**Supporting Information**

**Strong hybridization between Bi-6s and O-2p orbitals in Sillén–Aurivillius perovskite Bi₄MO₈X (M = Nb, Ta; X = Cl, Br), visible light photocatalysts enabling stable water oxidation**

Hironobu Kunioku, a Masanobu Higashi, a Osamu Tomita, a Masayoshi Yabuuchi, a Daichi Kato, a Hironori Fujito, a Hiroshi Kageyama, a,b,* and Ryu Abe a,b,*

a Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-Ku, Kyoto 615-8510, Japan. E-mail: kage@scl.kyoto-u.ac.jp, ryu-abe@scl.kyoto-u.ac.jp

b CREST, Japan Science and Technology Agency (JST), Kawaguchi, Saitama 332-0012, Japan

---

**Figure S1.** XRD patterns of Bi₄MO₈X (M = Nb, Ta; X = Cl, Br) samples.

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

<table>
<thead>
<tr>
<th></th>
<th>a / Å</th>
<th>b / Å</th>
<th>c / Å</th>
<th>V / Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi₄TaO₈Cl</td>
<td>5.4421(1)</td>
<td>5.4830(1)</td>
<td>28.7697(6)</td>
<td>858.46(4)</td>
</tr>
<tr>
<td>Bi₄TaO₈Br</td>
<td>5.4692(1)</td>
<td>5.5157(1)</td>
<td>29.2196(6)</td>
<td>881.45(5)</td>
</tr>
<tr>
<td>Bi₄NbO₈Cl</td>
<td>5.4559(1)</td>
<td>5.4999(1)</td>
<td>28.6750(7)</td>
<td>860.45(5)</td>
</tr>
<tr>
<td>Bi₄NbO₈Br</td>
<td>5.4823(1)</td>
<td>5.5421(1)</td>
<td>29.0952(5)</td>
<td>882.43(4)</td>
</tr>
</tbody>
</table>
Figure S2. SEM images of (a) Bi$_4$TaO$_8$Cl, (b) Bi$_4$TaO$_8$Br, (c) Bi$_4$NbO$_8$Cl, and (d) Bi$_4$NbO$_8$Br particles. The specific surface areas are indicated on the images.

Figure S3. Mott-Schottky plots of BiOX (X = Cl, Br) in Na$_2$SO$_4$ 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)RuOₓ-BiₓMO₈X and (b) Pt-BiₓMO₈X in an aqueous 20 vol% MeOH solution under photoirradiation (λ > 300 nm).
Figure S6. Enlarged view of PDOS near conduction band of (a) Bi₄TaO₈Cl, (b) Bi₄TaO₈Br, (c) Bi₄NbO₈Cl, and (d) Bi₄NbO₈Br.
Figure S7. PDOS of O-2p orbitals of O1–O8 in (a) Bi$_4$NbO$_8$Cl and (b) Bi$_4$NbO$_8$Br, where O1-O4 (upper) and O5-O8 (lower) represent oxygen atoms in the (Bi$_2$O$_2$)$_2$X layer and the A$_{n-1}$B$_n$O$_{3n+1}$ layer, respectively (Figure 1).

Figure S8. PDOS of Bi-6s and Bi-6p orbitals of Bi1–Bi4 in (a) Bi$_4$NbO$_8$Cl and (b) Bi$_4$NbO$_8$Br (Figure 1).