Supporting Information

Photocatalytic Degradation of RhB by Fluorinated Bi_2WO_6 and Distributions of the Intermediate Products

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Sample Preparation:

Fluorinated Bi_2WO_6 samples were prepared by a two–step hydrothermal process. The starting materials of WO_3, Na_2O and NaF were mixed and calcined at 1100 °C. The final Na_2WO_4 containing F^- ions was obtained from XRD patterns (Figure *S1*). In what followed, the value of $\boldsymbol{R_F}$ was used to describe the molar ratio of NaF to Na_2O; these were 0, 0.1, 0.2, 0.4 and 0.6 nominal ratios. The calcined sample and $Bi(NO_3)_3$ (the molar ratio of 1:1) were used to synthesis fluorinated Bi_2WO_6 by a hydrothermal process described as our previous report (*3*). The resulting products were collected by filtration, and then were washed by deionized water for several times until no F^- ions were left in the solution as tested. The samples were then dried at 80 °C for 4 h for characterization.

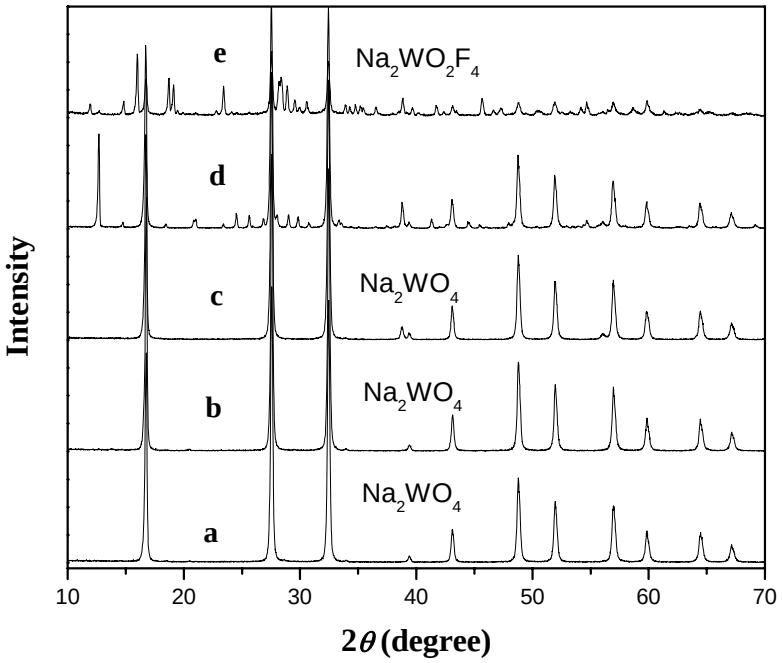


FIGURE *S1*. XRD patterns of Na_2WO_4 with the different F doping content prepared by high–temperature solid state reaction. $\boldsymbol{R_F}$ = 0 (a), $\boldsymbol{R_F}$ = 0.1 (b), $\boldsymbol{R_F}$ = 0.2 (c), $\boldsymbol{R_F}$ = 0.4 (d) and $\boldsymbol{R_F}$ = 0.6 (e).

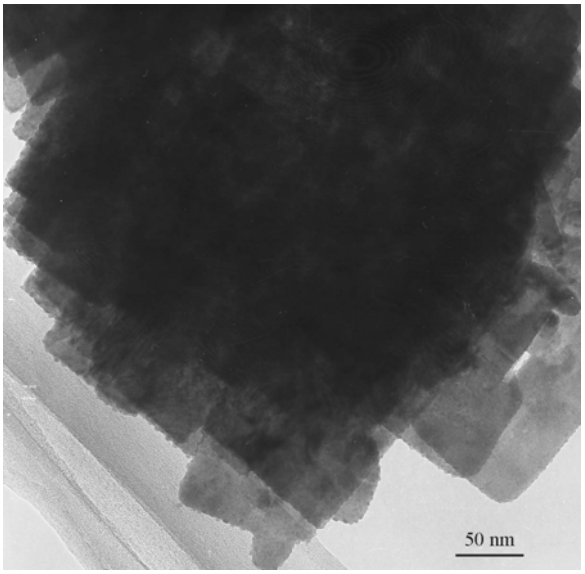


FIGURE *S2*. TEM image of the as–prepared sample ($\boldsymbol{R_F}$ = 0.4) prepared by the hydrothermal process at 180 °C for 24 h.

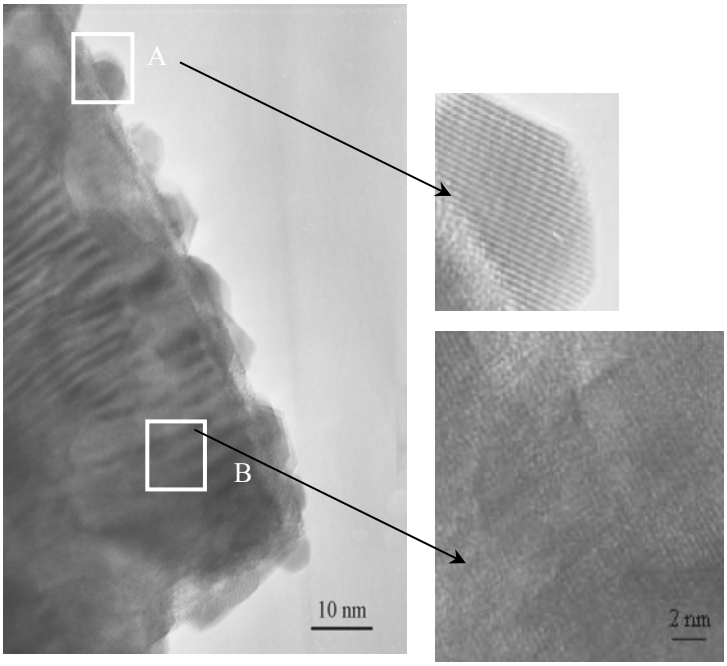


FIGURE *S3*. HRTEM image of the as–prepared sample ($\boldsymbol{R}_{\mathbf{F}}$ = 0.4) prepared by hydrothermal process at 180 °C for 24 h. One can see that the F–Bi_2WO_6 crystal is sheet–shaped, which is similar with that of Bi_2WO_6 in our previous publication (*5*). The growth orientation was the same in different areas, indicating a single-crystalline feature of the whole nanoplates. However, the growth orientations were different in the areas of A and B. The sample particles on the edges could be the impurities of Bi_2O_3.

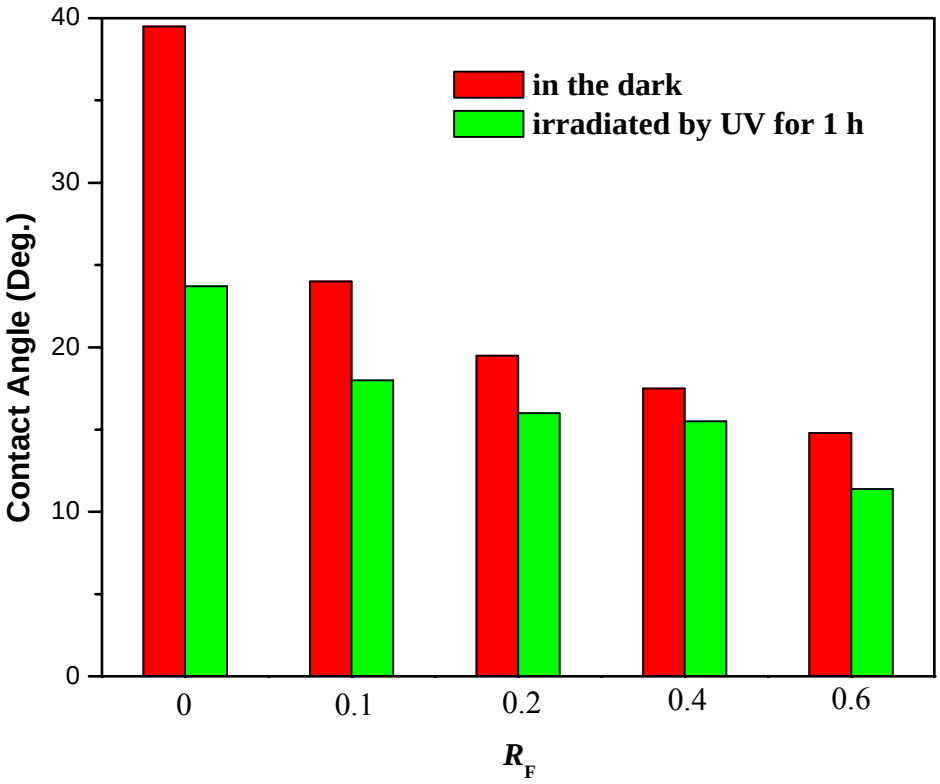


FIGURE *S4*. Change of the water CA under weak UV light irradiation (black light bulb, light intensity = 20 μW cm^{-2}) on the as–prepared samples.

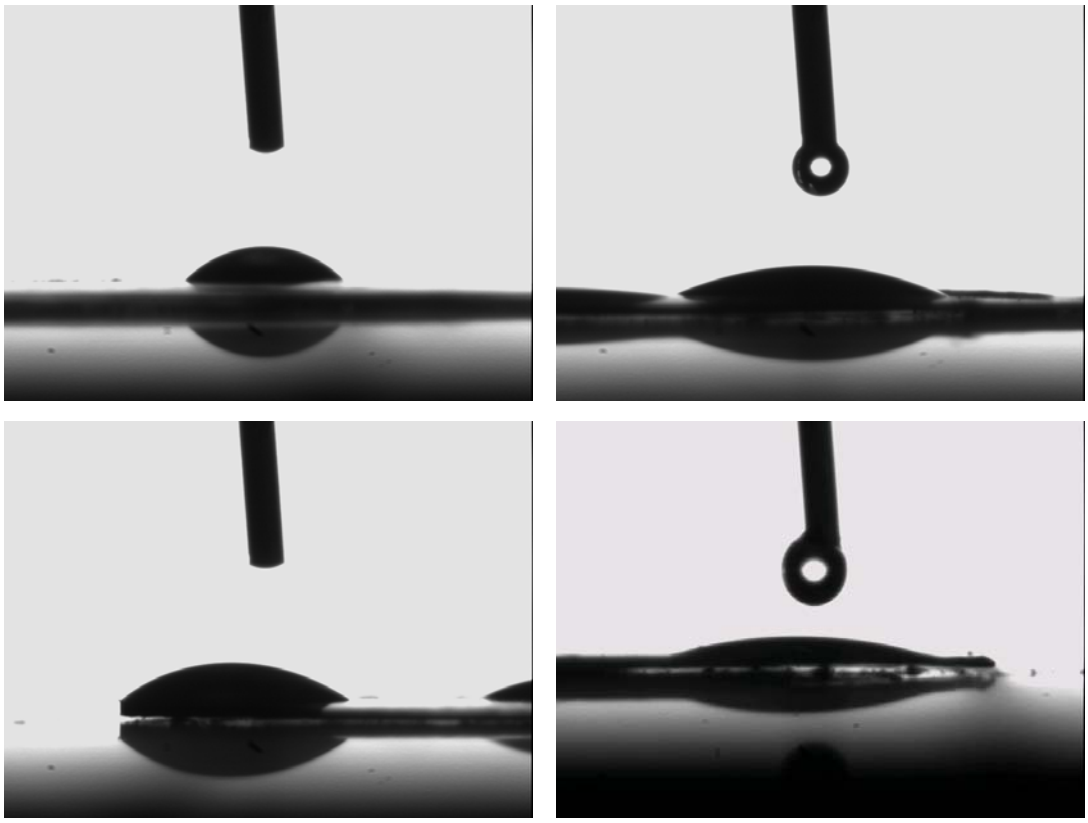


FIGURE *S5*. The CA variation of the as–prepared sample. Before (A) and after (B) irradiation of the sample ($\boldsymbol{R}_{\mathbf{F}} = 0$); before (C) and after (D) irradiation of the sample ($\boldsymbol{R}_{\mathbf{F}} = 0.4$).

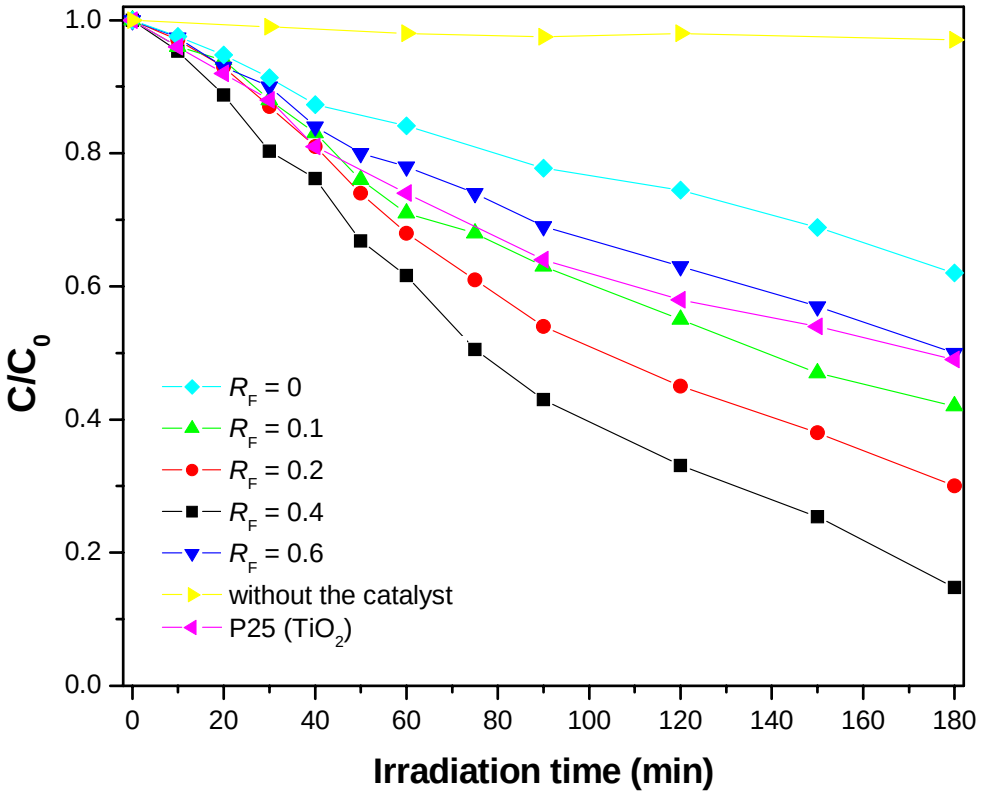


FIGURE *S6*. Photodegradation of RhB over the as–prepared samples as a function of UV irradiation time. Catalyst loading, 0.1 g; RhB concentration, 2×10^{-5} M. The data was gained by recording the variations in the absorption band (553 nm) in the UV–visible spectra of RhB.

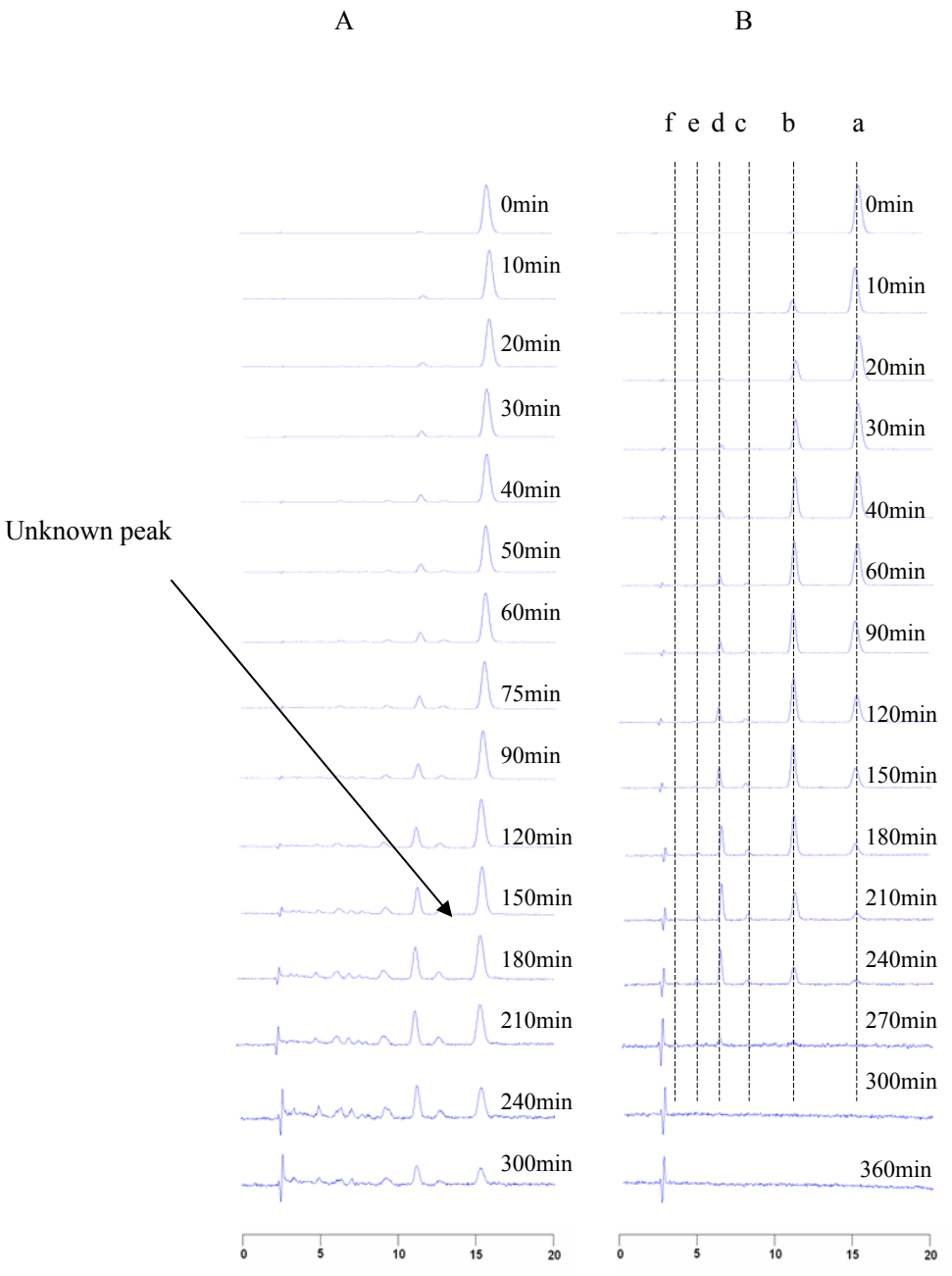


FIGURE *S7.* HPLC chromatograms of the *N*–deethylated intermediates at different irradiation intervals. Initial conditions are the same as those described in Figure 4; (A) $\boldsymbol{R_F}$ = 0, (B) $\boldsymbol{R_F}$ = 0.4.

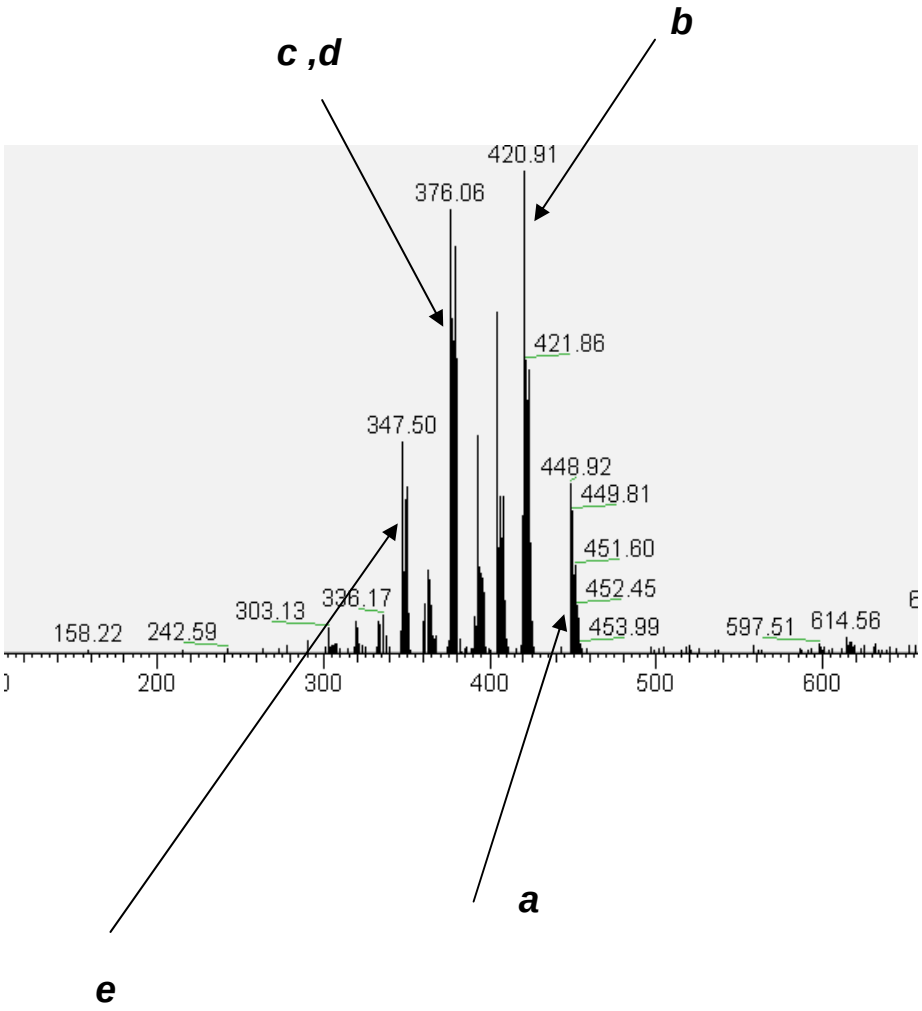
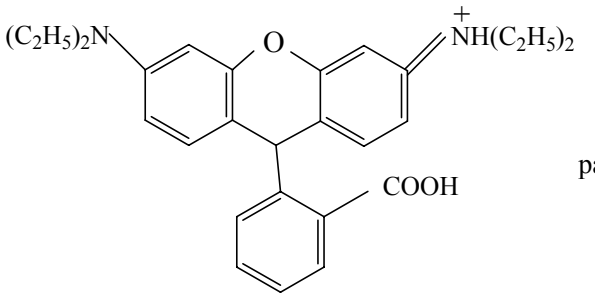
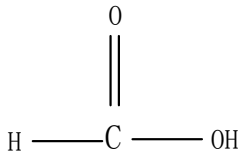


FIGURE *S8*. Identification of deethylation intermediates of RhB by GC–MS. Typical LC–MS chromatogram at the irradiation for 180 min.

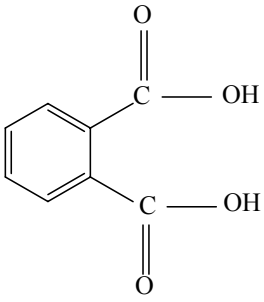
- ***a*** parent RhB
- ***b*** *N*, *N*–diethyl–*N´* –ethylrhodamine (DER)
- ***c*** *N*–ehyl–*N*–ethylrhodamine (EER)
- ***d*** *N*, *N*–diethylrhodamine (DR)
- ***e*** *N*–ethylrhodamine (ER)



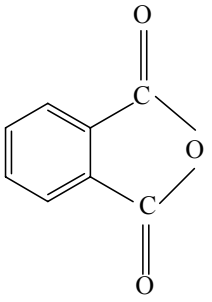
parent RhB



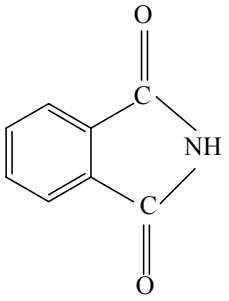
formic acid



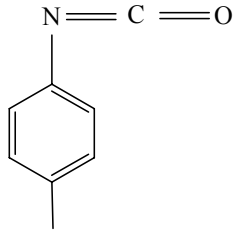
phthalic acid

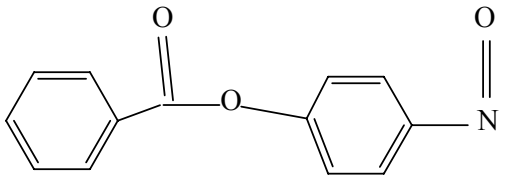


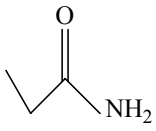
phthalic ester

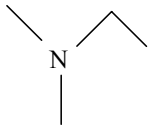


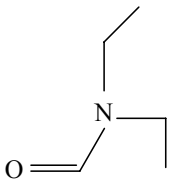
phthalic anhydride

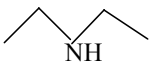


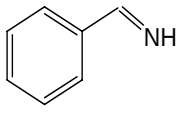












N-containing molecular fractions

FIGURE *S9*. Identification of the ring–open products of RhB by GC–MS in the presence of Bi_2WO_6 ($\boldsymbol{R_F}$ = 0 and $\boldsymbol{R_F}$ = 0.4).

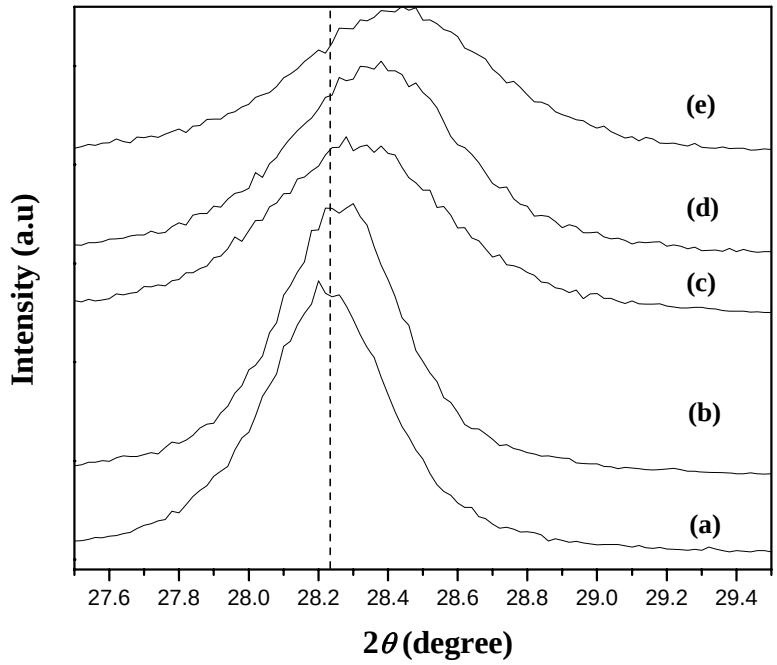


FIGURE *S10*. Diffraction peak positions of the (*113*) plane in the range of 2θ = 27.5–29.5°; $\boldsymbol{R}_{\mathbf{F}}$ = 0 (a), $\boldsymbol{R}_{\mathbf{F}}$ = 0.1 (b), $\boldsymbol{R}_{\mathbf{F}}$ = 0.2 (c), $\boldsymbol{R}_{\mathbf{F}}$ = 0.4 (d) and $\boldsymbol{R}_{\mathbf{F}}$ = 0.6 (e).