**Supplementary Information**

Photocatalytic decolorization of three commercial dyes using a new heteropolyoxotantalate catalyst

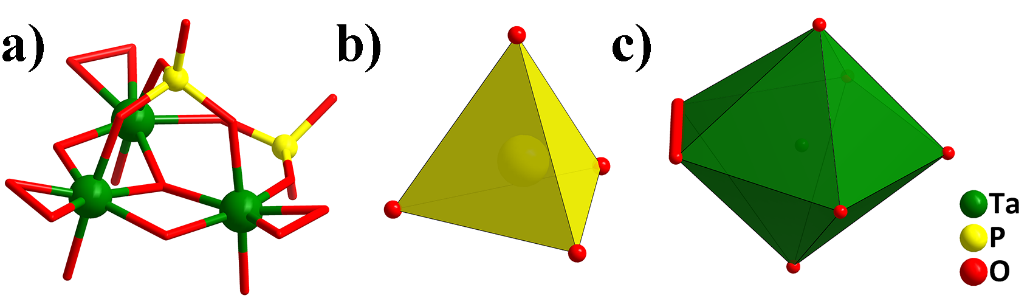
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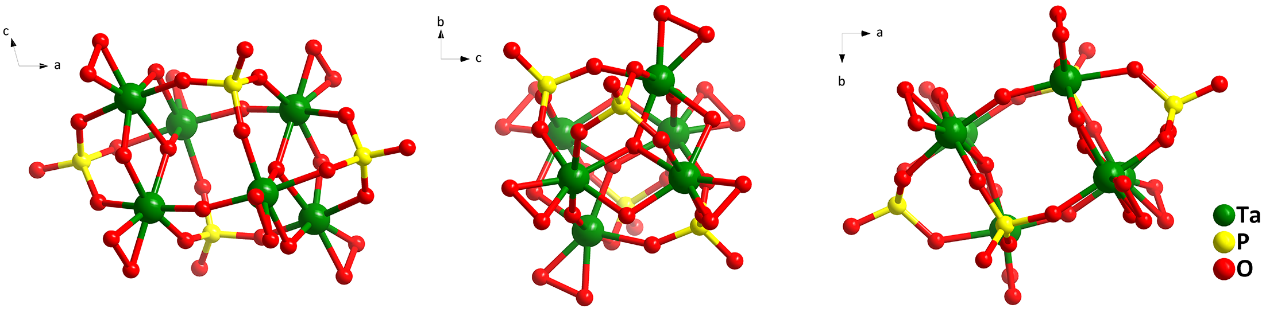
*b* *National Demonstration Center for Environmental and Planning, Henan University, Kaifeng, 475004 Henan, China.*

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**Figure S1. Ball-and-stick representation of P2Ta3 fragment (a), PO4 environment (b) and TaO7 coordination environment (c).**

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**Figure S2. Viewing from different direction of ball-and-stick representations of polyanion 1 (a-c) and the ellipsoid structure of polyanion 1 (d).**

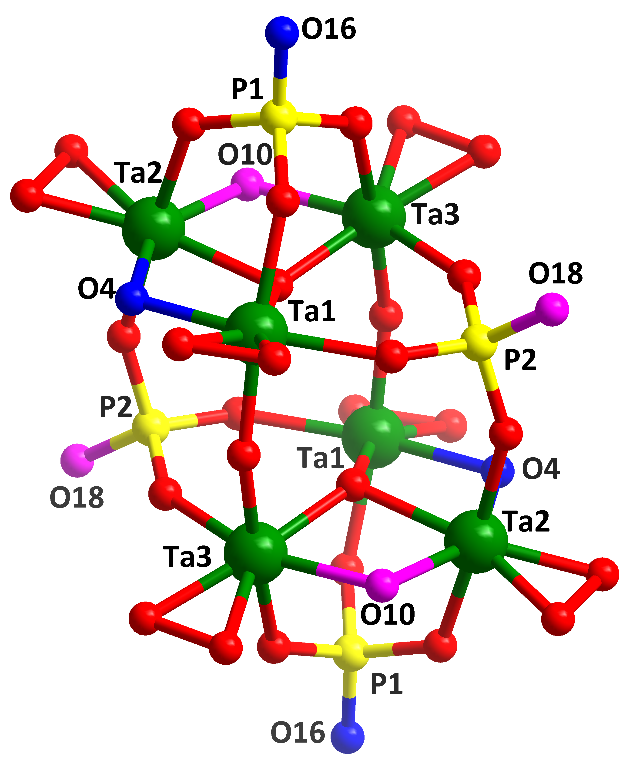
**Table S1. Bond lengths in 1a.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Ta–O distance (Å) | | | | | |
| Ta1–O1 | 1.918 | Ta2–O4 | 2.046 | Ta3–O1 | 1.916 |
| Ta1–O2 | 1.964 | Ta2–O5 | 2.096 | Ta3–O5 | 2.099 |
| Ta1–O3 | 1.946 | Ta2–O8 | 1.955 | Ta3–O10 | 2.094 |
| Ta1–O4 | 2.070 | Ta2–O9 | 1.946 | Ta3–O13 | 1.973 |
| Ta1–O5 | 2.096 | Ta2–O10 | 2.052 | Ta3–O14 | 1.957 |
| Ta1–O6 | 2.056 | Ta2–O11 | 2.022 | Ta3–O15 | 2.070 |
| Ta1–O7 | 2.047 | Ta2–O12 | 1.984 | Ta3–O17 | 2.027 |
| O–O distance (Å) | | | | | |
| O2–O3 | 1.477 | O8–O9 | 1.509 | O13–O14 | 1.496 |
| P–O distance (Å) | | | | | |
| P1–O6 | 1.549 | P1–O11 | 1.559 | P1–O15 | 1.560 |
| P1–O16 | 1.485 | P2–O7 | 1.528 | P2–O12 | 1.541 |
| P2–O17 | 1.524 | P2–O18 | 1.503 |  |  |

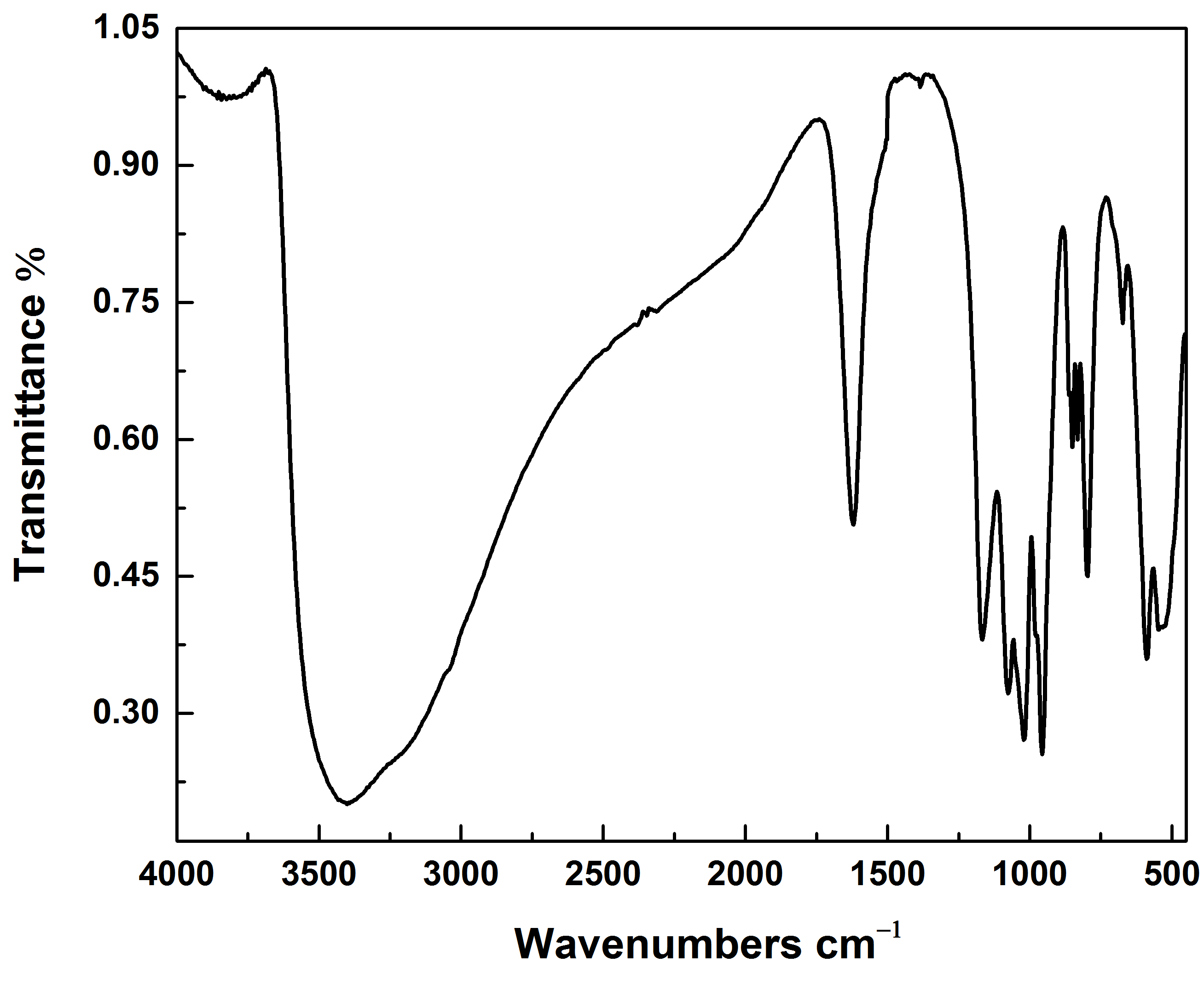
**Table S2. BVS calculation results of all the atoms on polyanion 1a.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom Code | Bond Valence | Atom Code | Bond Valence | Atom Code | Bond Valence |
| Ta1 | 5.52 | O3Ψ | 0.93 | O11 | 1.89 |
| Ta2 | 5.47 | O4\* | 1.38 | O12 | 2.02 |
| Ta3 | 5.44 | O5 | 1.86 | O13Ψ | 0.87 |
| P1 | 4.80 | O6 | 1.85 | O14Ψ | 0.90 |
| P2 | 4.97 | O7 | 1.94 | O15 | 1.80 |
|  |  | O8Ψ | 0.91 | O16\* | 1.38 |
| O1 | 2.02 | O9Ψ | 0.93 | O17 | 1.99 |
| O2Ψ | 0.89 | O10‡ | 1.32 | O18‡ | 1.32 |

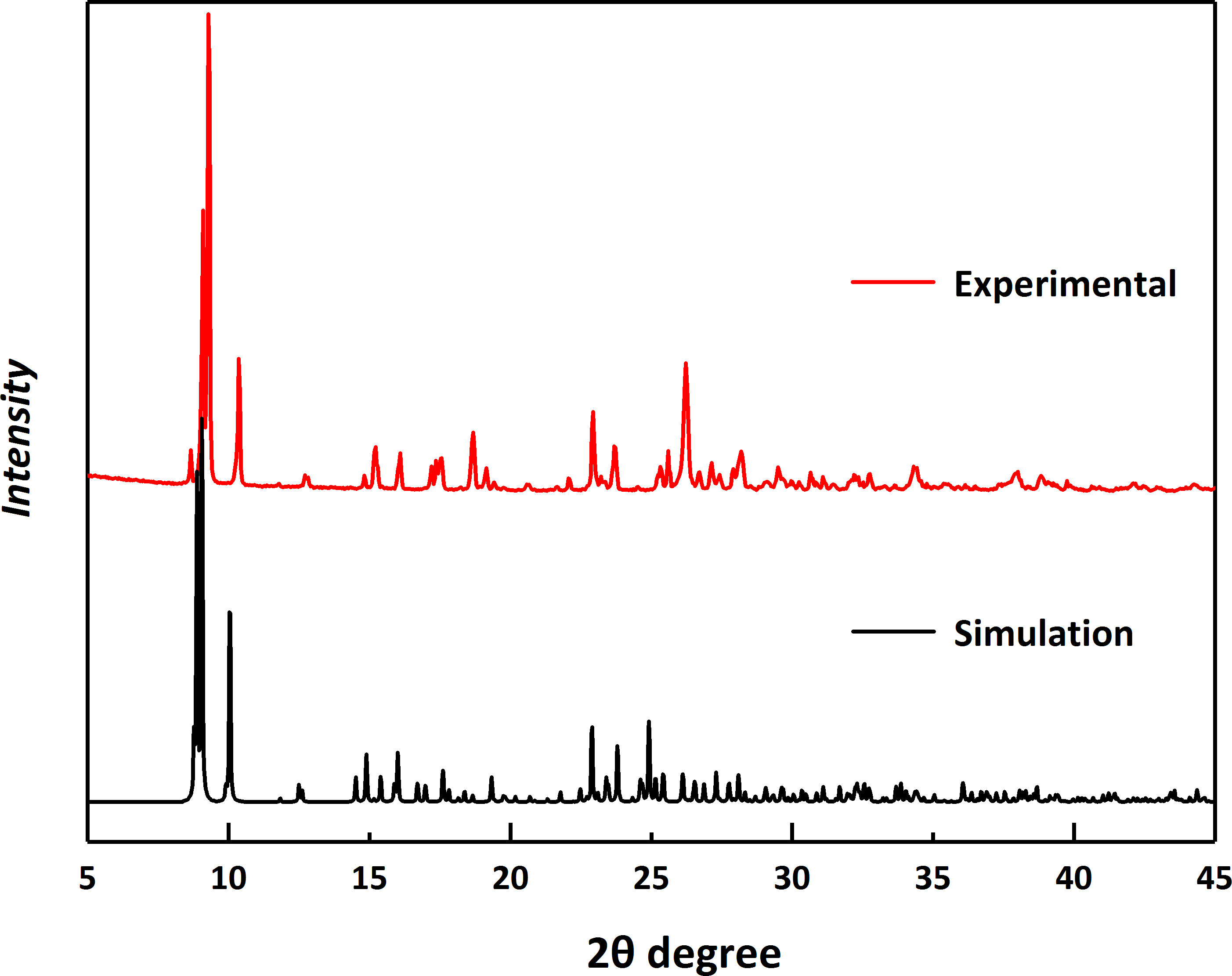
Ψ, ‡ and \* represent peroxooxygen atoms, mono-pronated groups and O/OH ligands, respectively.

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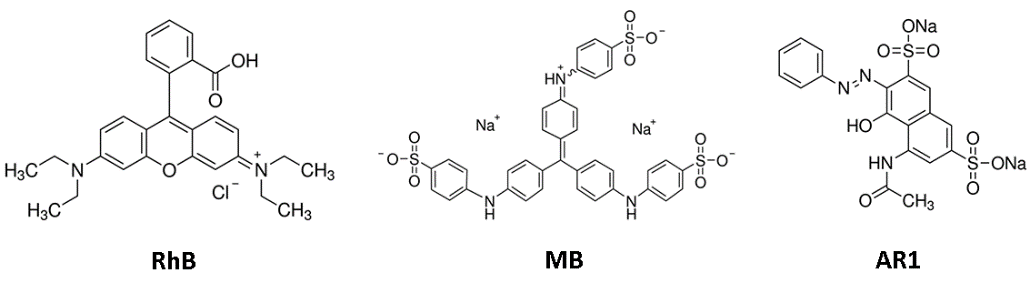
**Figure S3. Ball-and-stick representation of 1 highlighting the pronated oxygen atoms. Color code: Ta green balls; P yellow balls, O red balls, OH pink balls, disordered O/OH blue balls.**

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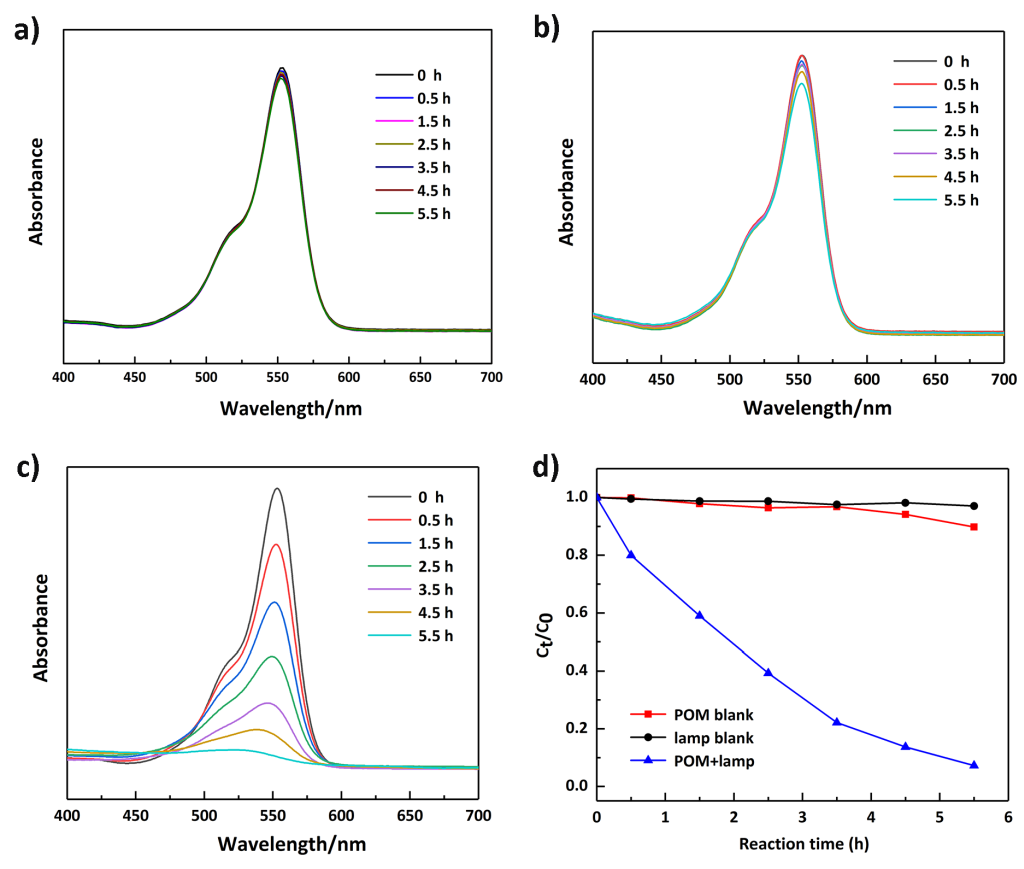
**Figure S4. IR spectrum of 1a in the region between 4000 to 500 cm−1.**



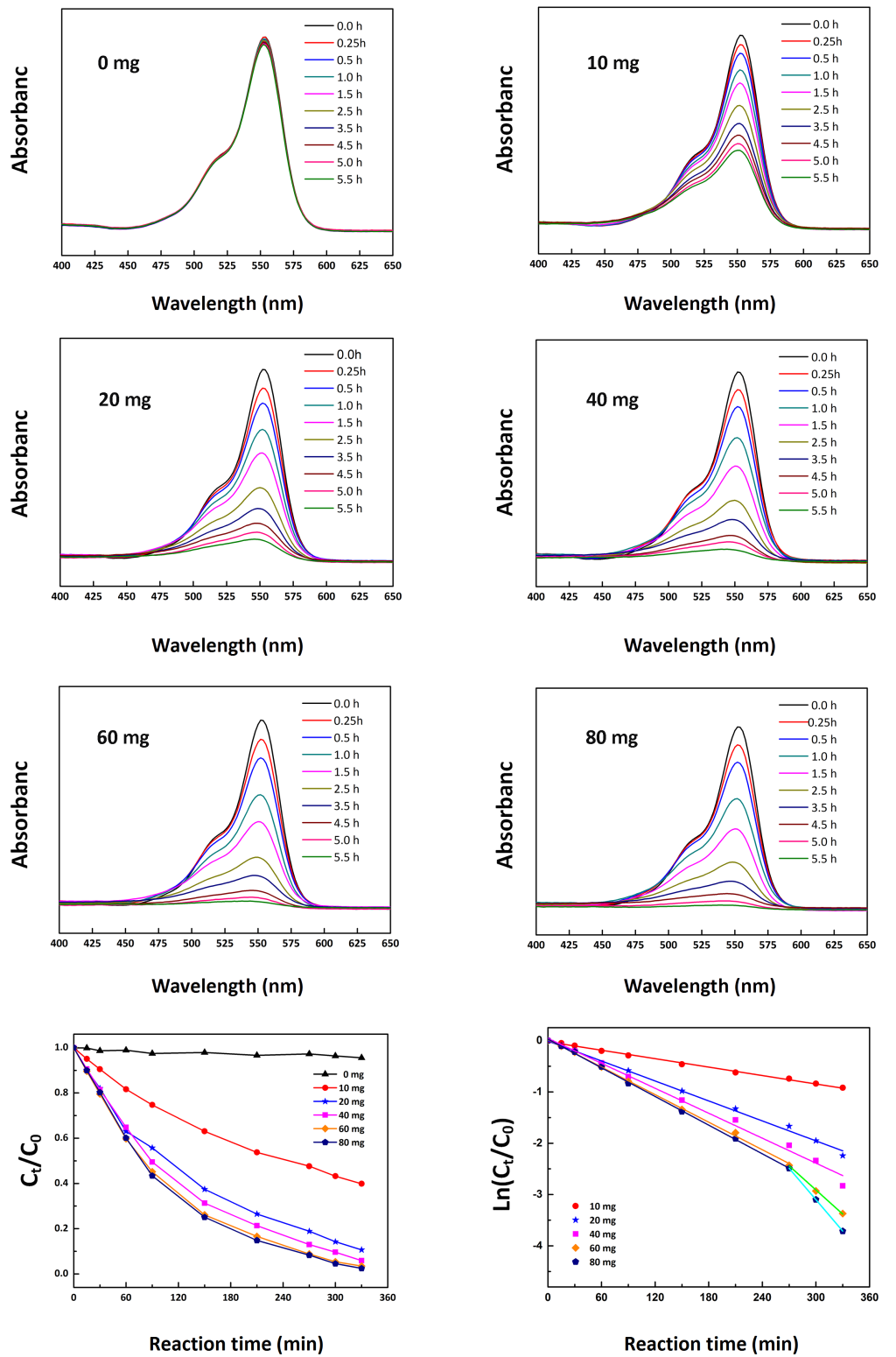
**Figure S5. XRD pattern of compound 1a (red) and its simulated XRD pattern (black).**

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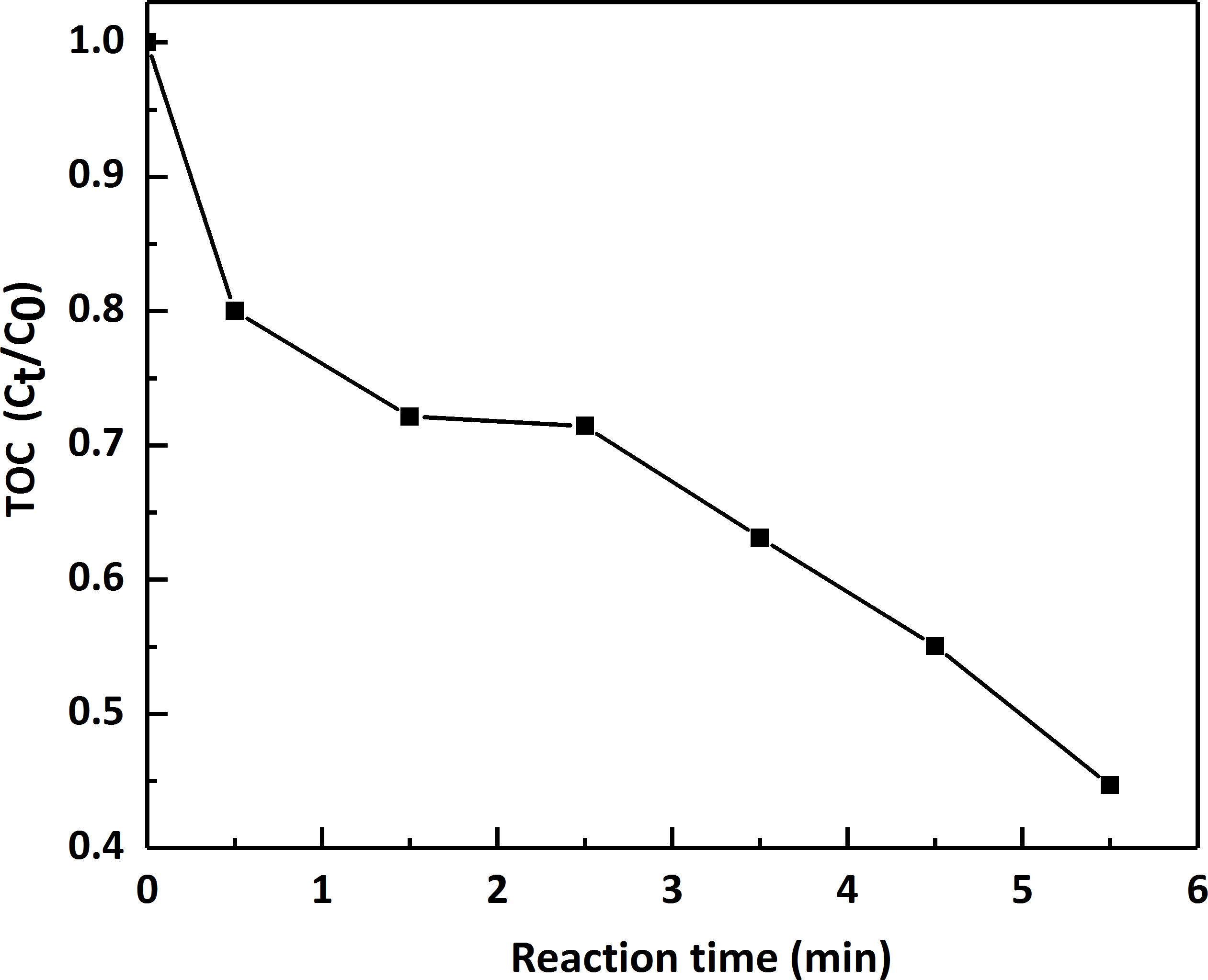
**Figure S6. Chemical structures of RhB, MB and AR1.**

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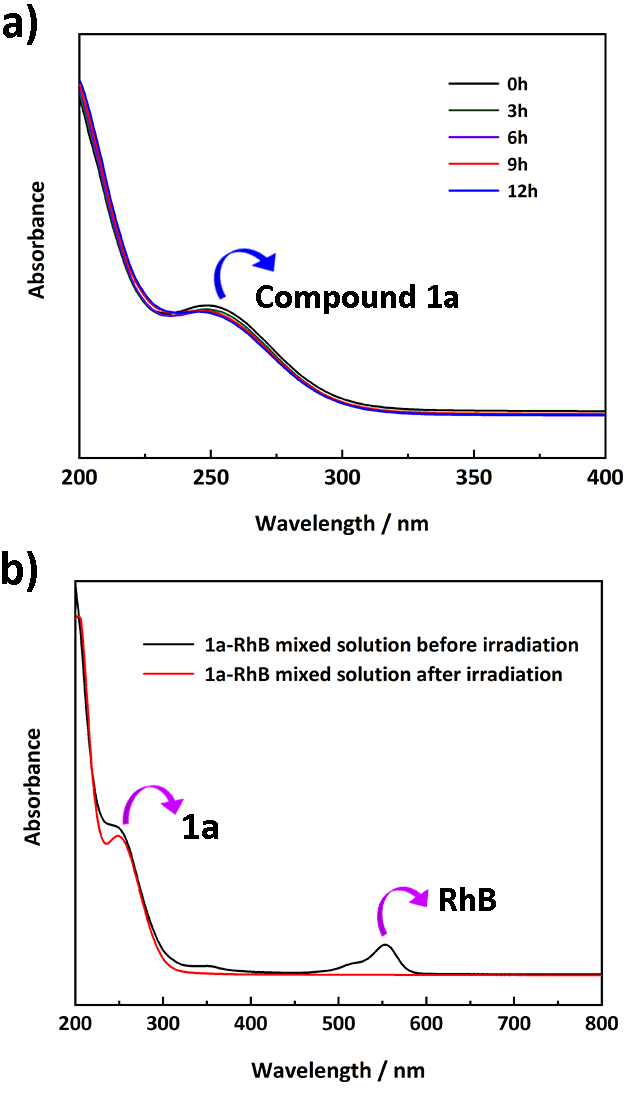
**Figure S7.** **Photocatalytic decolorization performance of compound 1a on RhB dye. a) Change in absorption of RhB in the absence of 1a with Xe lamp; b) Change in absorption of RhB in the presence of 1a (40 mg) without Xe lamp; c) Change in absorption of RhB in the presence of 1a (40 mg) with Xe lamp; d) Plot of *Ct*|*C0* vs time with 1a (blue), the absence of 1a (black) and the blank experiment without lamp (red).**

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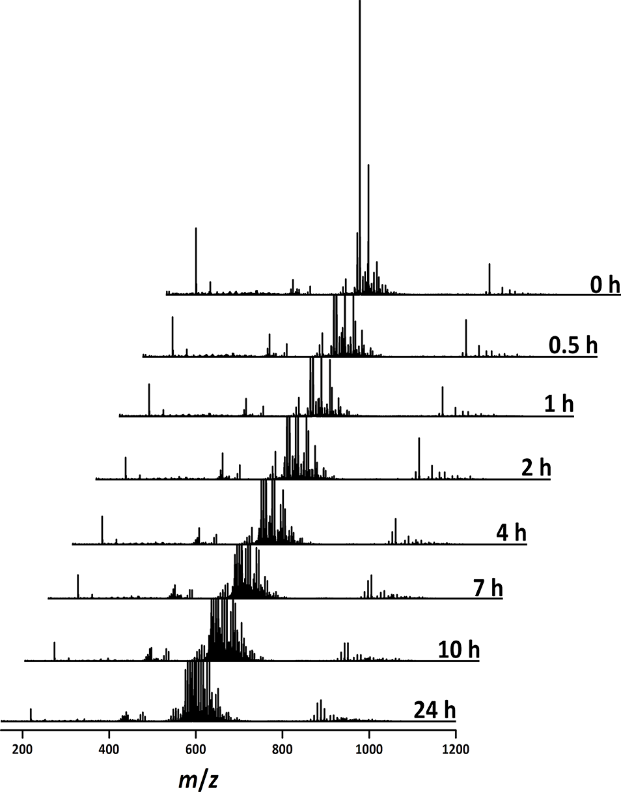
**Figure S8. Photocatalytic decolorization performance of compound 1a on RhB dye.**



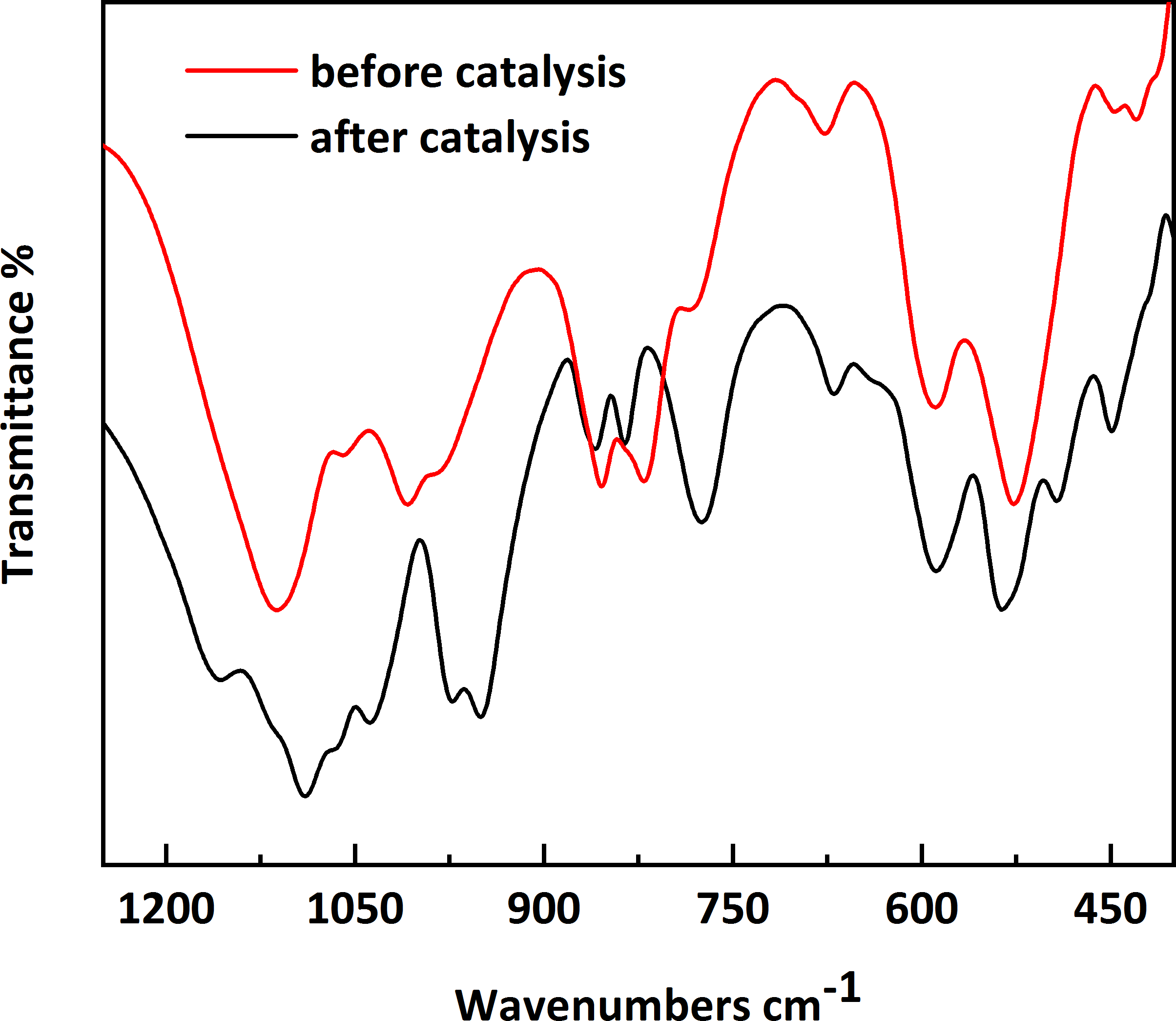
**Figure S9. The TOC removal of RhB dye treated by material 1a.**

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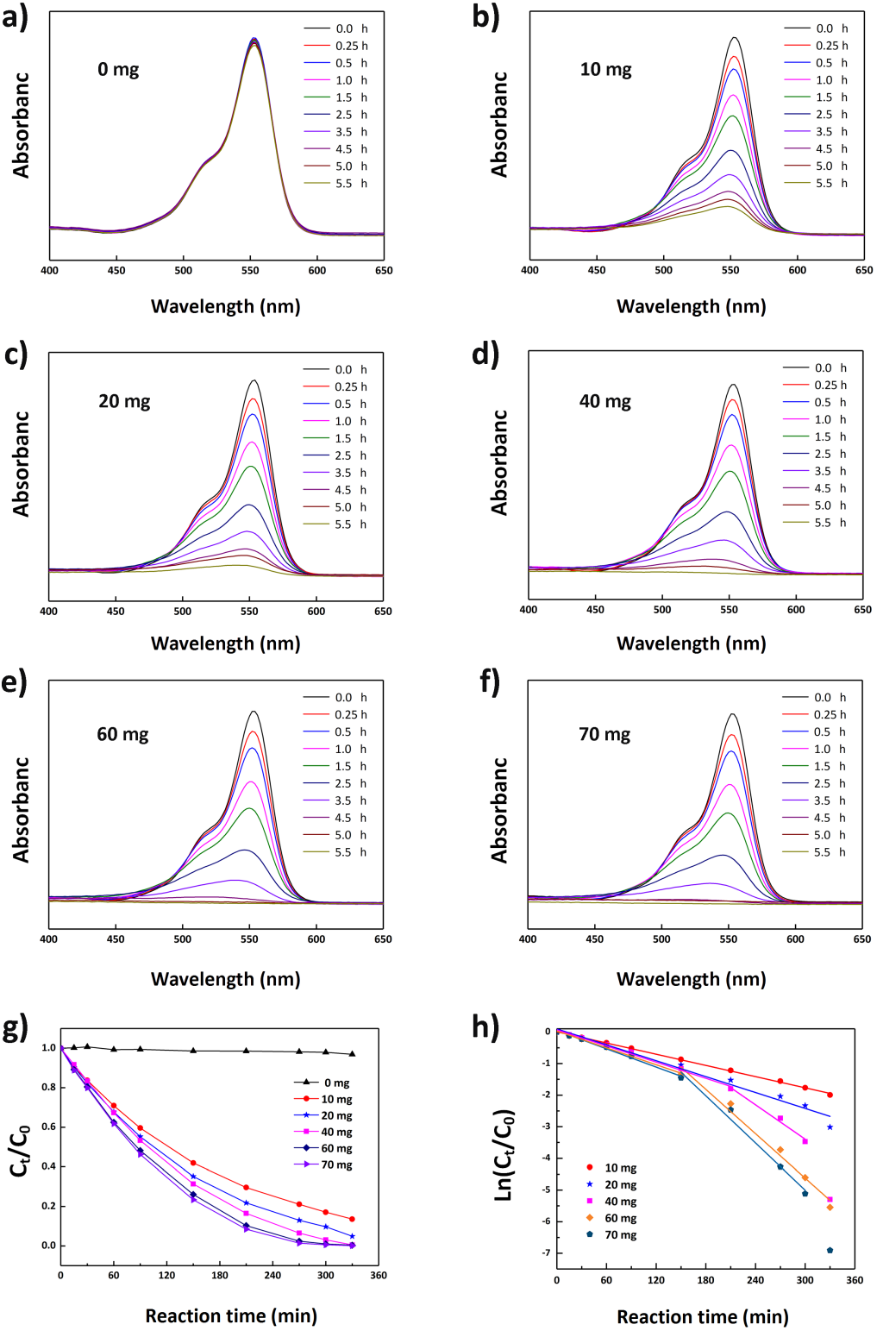
**Figure S10. a) The time-scale UV spectra for the solution of compound 1a; b) the UV spectra of compound 1a and RhB mixed solution before and after irradiation.**

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**Figure S11.** **Negative-ion ESI-MS spectra of cluster anion in compound 1a during 24 h.** To investigate the stability of POM cluster presented in this study, ESI-MS measurement was performed on an *AB SCIEX Triple TOF 4600* spectrometer operating in negative ion mode and data was analyzed using the *Peakview 2.0* software provided. ESI-MS sample was prepared by dissolving single crystal in mixed solvent CH3CN-H2O with HPLC grade and diluting to a concentration of ca. 1 x 10−6 M. It can be seen that the main envelope observed at *m/z* = 597.5 for **1a** could be assigned to the formula [H7{P4Ta6(O2)6O24}]3−, which can be also remained for 24 h.

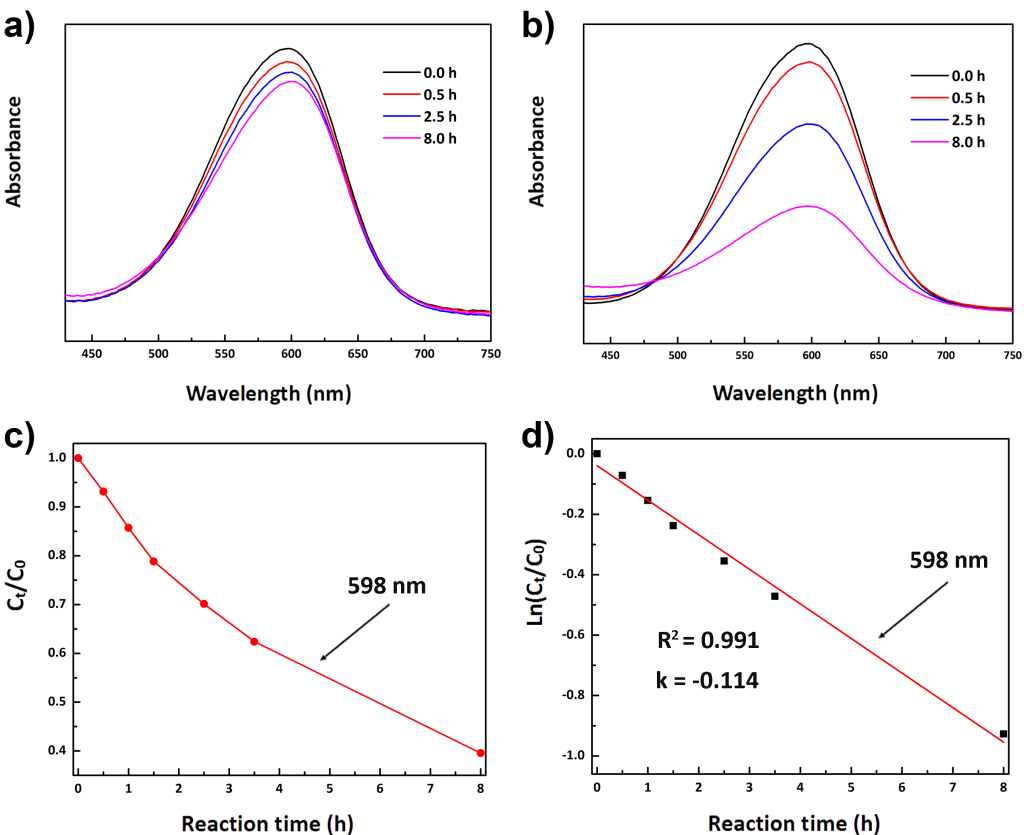
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**Figure S12. IR spectra of compound 1a before and after catalysis, highlight the region between 1250 to 400 cm−1.**

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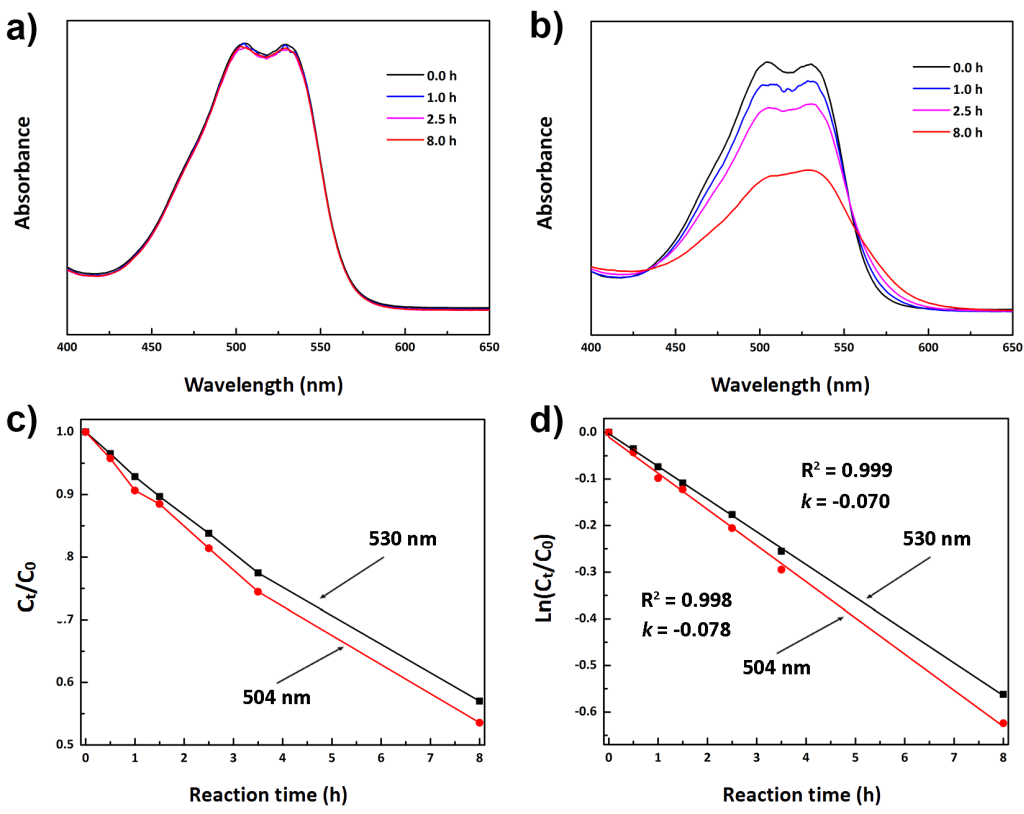
**Figure S13. Photocatalytic decolorization performance of compound 2a on RhB dye.**

For comparison, the photocatalytic performances of different amount **2a** (10, 20, 40, 60 and 70 mg) on the decolorization of RhB dyes have been also investigated. It can be seen that RhB dye can be completely decolorized within 5.5 h when the amount of compound **2a** is higher than 20 mg. This may be attributed the fact that **1a** is a structural analogue of **2a**.

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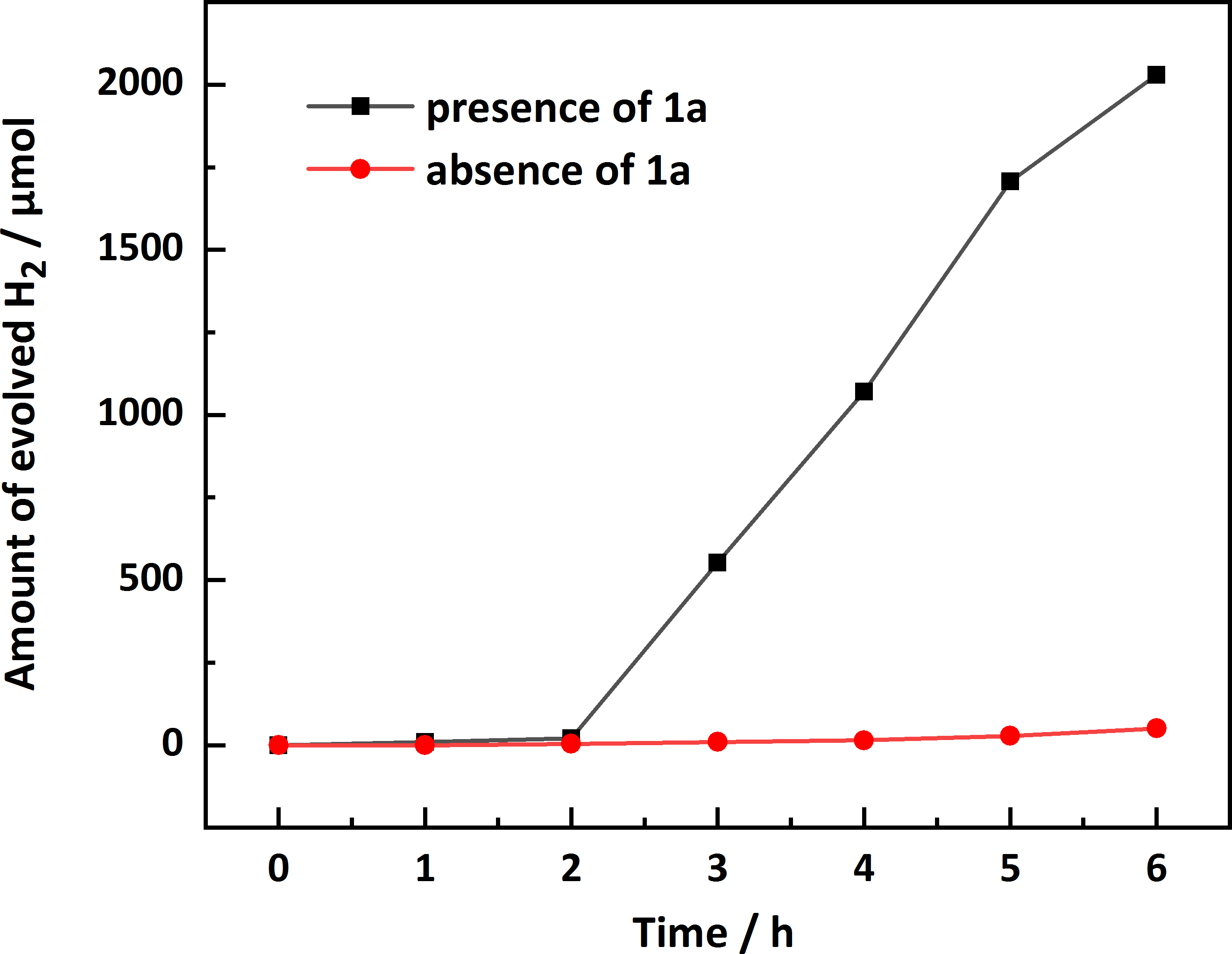
**Figure S14. a) Absorption spectrum of the MB solution in the absence of compound 1a; b) Absorption spectrum of the MB solution in the presence of compound 1a (40 mg); c) plots of the concentration ratios of MB *Ct*|*C0* vs time (h) in the presence of compound 1a under Xe lamp irradiation; d) The first order linear plot of *ln*(*Ct*|*C0*) vs. time for MB.**

It can be clearly seen that the absorbance peaks of MB (598 nm) decreased obviously along with the reaction time in the presence of **1a**, 60.4% of MB decolorized after 8 h of irradiation, which is higher than that of absence of **1a** (12.5%). The catalytic reaction could be considered as a pseudo first order kinetics with regard to the linear fit of the *ln*(*Ct*|*C0*) data. The calculated rate constant (*kapp*, h–1) for the reduction of MB in the presence of **1a** is 0.114 h–1.

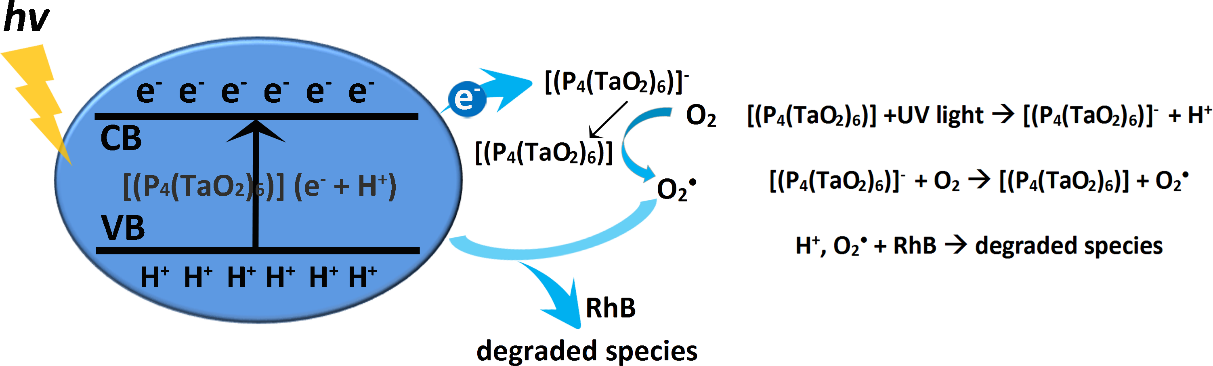
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**Figure S15. a) Absorption spectrum of the AR1 solution in the absence of compound 1a; b) Absorption spectrum of the AR1 solution in the presence of compound 1a (40 mg); c) plots of the concentration ratios of AR1 *Ct*|*C0* vs time (h) in the presence of compound 1a under Xe lamp irradiation; d) The first order linear plot of *ln*(*Ct*|*C0*) vs. time for AR1.**

It can be clearly seen that the absorbance peaks of AR1 (504 and 530 nm) decreased along with the reaction time in the presence of **1a**, 46.4% (504 nm) and 42.7% (530 nm) of AR1 decolorized after 8 h of irradiation, which is obviously higher than that of absence of **1a** (almost no decolorization). The catalytic reaction could be considered as a pseudo first order kinetics with regard to the linear fit of the *ln*(*Ct*|*C0*) data. The calculated rate constant (*kapp*, h–1) for the reduction of AR1 in the presence of **1a** is 0.078 h–1 (504 nm) and 0.070 h–1 (504 nm).

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**Figure S16. Time courses of photocatalytic H2 evolution under the presence of compound 1a (black) and the absence of compound 1a (red). Experiment condition: 100 mg of 1a and 0.05 mg of H2PtCl6 were dissolved in 100 mL of 10% methanol, which was irradiated under UV using a 500 W mercury lamp.**

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**Figure S17. Schematic illustration for the photocatalytic mechanism of compound 1a.**