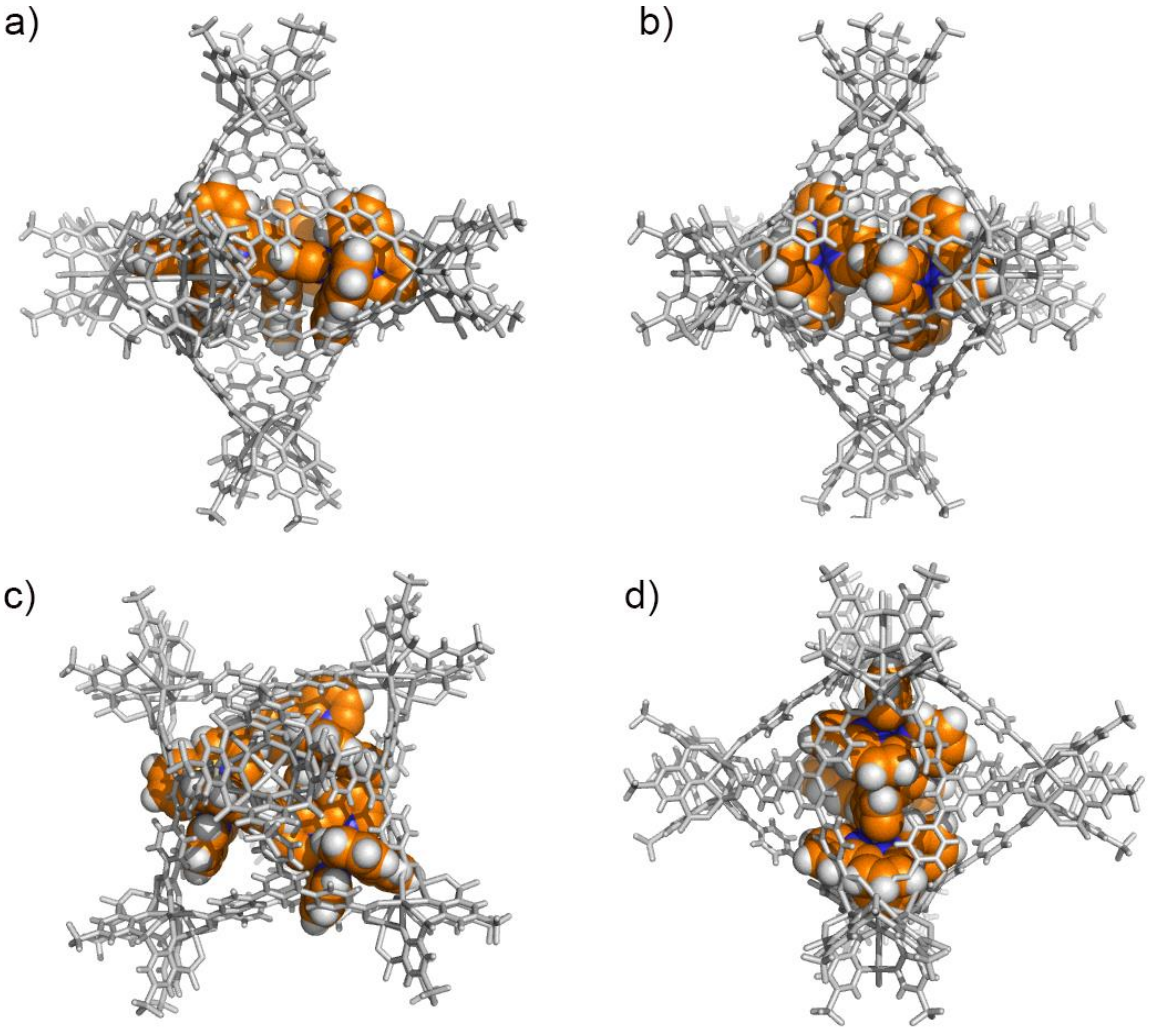

Fig. S5 Simulation of Ru@PCC-2 by molecular modeling.

Section 3. Dye Degradation

Reaction Rate

Photocatalytic degradation of MB was conducted to investigate the efficiency of photocatalysts. The photocatalytic activities of empty PCC-2, Ru and Ru@PCC-2 were monitored from the variation of the color in the reaction system by measuring the maximum absorbance intensity of the MB chromophoric group at λ_{max} = 654 nm. The reaction rate was record and shown in Figure 4 in the main context.
The experimental data was fitted by the first-order kinetic model as expressed by eqn (1).

$$-\ln(C/C_0) = kt \qquad (1)$$

The C_0 and C are the initial and current concentration of the MB, respectively, and k is the kinetic rate constant. The values of k were obtained from the slope between 20 min and 120 min, and the intercept of the linear plot. Reaction rate was calculated and shown in Fig S56 and S7.

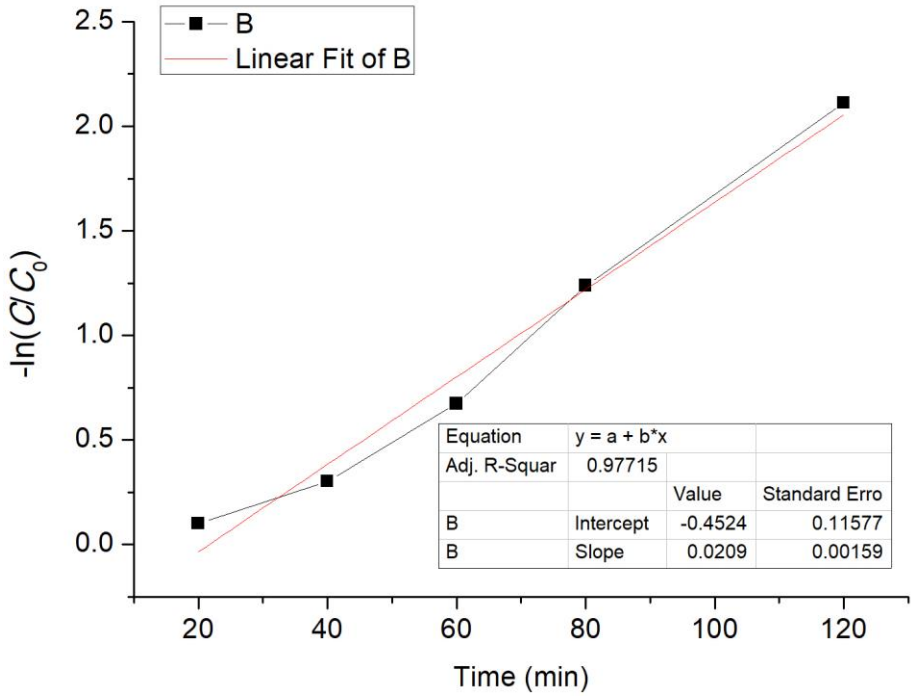

Fig. S6 First-order kinetics plot for the photodegradation of MB by Ru@PCC-2 under visible light irradiation.

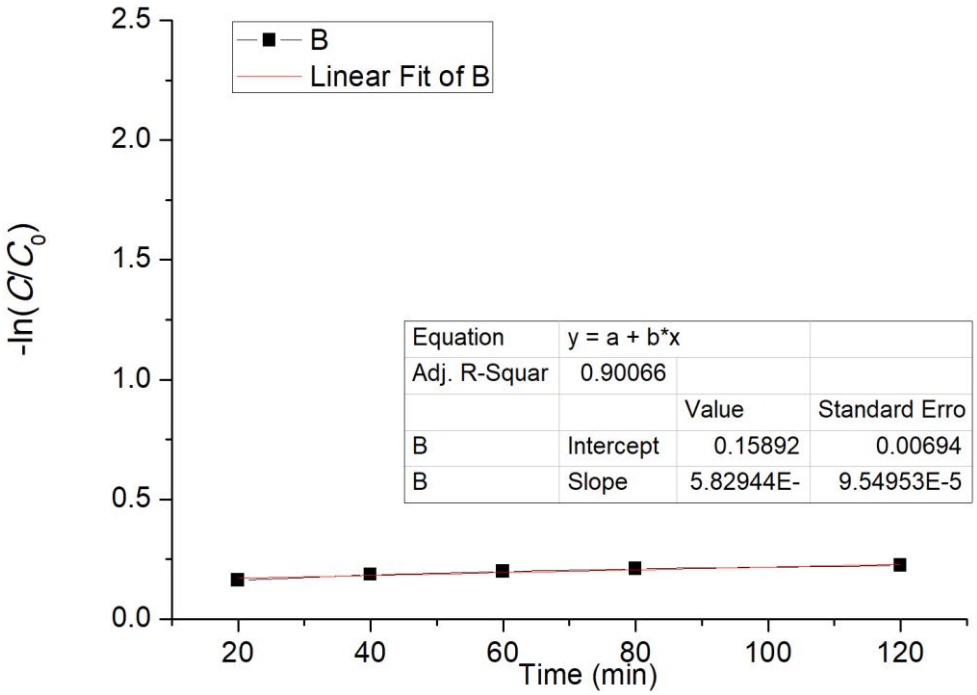

Fig. S7 First-order kinetics plot for the photodegradation of MB by Ru under visible light irradiation.

Stability Test

After degradation reaction, the catalyst Ru@PCC-2 was precipitated by adding excess amount of MeOH and filtrated as orange powder. The orange powder was washed by MeOH and acetonitrile for three times, then tried in air. Then the orange powder was dissolved in DMF and put into 1 mm cell for UV-Vis measurement. UV-Vis spectra (Fig. S8) and ESI-MS spectra (Fig. S9) were record for Ru@PCC-2 before and after reaction. UV-Vis spectra indicate that Ru@PCC-2 was intact after reaction, showing no change of position and intensity of UV peaks. ESI-MS spectrum of PCC-2 after reaction still contains significant amount of ionic peaks, suggesting the structure of PCC-2 are still maintained.

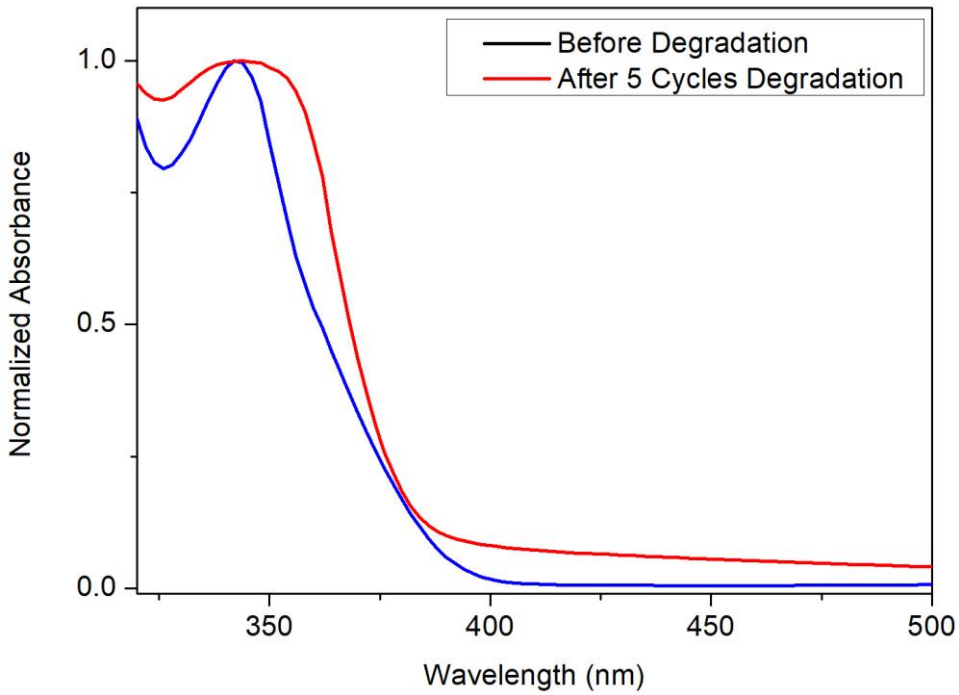

Fig. S8 UV-Vis spectrum of Ru@PCC-2 before and after 5 times of degradation reactions.

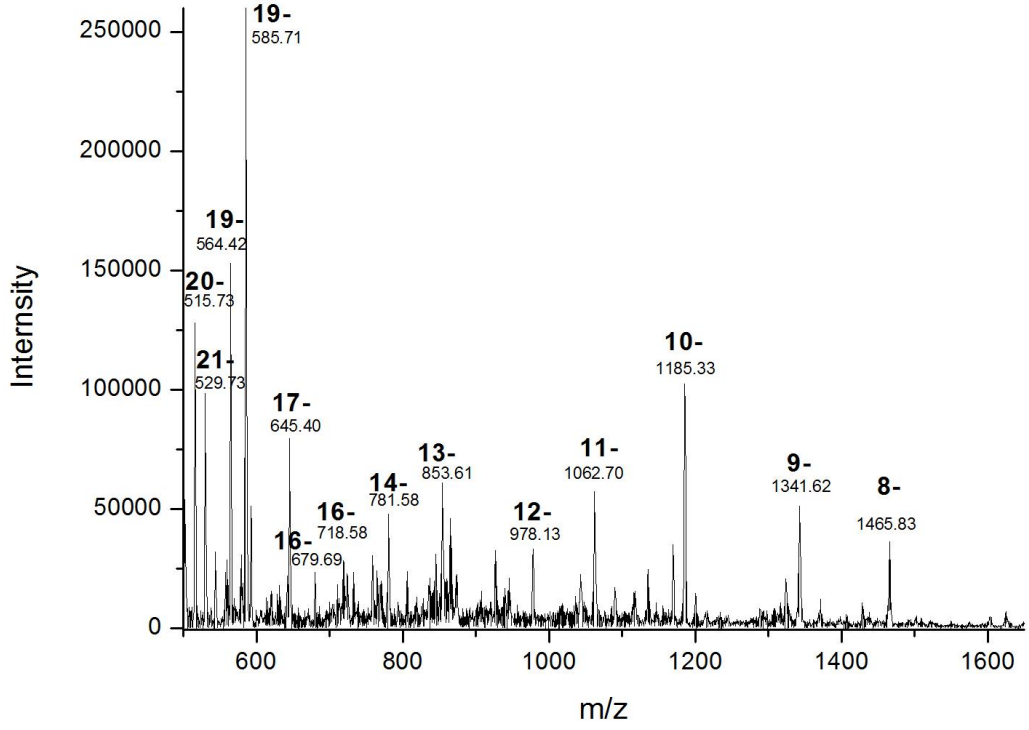

Fig. S9 ESI-MS Spectrum of PCC-2 before reaction.

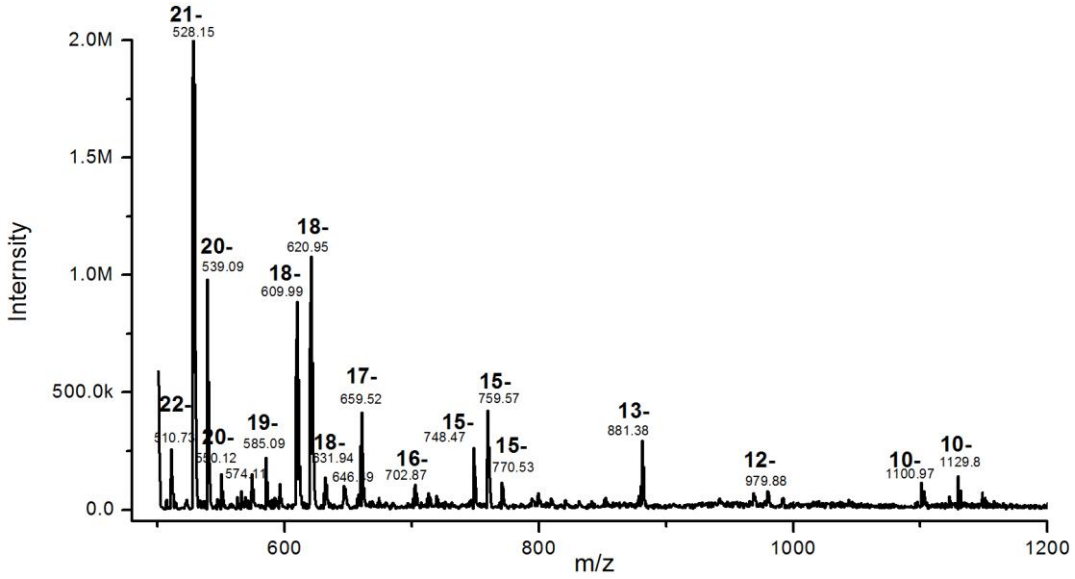

Fig. S10 ESI-MS spectrum of Ru@PCC-2 after 5 times of degradation reactions.

References

(1) Iki, N.; Horiuchi, T.; Oka, H.; Koyama, K.; Morohashi, N.; Kabuto, C.; Miyano, S. *J. Chem. Soc., Perkin, Trans.* **2001**, *2*, 2219-2225.