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Supporting Information for

Surface polycondensation as an effective tool to activate organic crystals: from “boxed” semiconductors for water oxidation to 1d car-bon nanotubes

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Experiment section

All chemicals were purchased from Sigma-Aldrich Inco.

First, 492 mg melamine (M) and 408 mg chloranilic acid (CLA) were shaken overnight in 40 mL water with a vibration speed of 350 times per minute. The liquid shows purple while the crystal is orange. After that, the formed crystals were centrifuged with the speed of 8000 r/min, and then fully dried at 60 °C, given a solid powder B-M-CLA with orange colour.

These complex crystals were slightly ground and heated at different temperature for 4 h. The heating speed was 2 °C per minute. The final products are named as M-CLA-heating temperature (i.e. M-CLA-300 stands for the sample synthesized at 300 °C). The colour ranges step by step from orange to black with increasing temperature.

MB (Methylene Blue, 5 mg L^{-1}) and RhB (Rhodamine B,1 mg L^{-1}) solution were prepared in advance with deionized water. For photodegradation test, 5 mg of photocatalyst was dispersed in 20 ml MB or RhB solution. After saturation in the dark for 1 hour, the degradation system was illuminated by 50 W LED light with constant stirring.

Peroxide detection:

5 mg CLA-M-250 material was added into 20 mL RhB water solution (0.2mg L^{-1}) and then the reaction system was kept stirring under white light illumination (350 nm~infrad radiation). The peroxide test from was dipped in to the solution for 1 second, after the visible fade of dye, which would not be affected by the color of dye molecule itself. After 5 seconds, the color of test was compared with stardard color card and got the result. The peroxide test we use is from MQuant with the item number 110081.

Oxygen production experiment:

The preparation of cocatalyst doped M-CLA-250: it was synthesized by using 400 mg M-CLA-250 and 48 mg $Co(NO_3)_2$ that were mixed together with 50 mL water. Then the solution was constantly stirred while heated at around 80 °C for 2 hours. After that, $Co(NO_3)_2$ was converted to CoO at 200 °C.

For the oxygen evolution reaction measurement, 100 mg Co doped M-CLA-250 material was added into the reaction flask together with 200 mg $AgNO_3$ and 100 mL water. Then the whole reaction system was flushed with nitrogen for 5 minutes to remove dissolved oxygen. During the experiment process, an oxygen sensor was inserted under the water level while nitrogen was continuously coming above the liquid level to prevent no oxygen leakage from the outside. The experiment setup was exposed to visible light at around 20 centigrade, while the oxygen content was monitored by oxygen dipping probe sensor from PreSens. The control experiments were conducted also as above mentioned, only without one factor each time, such as illumination, $AgNO_3$ or cocatalyst.

Characterization device

PXRD patterns were recorded with a Bruker D8 Advance instrument with Cu Kα radiation.

SEM images were obtained on a LEO 1550-Gemini microscope.
Shimadzu UV 2600 was used to reveal the optical absorbance spectra of powders.
The structures of materials in this work is observed by scanning electron microscope (SEM) on JSM-7500F (JEOL) equipped with an Oxford Instruments X-MAX80 mm^2 detector. The morphology of samples were also checked by transmission electron microscopy (TEM) with an EM 912 Omega microscope ar120 kV.
The STEM images were acquired using a double-corrected Jeol ARM200F, equipped with a cold field emission gun. For the investigation, the acceleration voltage was put to 200kV, the emission was set to 15µA and a condenser aperture with a diametre of 30µm was used.
Thermo Scientific™ Nicolet™ iS™5 FT-IR spectrometer was used for Fourier transform infrared spectroscopy measurement.
Elemental analysis result was revealed through combustion analysis with the Vario Micro device.
The information about surface area was calculated based on 77K N_2 adsorption-desorption in Brunauer-Emmett-Teller (BET) model. Before measurement, the samples were heated at 120 °C for 6 hours.
Elemental composition of products and chemical states of the surface elements were analyzed by X-ray photoelectron spectroscopy using ESCALab220i-XL electron spectrometer from VG Scientific and 300W AlKα radiation.

Table S1 the yield of B-M-CLA with different CLA/M molar ratio

CLA (mg)	M (mg)	molar ratio of CLA:M	Yield
408	82	3:1	37%
408	123	2:1	49%
305	246	3:4	89%
204	246	1:2	99%
153	367	1:4	48%
108	367	1:6	24%

Table S2 Element analysis results of materials synthesized at different temperature

	N%	C%	H%	S%	C/N
B-CLA-M	33.40	29.14	3.569	0.584	0.8720
CLA-M-200	33.46	29.05	3.592	0.618	0.8682
CLA-M-250	33.21	29.01	3.460	0.607	0.8739
CLA-M-280	41.88	35.73	3.278	0.778	0.8536
CLA-M-300	40.99	34.63	3.052	0.640	0.8447
CLA-M-550	40.41	46.80	1.285	0.683	1.1580
CLA-m700	31.93	35.73	1.679	0.688	1.7744
CLA-M-800	24.62	66.20	0	0.8507	2.6790

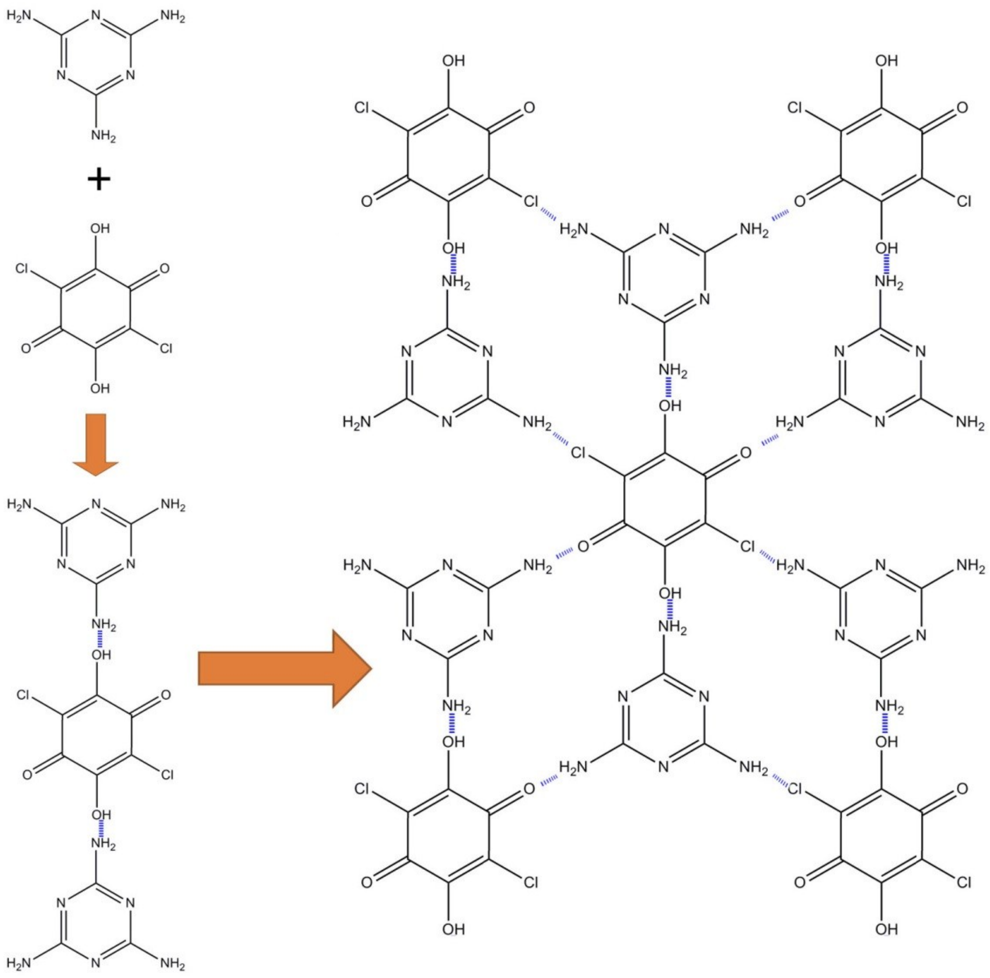

Figure S1 monomers and complex structure

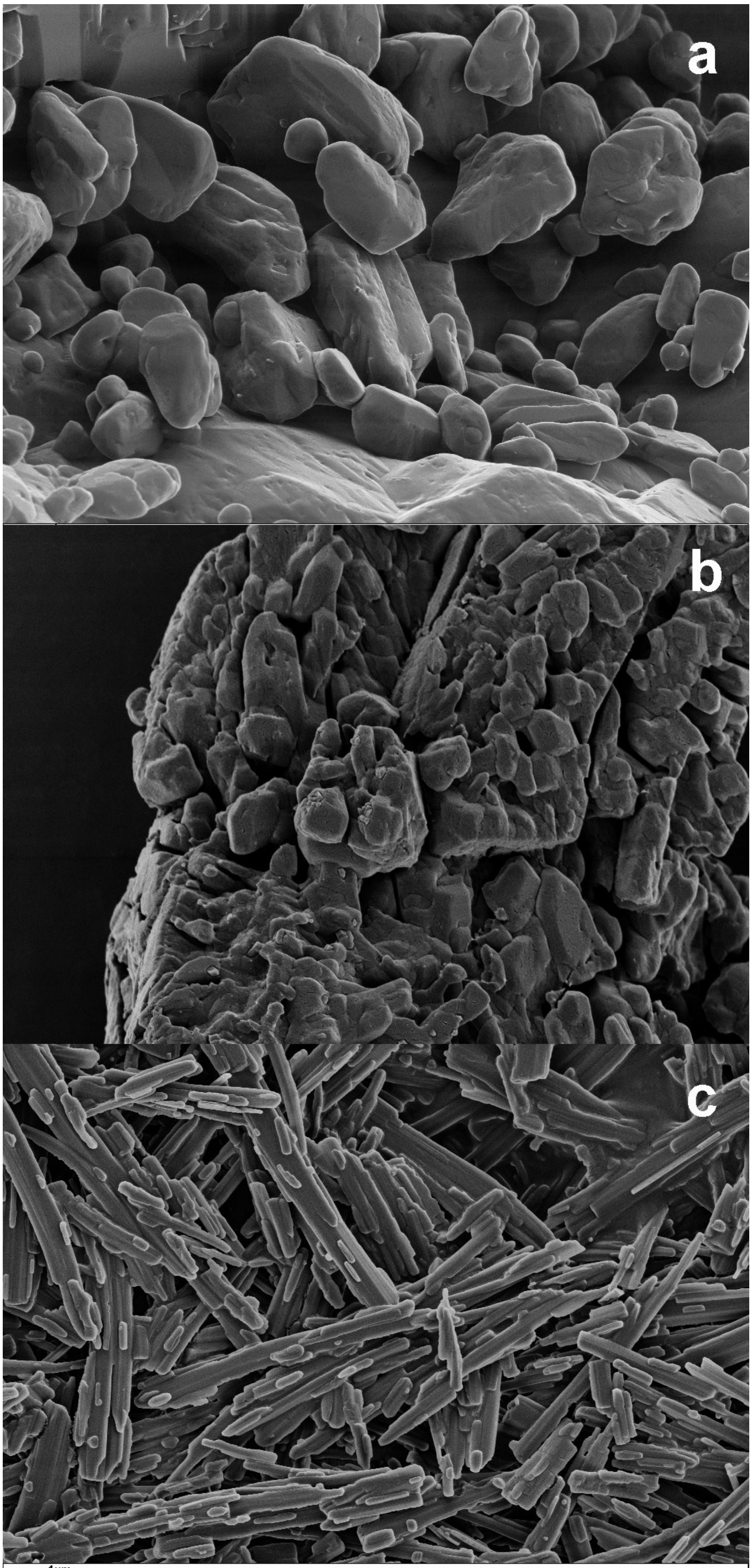

Figure S2 SEM graphs of monomer melamine (a), chloranillic acid (b) and the complex of B-CLA-M (c).

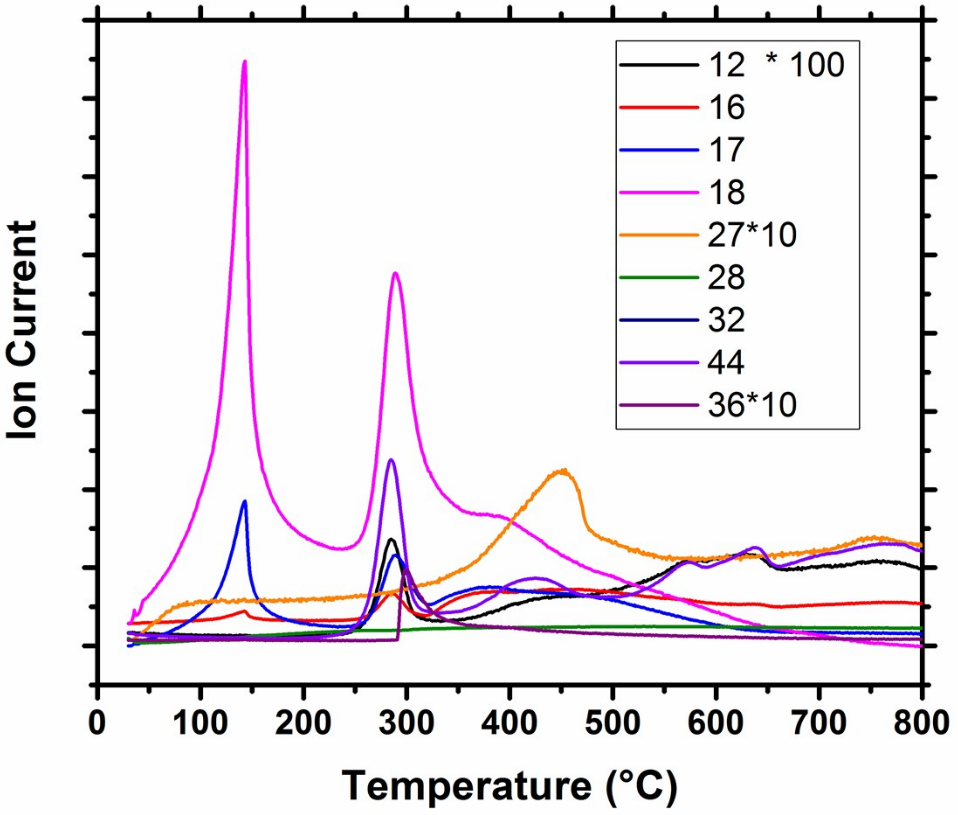

Figure S3. Corresponding MS ion currents of different weight fraction released from the reaction with temperature.

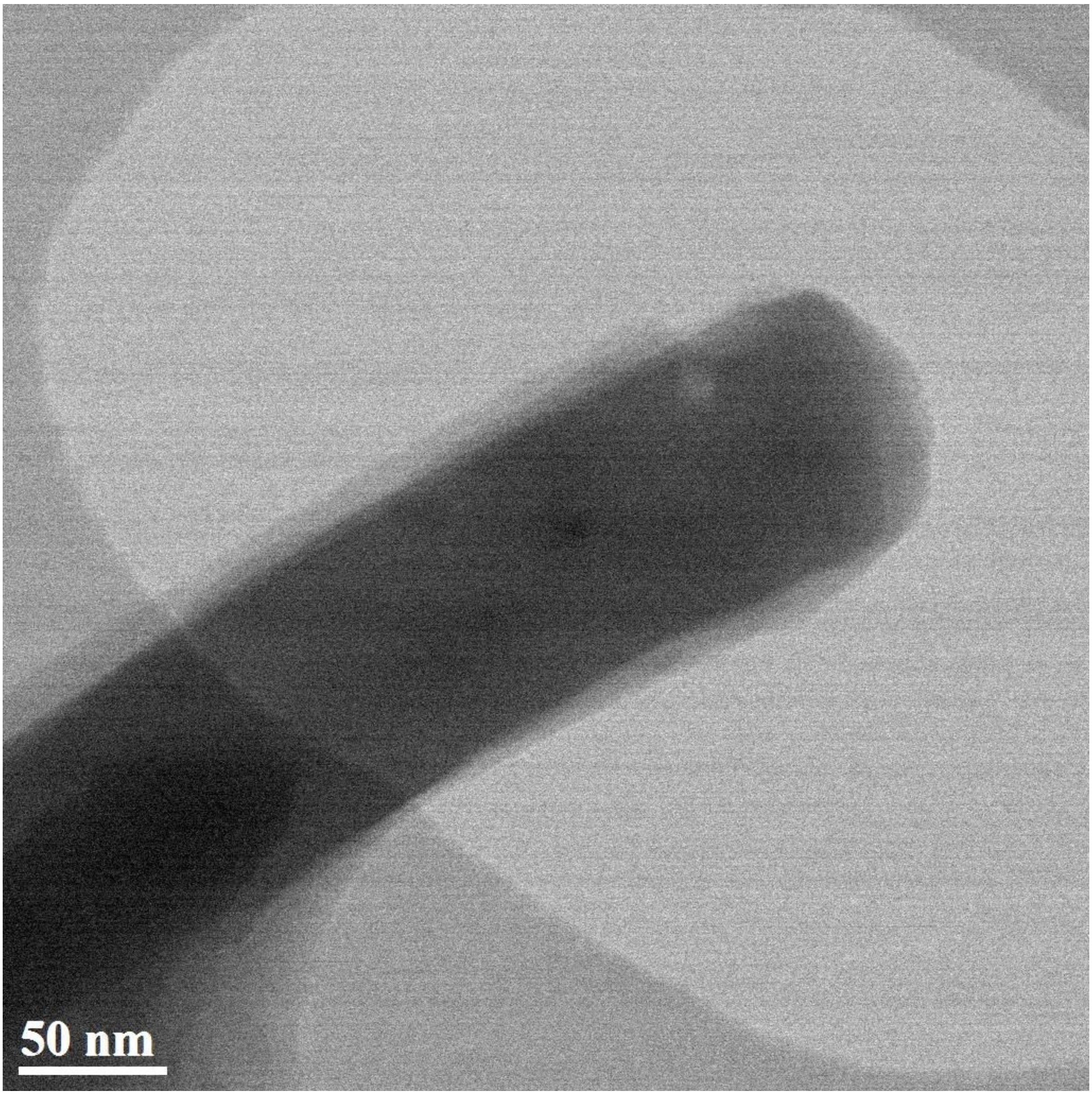

Figure S4 high resolution TEM graphs of CLA-M-250

Table S3 kinetics of the degradation reaction with different catalysts

	K
B-M-CLA	0.004555
M-CLA-200	0.004806
M-CLA-250	0.010879
M-CLA-300	0.006134
M-CLA-550	0.005148
M-CLA-250 with O2	0.011670
M-CLA-250 with Ag+	0.017420
M-CLA-250 with MeOH	0.004100
M-CLA-250 with tertbutanol	0.001582

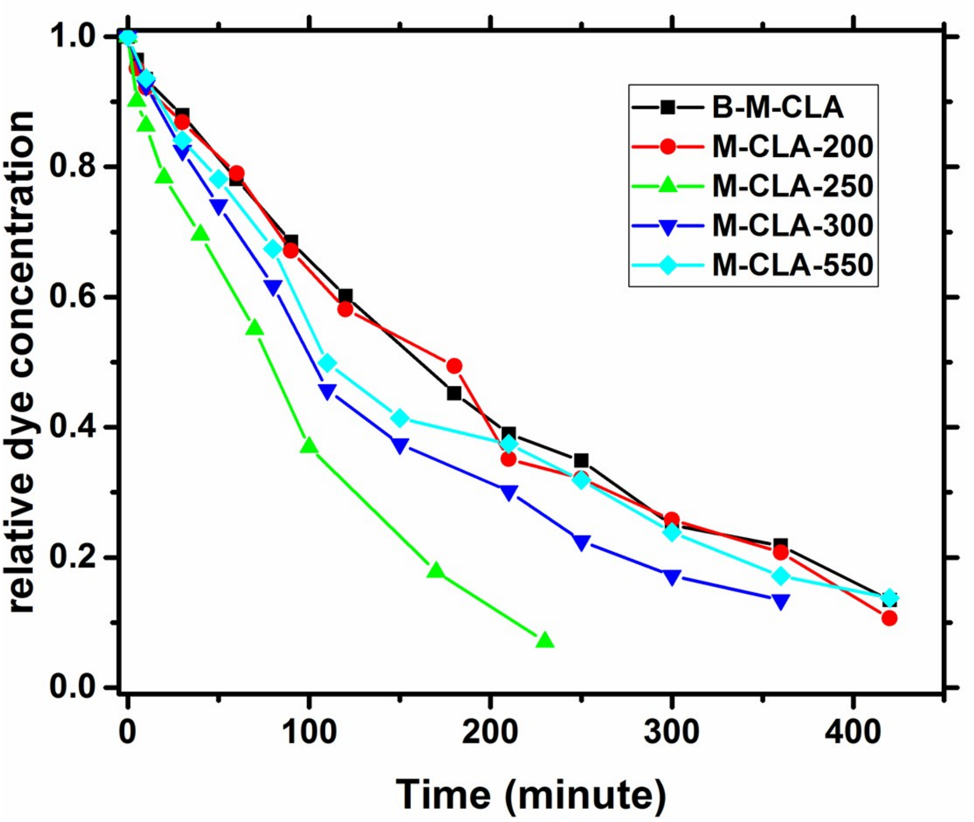

Figure S5. Photochemical RhB degradation curves with different catalysts.

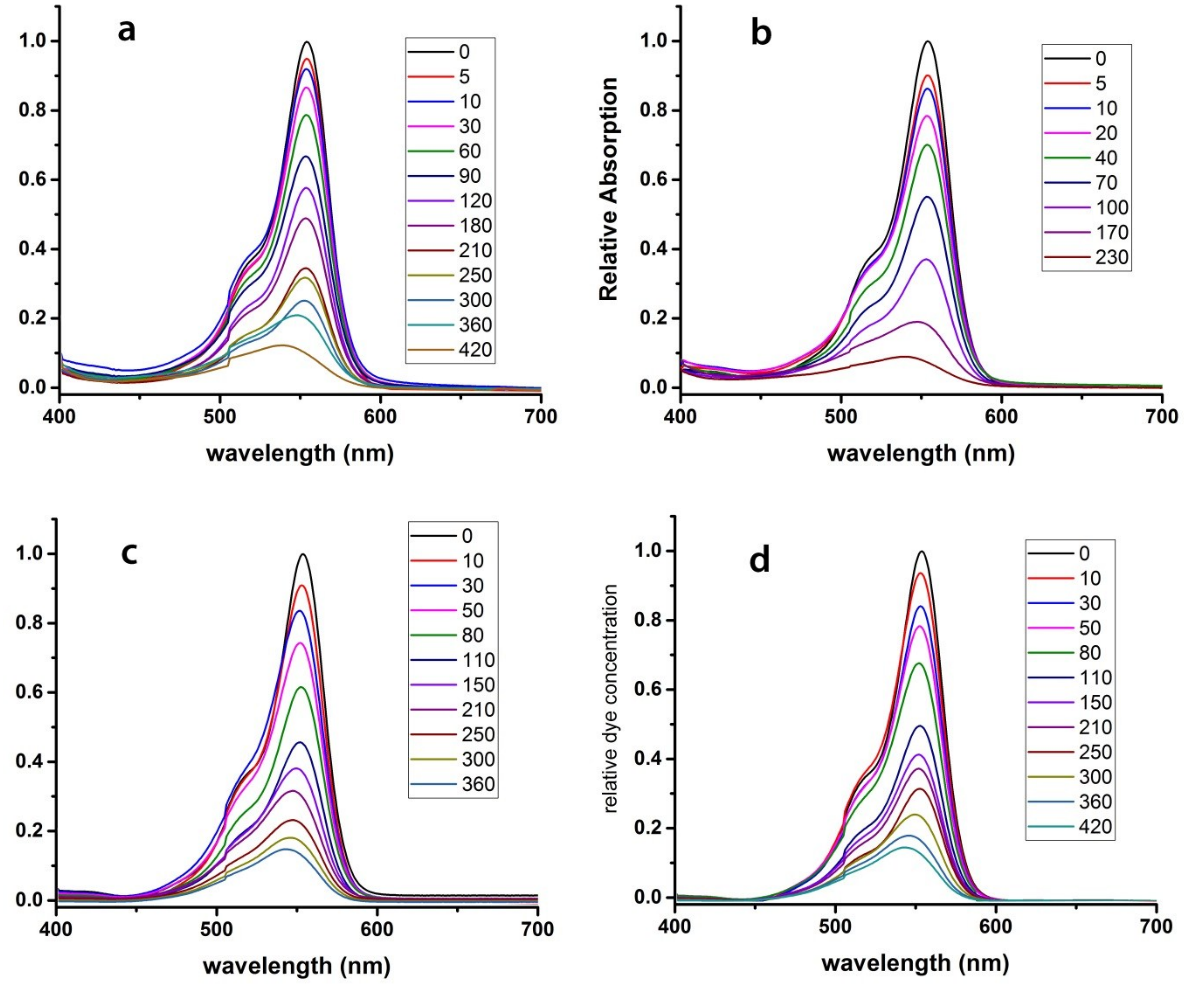

Figure S6. Degradation of RhB with CLA-M-200(a), CLA-M-250(b), CLA-M-300(c) and CLA-M-550(d) as Catalysts respectively.

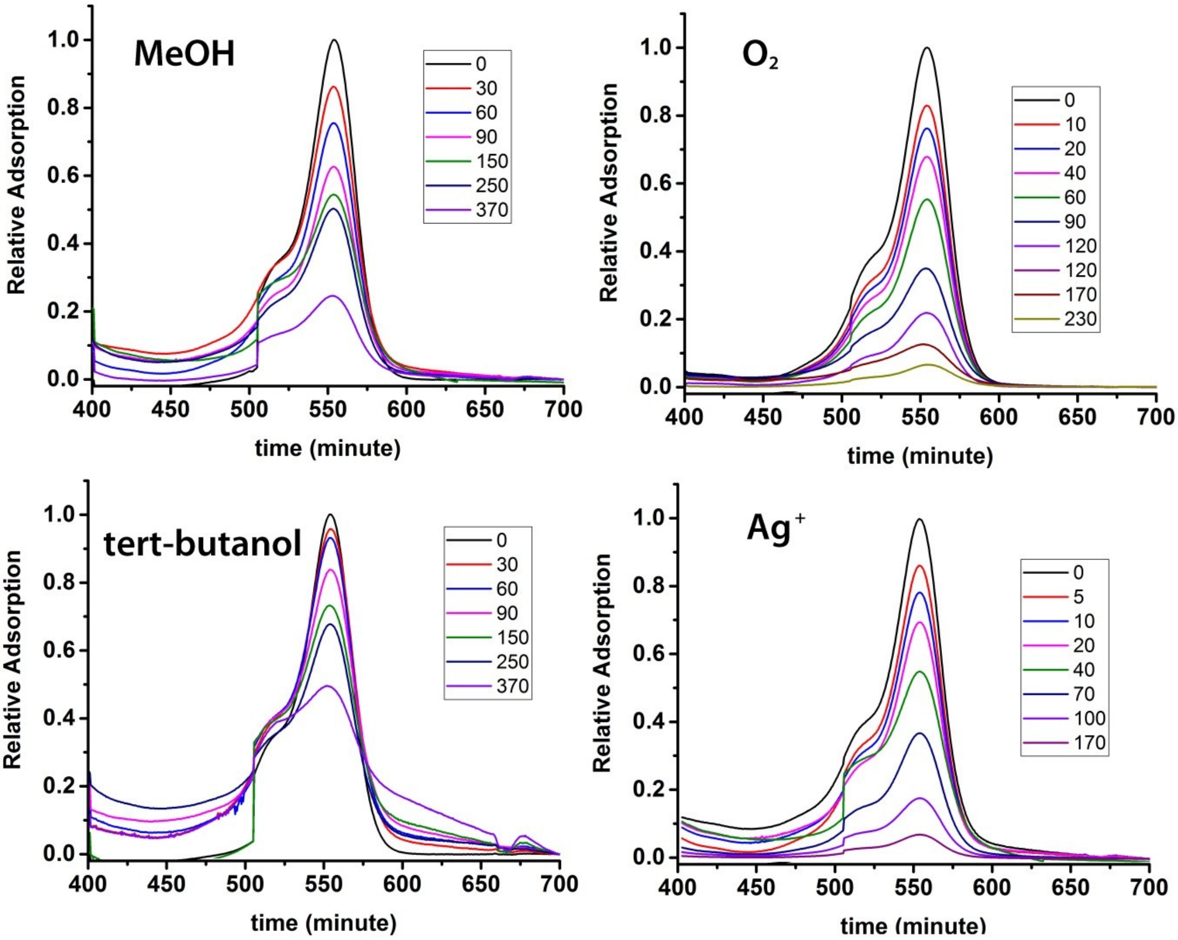

Figure S7. Photochemical RhB degradation curves with different (CLA-M-250 as the catalyst).

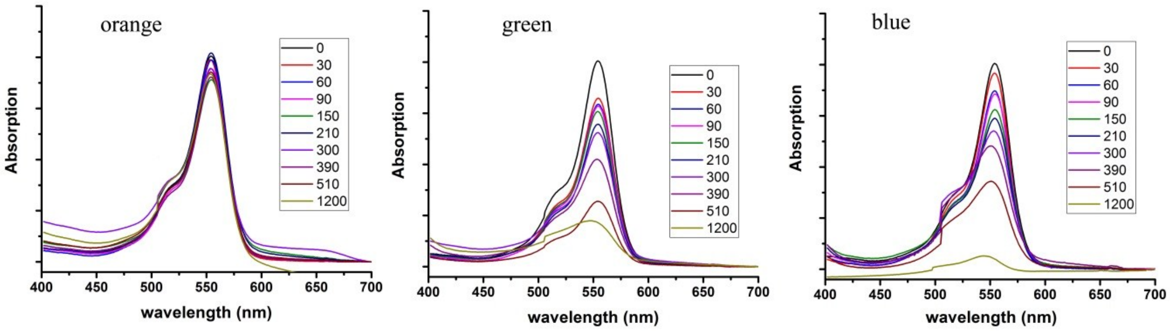

Figure S8. RhB Degradation with CLA-M-250 in 3 pure lights, blue (445 nm), green (520 nm) and orange (590 nm), respectively.

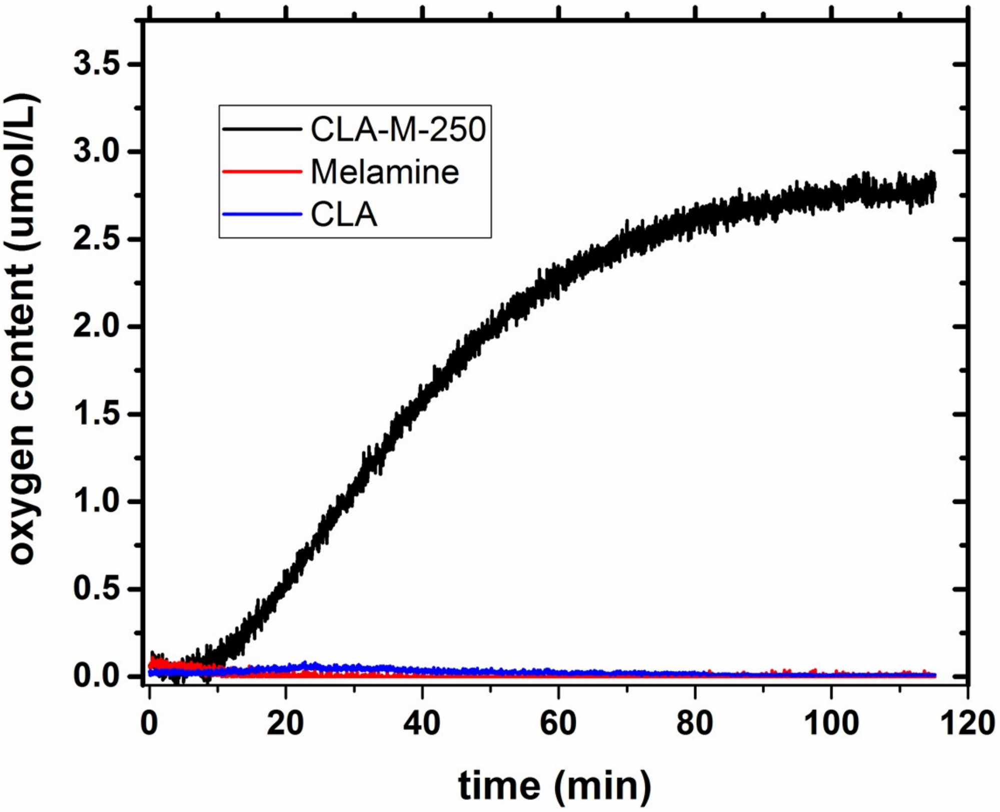

Figure S9 comparison of oxygen production experiments with CLA-M-250 and monomers.

The degradation of phenol:

20 mg CLA-250 was added into 30 mL glass bottle with 20 mL 1mg/L phenol water solution. After stirring in dark for 1 hour, the whole system was placed under illumination for one day. Before and after the degradation, both of the solution was checked with GC-MS. Before that, the signal of phenol could be detected, however after that this signal disappears. In addition, the pH of this system drop to 4 from the beginning 5.5, which could represent the final degradation products, could be acidic substances, such as oxalic acid or succinic acid. That information could be used to prove the degradation of phenol.

Besides, 20mg CLA-250 was added into 30 mL glass bottle with 20 mL 1mg/L phenol water solution. After stirring in dark for 1 hour, the whole system was placed under illumination. With the process of photo reaction, the solution was measured with GC-FID, the peak area of phenol could be observed slowly decreasing with time as shown below.

time	Integral Peak area (unit: million)
0h	6.62
4h	6.44
12h	5.97
16h	5.77
24h	5.34
36h	4.06