Electronic Supplementary Information

Four types of 1D or 2D organic–inorganic hybrids assembled by arsenotungstates and Cu^{II}–$Ln^{III/IV}$ heterometals

Dong-Ying Shi,[a] Jun-Wei Zhao,*[a] Li-Juan Chen,[a,b] Peng-Tao Ma,[a] Jing-Ping Wang[a] and Jing-Yang Niu*[a]

[a] *Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, P. R. China. Fax: (+86) 378 3886876; E-mail: zhaojunwei@henu.edu.cn, jyniu@henu.edu.cn*

[b] *Basic Experiment Teaching Center, Henan University, Kaifeng, Henan 475004, P. R. China*

Fig. S1 Comparison of the simulated and experimental PXRD patterns: **1** a), **2** b), **3** c), **4** d), **5** e), **6** f), **7** g), **8** h), **9** i), **10** j).

Fig. S2 The square antiprismatic geometry of the $Ce1^{IV}$ cation in **1**.

Fig. S3 IR spectra of **1**–**10**.

Fig. S4 The solid-state UV absoption spectra of **1**–**10**.

Fig. S5 UV-visible absorption spectral changes for the RhB solutions at various irradiation times: a) in the presence of **3**; b) in the presence of **4**; c) in the presence of **5**; d) in the presence of **6**; e) in the presence of **8**; f) in the presence of **10**. Inset: the conversion of RhB (*K*) with reaction time (*t*).

Fig. S6 UV-visible absorption spectral changes for the RhB solutions in darkness: a) in the absence of **1**, **2**, **7**, **9**, or $Na_8[A\text{-}\alpha\text{-}HAsW_9O_{34}]\cdot 11H_2O$; b) in the presence of **1**; c) in the presence of **2**; d) in the presence of **7**; e) in the presence of **9**; f) in the presence of $Na_8[A\text{-}\alpha\text{-}HAsW_9O_{34}]\cdot 11H_2O$.

Fig. S7 (a) The PXRD patterns of **1** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis. (b) The PXRD patterns of **2** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis. (c) The PXRD patterns of **7** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis. (d) The PXRD patterns of **9** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis.

The details during the course of the refinements of structures of 1-10:

Due to the large structures of **1-10** and the existence of a large amount of weight atoms, their intensity data are not very good, leading to the ADP max/min ratio of some atoms, and it is very difficult to refine these large structures, therefore, some unit-occupancy atoms have been refined isotropically and restrainedly refined.

1: The ISOR instruction is used for O5, O6, O8, O23, O30, O31, O46, O48, O58, O88, O89, O62, O25, N14, N9, O14W, O113, O107, O148, O149, N12, N20, N21, C11, C12, C14, C16, C26, C28, O26, N27, O147, O155, N10, O17W, O19W, O20W, O18, O27, O44, O150, O77, N15, O126, O128, O12, O106, O124, O143, C20, O109, C27, O9, C25, C9, N11, N13, O82, O105, O146, O4, O16, O60, O74, O86, O22 and O75. The DFIX instruction is used for N1 and C1, N2 and C2, N4 and C4, N5 and C5, N7 and C7, C1 and C2, C3 and C4, C7 and C8, C21 and C22, Cu1 and N4, Cu9 and O7W, O8W and O15W, O22W and O46, O19W and O22W, O22W and O38, O16W and O22W. O4W-O11W, O15W, O16W, O18W, O22W, O129, N1-N8, N16, N23, C1-C8, C13, C18, C21 and C23 are refined isotropically. Now, there are now 67 Uiso/Uij restrained atom sites, 24 distance or angle restraints and 418 least-squares restraints were used in the refinement.

2: The ISOR instruction is used for O1, O6, O10, O11, O20, O65, O66, O74, O12, O59, O72, O78, O42, N10 and C10. The DFIX instruction is used for O71 and O8W. The ISOR instruction is used for W19 and O71, W22 and O72, As2 and O61, W20 and O74. The O4W, O5W, O7W, O8W, O14, O17, O31, O71 and O77 atoms are refined isotropically. Now, there are now 15 Uiso/Uij restrained atom sites, 2 distance or angle restraints and 94 least-squares restraints used in the refinement.

3: The ISOR instruction is used for O1, O2, O4, O5, O7, O10, O12, O20, O24, O25, O41, O44, O45, C8, O21, O19 ,NA1, O48, O54, O56, O57, O58, O61, O63, O69, O77, O78, N8, N9, N10, C9, O62, O3W, O7W, O18, O67, O9, O37, O50, O70, O75, N2, C4, N6, O15, O46, O30, N5, O29, O36, O43, O17, O52, W22 and O35. The DFIX instruction is used for O1W and O71. The DELU instruction is used for C3 and N3. The Na2, Na2', O5W, O6W, C7 and C10 atoms are refined isotropically. Now, there are 56 Uiso/Uij restrained atom sites, 1 distance restraint and 338 least-squares restraints were used in the refinement.

4: The ISOR instruction is used for NA1, O29, O45, O48, O52, O54, O56, O67, O72, O11, N9, O36, C10, Na3, O6, O27, O76, C2, O5, O60 and Na2. The DFIX instruction is used for O1W and O71. The O14, O17, O31, O41, O46, O50, O59, C1, C8 and O1W-O10W atoms are refined isotropically. Now, there are 21 Uiso/Uij restrained atom sites, 1 distance restraint and 127 least-squares restraints were used in the refinement.

5: The ISOR instruction is used for O2, O3, O10, O18, O20, O44, O45, O29, O47, O52, O55, C1, C2, O24, O72, O75, O30, O49, O70, O73, N2, N9, C5, C7, C8, C9, C6, O5, O8, O23, O32, O1, O53, O74, O9, O36, Na1, O77 and O38. The DFIX instruction is used for C2 and N2. The SIMU and DELU instructions are used for W16 and O62, N8 and C8, W21 and O62. The Na3, O1W-O7W, O14, O17, O19, O23, O31, O41, O46, O59 and O78 atoms are refined isotropically. Now, there are 42 Uiso/Uij restrained atom sites, 2 distance or angle restraints and 238 least-squares restraints used in the refinement.

6: The ISOR instruction is used for Na2, O2, O5, O10, O19, O27, O35, O39, O40, O44, O45, O48, O51, O60, O65, O70, O71, O72, O77, O78, N3, N9, C4, C5, O46, O49, O59, O63, O18, O12, O31, N2, O46, O49, O59, O63, O18, O25, C7, Na2, W22 and O38. The O1, O7, O17, O25, O47, O55, O69, O73, C2, C6, C8, C10 and O1W-O7W atoms are refined isotropically. Now, there are 35 Uiso/Uij restrained atom sites, and 246 least-squares restraints used in the refinement.

7: The ISOR instruction is used for O10, O13, O19, O30, O34, O37, O40, O46, O54, O57, O58, O66, O76, N22, O4W, N6, N14, O27, O75, O15, N6, N14, O49, O68, N18, O50, N16 and O4. The DFIX instruction is used for C14 and C15, C14 and N10, C13 and C14, C1 and N1, C10 and C11, C13 and N9, C19 and C20, C20 and C21, C32 and N22, C31 and N21, Cu3 and N9, Cu6 and N22, Cu6 and O4W, Cu3 and C15, Cu3 and C14, C1 and C3. The DELU instruction is used for N11 and C16. The C1-C5, C9-C15, C19-C23, C26, C31-C33, N2, N3, N9, N10,

N21, O5W and O6W atoms are refined isotropically. Now, there are 28 Uiso/Uij restrained atom sites, 20 distance or angle restraints and 185 least-squares restraints used in the refinement.

8: The ISOR instruction is used for O9, O15, O16, O61, O72, O74, N11, N13, N21, N22, C32, C19 and O3W. The N3, N9, N10, C1-C6, C7-C15, C18, C20, C23, C26, C31, C33 and O1W-O7W atoms are refined isotropically. The DFIX instruction is used for C13 and C14, C7 and C8, C8 and C9, C8 and N6, C14 and N10, C19 and N13, C31 and C32, C20 and C21, C32 and N21, C32 and C33, C14 and C15, Cu6 and C31, Cu6 and C32, Cu6 and C33, Cu6 and N22. The DELU instruction is used for N13 and C19, N17 and C25, C16 and C17, Cu1 and N1. Now, there are 18 Uiso/Uij restrained atom sites, 18 distance or angle restraints and 91 least-squares restraints used in the refinement.

9: The ISOR instruction is used for O13, O20, O34, O40, O66, O1, O2, O29, N21, O19, O60, O18, N5, O5, O21 and O27. The DFIX instruction is used for N7 and C11, N12 and C17, N21 and C31, C26 and C27, C2 and C3, C4 and C6, C8 and C9, C25 and C26, C31 and C32. The O29, O78, N4, N8, N10, N11, N16, C1-C7, C9-C13, C15-C27, C31-C33 and O1W-O7W atoms are refined isotropically. Now, there are 15 Uiso/Uij restrained atom sites, 16 distance or angle restraints and 99 least-squares restraints were used in the refinement.

10: The ISOR instruction is used for N22. The DFIX instruction is used for C28 and C29, C20 and C21, C1 and C2, C10 and C11, C32 and C33, C25 and C26, C26 and C27, N19 and C28, N20 and C29, N4 and C5, N15 and C22, N21 and C31. The O16, N14, N18-N22, C1-C6, C10-C33 and O1W-O6W atoms are refined isotropically. Now, there are 1 Uiso/Uij restrained atom site, 21 distance or angle restraints and 12 least-squares restraints were used in the refinement.

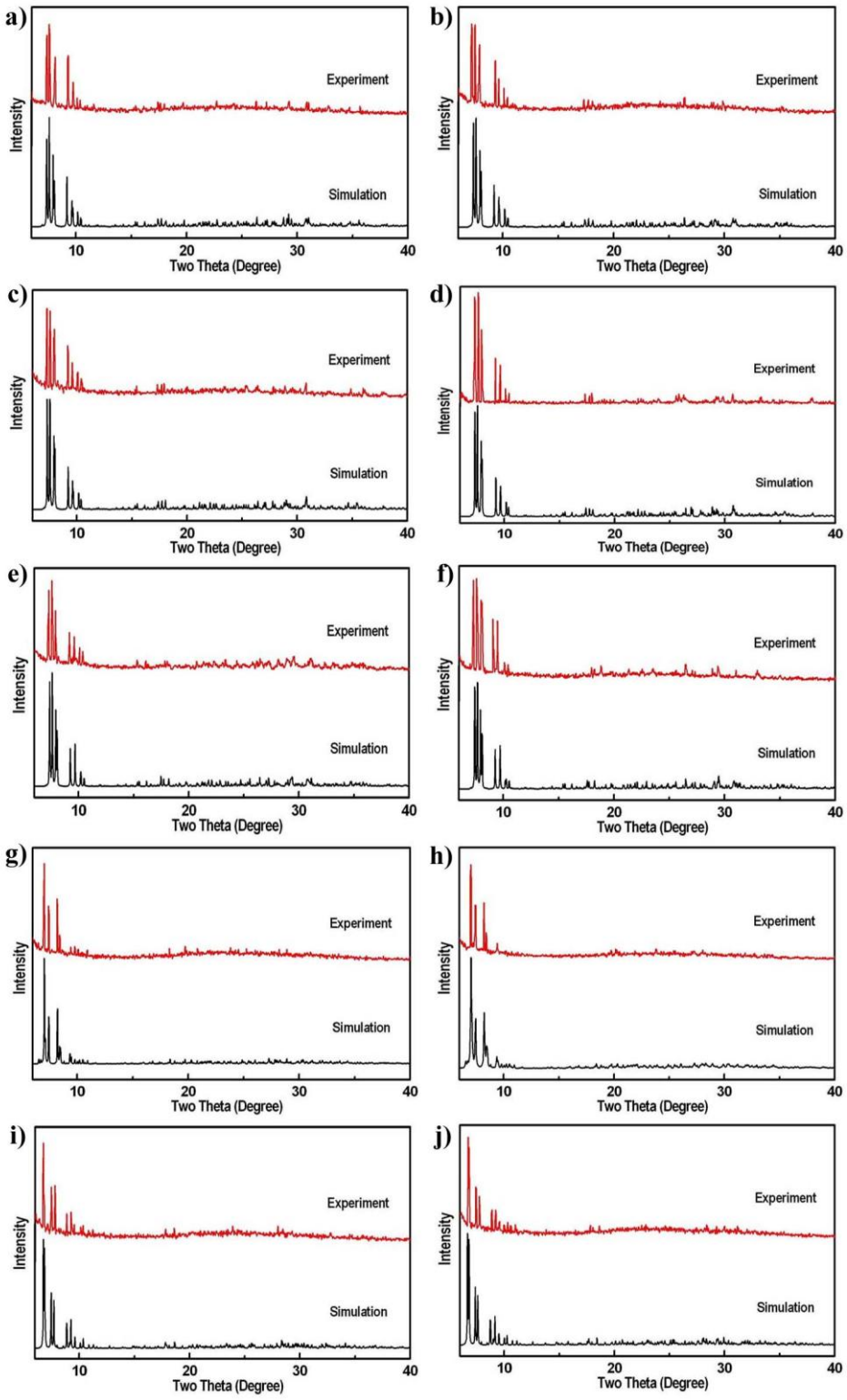

Fig. S1 Comparison of the simulated and experimental PXRD patterns: **1** a), **2** b), **3** c), **4** d), **5** e), **6** f), **7** g), **8** h), **9** i), **10** j).

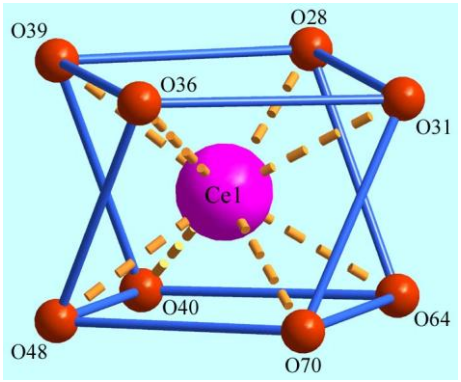

Fig. S2 The square antiprismatic geometry of the $Ce1^{IV}$ cation in **1**.

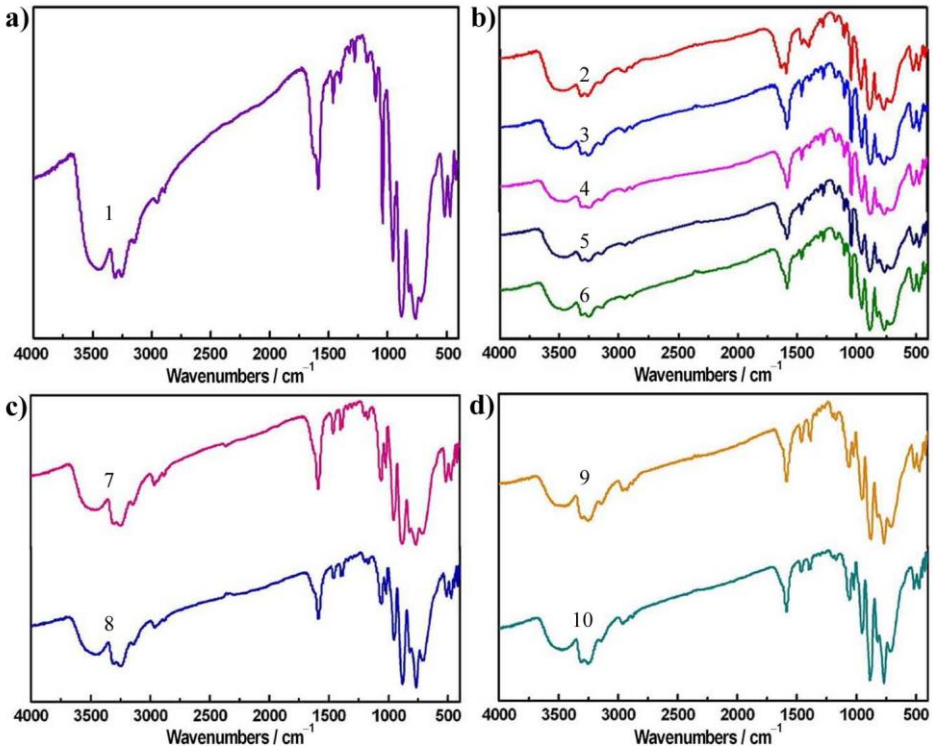

Fig. S3 IR spectra of **1**–**10**.

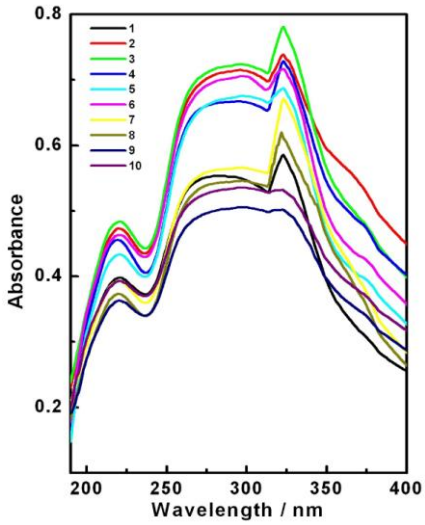

Fig. S4 The solid-state UV absoption spectra of **1**–**10**.

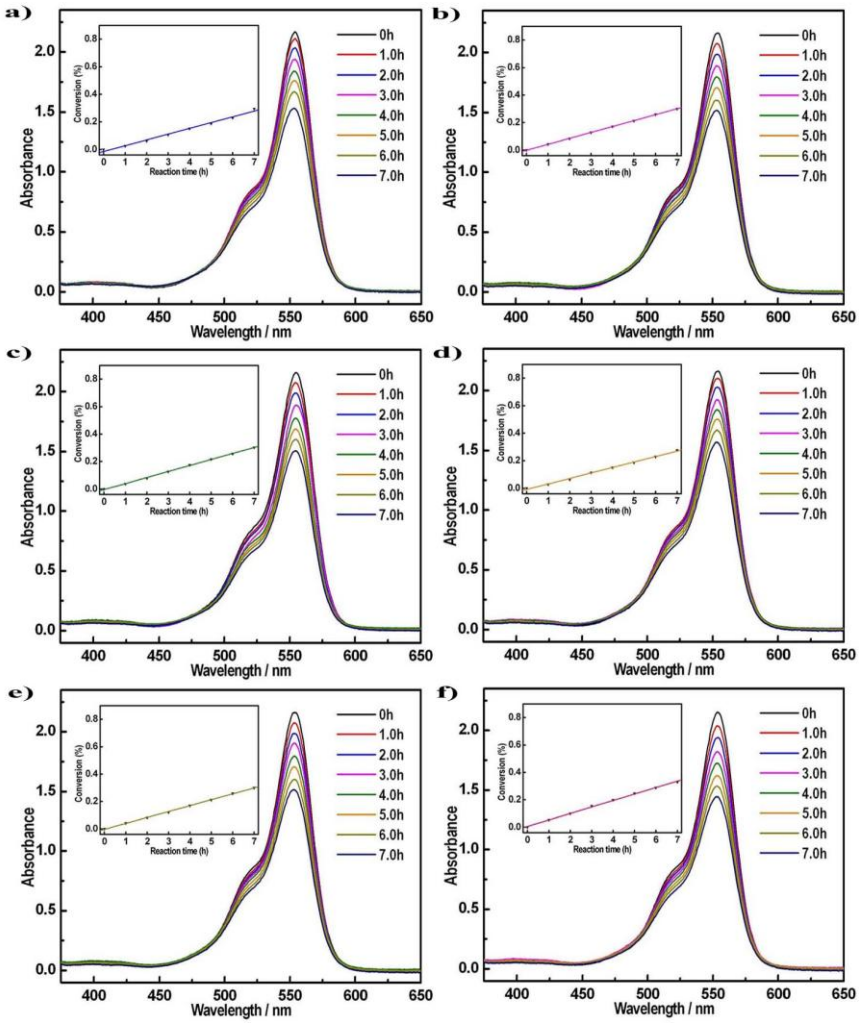

Fig. S5 UV-visible absorption spectral changes for the RhB solutions at various irradiation times: a) in the presence of **3**; b) in the presence of **4**; c) in the presence of **5**; d) in the presence of **6**; e) in the presence of **8**; f) in the presence of **10**. Inset: the conversion of RhB (*K*) with reaction time (*t*).

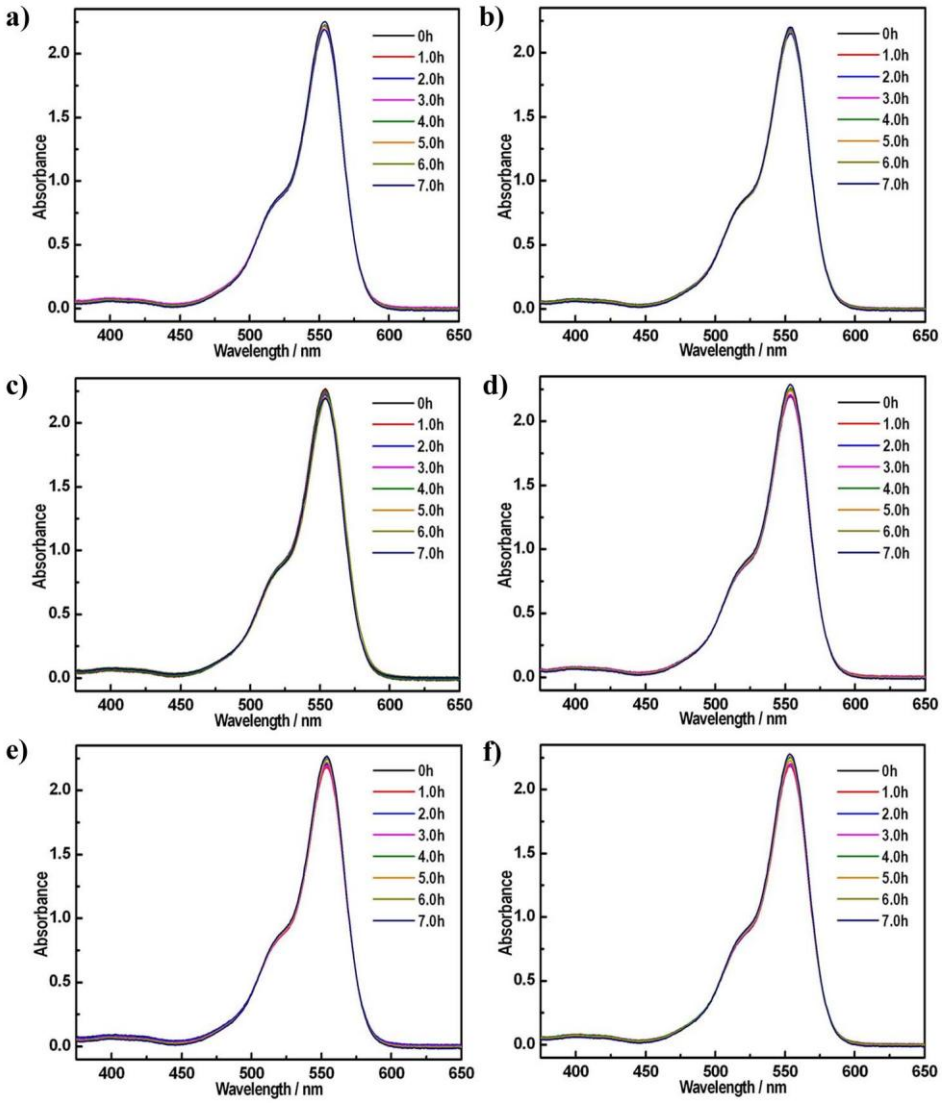

Fig. S6 UV-visible absorption spectral changes for the RhB solutions in darkness: a) in the absence of **1**, **2**, **7**, **9**, or $Na_8[A\text{-}\alpha\text{-}HAsW_9O_{34}]\cdot 11H_2O$; b) in the presence of **1**; c) in the presence of **2**; d) in the presence of **7**; e) in the presence of **9**; f) in the presence of $Na_8[A\text{-}\alpha\text{-}HAsW_9O_{34}]\cdot 11H_2O$.

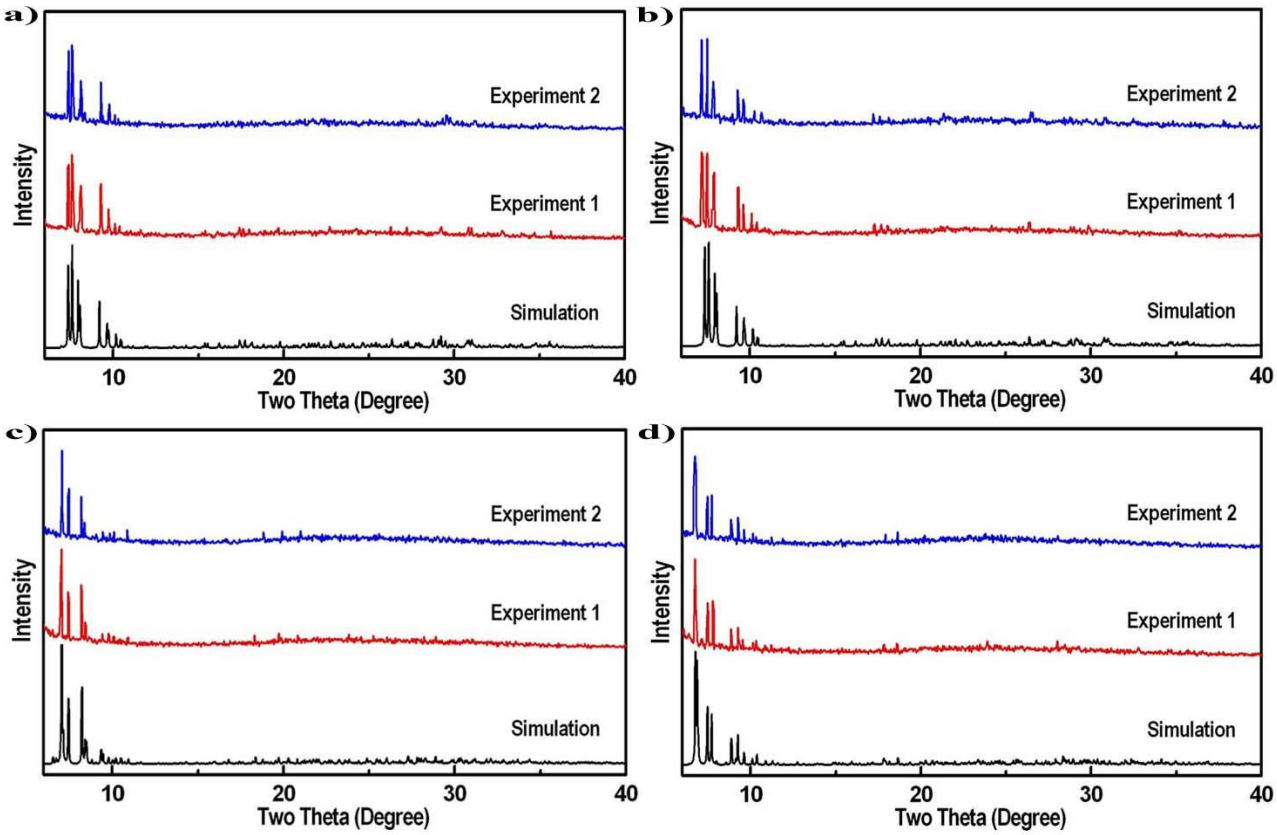

Fig. S7 (a) The PXRD patterns of **1** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis. (b) The PXRD patterns of **2** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis. (c) The PXRD patterns of **7** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis. (d) The PXRD patterns of **9** before (Experimental1) and after (Experimental2) after the photocatalytic degradations of RhB and its calculated pattern based on the single-crystal structural analysis.