Supplemental Material for:

Assembly of 3D hybrids with improved properties by using the

transition-metal-monosubstituted Keggin polyoxometalate chains

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Fig. S1. Detail view of the Keggin anion-chain in 1.



Fig. S2 View of coordination details of POM clusters: (left) $PW_{11}Cu$ in 1 and (right) PW_{12} in 4.



Fig. S3 View of connection details between $PW_{11}Cu$ chain and Ag3 cations in 1.



Fig. S4 IR spectra of compounds 1–5.



Fig. S5 XPS of compounds 4 and 5.



Fig. S6 The simulative (bottom) and experimental (top) powder X-ray diffraction patterns for **1** and **3–5**.



Fig. S7 The crystal picture of 2.



Fig. S8 The TG curves of compounds 1–5.



Fig. S9 The plot of relative concentration (C_t/C_o) of the RhB solution *versus* reaction time: direct photodecolorization (black), photodecolorization in the presence of 1 (blue) and 4 (red).



Fig. S10 PXRD patterns of **1** (left) and **4** (right): simulative (bottom), experimental (middle) and after the photocatalytic reaction (top).



Fig. S11 Emission spectrum and absorption spectrum (inset) of btp in the solid state.