Supporting Information

Strong hybridization between Bi-6s and O-2p orbitals in Sillén–Aurivillius perovskite Bi_4MO_8X (M = Nb, Ta; X = Cl, Br), visible light photocatalysts enabling stable water oxidation

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Figure S1. XRD patterns of Bi_4MO_8X (M = Nb, Ta; X = Cl, Br) samples.

Table S1. Lattice constants of Bi₄MO₈X calculated by Le Bail analysis.

19-1-1 	a/Å	b/Å	c / Å	V / Å ³
Bi ₄ TaO ₈ Cl	5.4421(1)	5.4830(1)	28.7697(6)	858.46(4)
Bi₄TaO ₈ Br	5.4692(1)	5.5157(1)	29.2196(6)	881.45(5)
Bi ₄ NbO ₈ Cl	5.4559(1)	5.4999(1)	28.6750(7)	860.45(5)
Bi ₄ NbO ₈ Br	5.4823(1)	5.5421(1)	29.0952(5)	882.43(4)



Figure S2. SEM images of (a) Bi₄TaO₈Cl, (b) Bi₄TaO₈Br, (c) Bi₄NbO₈Cl, and (d) Bi₄NbO₈Br particles. The specific surface areas are indicated on the images.



Figure S3. Mott-Schottky plots of BiOX (X = Cl, Br) in Na₂SO₄ aqueous solution (0.1 M, pH 2.0).



Figure S4. PYS spectrum of BiOBr. Each line was determined as the pair of a base and a rise to calculate an onset (= VBM).



Figure S5. Time courses of H₂ evolution over (a)RuO_x-Bi₄MO₈X and (b) Pt-Bi₄MO₈X in an aqueous 20 vol% MeOH solution under photoirradiation ($\lambda > 300$ nm).



Figure S6. Enlarged view of PDOS near conduction band of (a) Bi_4TaO_8Cl , (b) Bi_4TaO_8Br , (c) Bi_4NbO_8Cl , and (d) Bi_4NbO_8Br .



Figure S7. PDOS of O-2p orbitals of O1–O8 in (a) Bi_4NbO_8Cl and (b) Bi_4NbO_8Br , where O1-O4 (upper) and O5-O8 (lower) represent oxygen atoms in the $(Bi_2O_2)_2X$ layer and the $A_{n-1}B_nO_{3n+1}$ layer, respectively (Figure 1).



Figure S8. PDOS of Bi-6s and Bi-6p orbitals of Bi1–Bi4 in (a) Bi₄NbO₈Cl and (b) Bi₄NbO₈Br (Figure 1).