

Electronic Supporting Information

Syntheses, structural characterization and photophysical properties of two series of rare-earth-isonicotinic-acid containing Waugh-type manganomolybdates

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1. Some typical examples of REPOMBMs
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Fig. S1 IR spectra of 1–13.

Fig. S2 a) The Mn-centered triangular $\{MnMo_3O_{18}\}$ cluster; b) Three triangles ($\Delta 1$, $\Delta 2$, $\Delta 3$) in the $[MnMo_9O_{32}]^{6-}$ polyoxoanion.

Fig. S3 a) The 3-D supramolecular packing of **1** viewed along the a axis; b) The 3-D supramolecular packing of **1** viewed along the c axis.

Fig. S4 (a) The UV spectrum of **3** in the range of 400–200 nm. (b) The UV spectrum of **8** in the range of 400–200 nm. (c) The UV spectral evolution of **3** in the acidic region. (d) The UV spectral evolution of **3** in the alkaline region. (e) The UV spectral evolution of **8** in the acidic region. (f) The UV spectral evolution of **8** in the alkaline region.

Fig. S5 a) The UV spectral evolution of **3** in aqueous solution with time; b) The UV spectral evolution of **8** in aqueous solution with time.

Fig. S6 a) The visible spectrum of $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$ in aqueous solution; b) The visible spectrum of **3** in aqueous solution; c) The visible spectrum of **8** in aqueous solution.

Fig. S7 Plots of Kunelka-Munk function versus energy E (eV) for **3**, **8** and $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$.

Fig. S8 UV-visible absorption spectral changes for the azophloxine solutions at various irradiation times: a) in the presence of **1** (19.9 mg); b) in the presence of **2** (19.9 mg); c) in the presence of **4** (20.7 mg); d) in the presence of **5** (20.7 mg); e) in the presence of **6** (20.8 mg); f) in the presence of **7** (20.8 mg); g) in the presence of **9** (20.9 mg); h) in the presence of **10** (20.9 mg); i) in the presence of **11** (20.9 mg); j) in the presence of **12** (21 mg); k) in the presence of **13** (20.1 mg); l) in the presence of $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$. Inset: the conversion of azophloxine (y) with reaction time (t). Experimental conditions: the initial concentration of azophloxine: $6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; the dye solution volume: 50 mL; the catalyst amount: $9.8 \times 10^{-6} \text{ mol}$ (based on $[MnMo_9O_{32}]^{6-}$); pH = 2.6.

Fig. S9 UV-visible absorption spectral changes for the azophloxine solutions at various catalyst dosages of **3**: a) $2.46 \times 10^{-6} \text{ mol}$ (5 mg); b) $9.82 \times 10^{-6} \text{ mol}$ (20 mg); c) $1.72 \times 10^{-5} \text{ mol}$ (35 mg); d) $2.46 \times 10^{-5} \text{ mol}$ (50 mg); e) $3.19 \times 10^{-5} \text{ mol}$ (65 mg); f) $3.93 \times 10^{-5} \text{ mol}$ (80 mg); g) $4.66 \times 10^{-5} \text{ mol}$ (95 mg), and **8**: h) $2.46 \times 10^{-6} \text{ mol}$ (5.2 mg); i) $9.82 \times 10^{-6} \text{ mol}$ (20.9 mg); j) $1.72 \times 10^{-5} \text{ mol}$ (36.6 mg); k) $2.46 \times 10^{-5} \text{ mol}$ (52.3 mg); l) $3.19 \times 10^{-5} \text{ mol}$ (67.9 mg); m) $3.93 \times 10^{-5} \text{ mol}$ (83.6 mg); n) $4.66 \times 10^{-5} \text{ mol}$ (99.1 mg). Experimental conditions: the initial concentration of azophloxine: 6×10^{-5}

$5 \text{ mol}\cdot\text{L}^{-1}$, the dye solution volume: 50 mL, pH = 2.6.

Fig. S10 The effect of the molar ratio of the doped VK-TA18-TiO₂ : **3** on the degradation of azophloxine: a) 0, b) 1:2, c) 1:1, d) 2:1, e) 4:1; The effect of the molar ratio of the doped VK-TA18-TiO₂ : **8** on the degradation of azophloxine: f) 0, g) 1:2, h) 1:1, i) 2:1, j) 4:1. Experimental conditions: the initial concentration of azophloxine: $6\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, the dye solution volume: 50 mL, pH = 2.6.

Fig. S11 Effect of different light intensities and different catalysts on the azophloxine degradation: Under UV light: a) 0.4 mg VK-TA18-TiO₂; b) 20 mg-**3**; c) VK-TA18-TiO₂-TiO₂:**3** (mole ratio) = 1:2 (20 mg **3** and 0.4 mg VK-TA18-TiO₂-TiO₂); d) 20.9 mg-**8**; e) VK-TA18-TiO₂-TiO₂:**8** (mole ratio) = 1:2 (20.9 mg **8** and 0.4 mg VK-TA18-TiO₂-TiO₂). Under visible light: f) 0.4 mg VK-TA18-TiO₂; g) 20 mg-**3**; h) VK-TA18-TiO₂-TiO₂:**3** (mole ratio) = 1:2 (20 mg **3** and 0.4 mg VK-TA18-TiO₂-TiO₂); i) 20.9 mg-**8**; j) VK-TA18-TiO₂-TiO₂:**8** (mole ratio) = 1:2 (20.9 mg **8** and 0.4 mg VK-TA18-TiO₂-TiO₂); k) without any catalyst. Experimental conditions: Initial concentration of azophloxine: $6\times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$, Volume: 50 mL, pH = 2.6.

Fig. S12 (a) The emission spectrum of (NH₄)₆[MnMo₉O₃₂]·8H₂O under excitation at 340 nm at room temperature; (b) The excitation spectrum of (NH₄)₆[MnMo₉O₃₂]·8H₂O obtained by monitoring the emission at 705 nm; (c) The luminescence decay curve of (NH₄)₆[MnMo₉O₃₂]·8H₂O.

Table S1 Bond valence sum (BVS) parameters for the La1, Mn1, Mo1 and Mo2 in **1**.

Table S2 Summary of RE³⁺ ionic radii, RE–O bond lengths, RE–O Average bond length and RE³⁺ coordination numbers of **1–13**.

1. Some typical examples of REPOMBMs

For instance, in 2002, Das et al. for the first time reported a chain-like extended structure $[\text{La}(\text{H}_2\text{O})_7\text{Al}(\text{OH})_6\text{Mo}_6\text{O}_{18}]_n \cdot 4n\text{H}_2\text{O}$ based on Anderson-type POMB polyanions and lanthanide linkers.¹⁷ Thereafter, Krebs and Wang also communicated Anderson-type REPOMBMs $[(\text{RE}(\text{H}_2\text{O})_6)_2(\text{TeMo}_6\text{O}_{24})] \cdot 10\text{H}_2\text{O}$ ($\text{RE} = \text{Ho}^{3+}, \text{Yb}^{3+}$) and $(\text{C}_6\text{NO}_2\text{H}_5)_2[\text{RE}(\text{H}_2\text{O})_5(\text{CrMo}_6\text{H}_6\text{O}_{24})] \cdot 0.5 \text{H}_2\text{O}$ ($\text{RE} = \text{Ce}^{3+}, \text{La}^{3+}$).¹⁸ In 2003, Wang and co-workers synthesized a series of REPOMBMs consisting of Keggin-type germanomolybdate polyanions $[\text{RE}(\text{NMP})_4(\text{H}_2\text{O})_4][\text{H}_x\text{GeMo}_{12}\text{O}_{40}] \cdot 2 \text{NMP} \cdot 3\text{H}_2\text{O}$ ($\text{RE} = \text{Ce}^{4+}, x = 0$; $\text{RE} = \text{Pr}^{3+}, \text{Nd}^{3+}, x = 1$; NMP = N-methyl-2-pyrrolidone).¹⁹ Soon afterward, Niu's group prepared the RE-supported 1-D polymeric chain phosphomolybdates $[\{\text{RE}(\text{NMP})_6\}(\text{PMo}_{12}\text{O}_{40})]_n$ ($\text{RE} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}$).²⁰ In 2012, Chen et al. published two POMB-based RE-pdc metal-organic frameworks $\{[\text{Sm}(\text{H}_2\text{O})_4(\text{pdc})]_3\} \{[\text{Sm}(\text{H}_2\text{O})_3(\text{pdc})]\} [\text{SiMo}_{12}\text{O}_{40}] \cdot 3\text{H}_2\text{O}$ and $\{[\text{La}(\text{H}_2\text{O})_4(\text{pdc})]_4\} [\text{PMo}_{12}\text{O}_{40}] \text{F}$ ($\text{H}_2\text{pdc} = \text{pyridine-2,6-dicarboxylic acid}$).²¹

2. The structural refinement details in 1-13

Thanks to the large structures of **1-13** 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.

For **1**: O6W-O8W and N6 are refined isotropically. 636 parameters and 1 restraint is used in the refinement.

For **2**: O6W-O8W and N6 are refined isotropically. 637 parameters and 1 restraint is used in the refinement.

For **3**: O6W-O8W and N6 are refined isotropically. 637 parameters and 1 restraint is used in the refinement.

For **4**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **5**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **6**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **7**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **8**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **9**: The "ISOR" instruction is used for C1. O9W, O10W, O13W, O14W, and N5 are refined isotropically. 678 parameters and 8 restraint is used in the refinement.

For **10**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **11**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **12**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 679 parameters and 2 restraint is used in the refinement.

For **13**: O9W, O10W, O13W, O14W, and N5 are refined isotropically. 678 parameters and 2 restraint is used in the refinement.

3. Some examples of Mo-containing heterometallic cubane-like clusters, the isometallic cubane $\{\text{M}_4\text{O}_4\}$ or heterometallic cubane $\{\text{M}_x\text{M}_{4-x}\text{O}_4\}$ containing POMs and multi- $\{\text{M}_4\text{O}_4\}$ cubane encapsulated POM oligomers

For instance, in 2001, Llusar et al prepared two heterobimetallic cuboidal clusters $[\text{Mo}_3\text{CuS}_4\text{Cl}_4(\text{dmpe})_3](\text{PF}_6)$ and $[\text{Mo}_3\text{CuS}_4\text{Br}_4(\text{dmpe})_3](\text{PF}_6)$ with fine optical-limiting properties by reacting the incomplete cuboidal trimers

[Mo₃S₄Cl₃(dmpe)₃](PF₆) and [Mo₃S₄Br₃(dmpe)₃](PF₆) with CuX (X = Cl⁻, Br⁻) in THF.^{30a} Later, Llusar's group synthesized a pair of enantiomerically pure cuboidal complexes (*P*)-[Mo₃CuS₄{(*R,R*)-Me-BPE}₃Cl₄]⁺ and (*M*)-[Mo₃CuS₄{(*S,S*)-Me-BPE}₃Cl₄]⁺.^{30b} In 2009, Zheng and co-workers reported three new heterothiometallic cluster polymers with fascinating topologies [Mo₂O₂S₆Cu₆I₂(4,4'-bipy)₃(H₂O)]_n, [WS₄Cu₄I₂(bpe)₃(H₂O)]_n and [WS₄Cu₆I₄(timtz)_{8/3}(H₂O)₁₂]_n.³¹ In addition, the isometallic cubane {M₄O₄} or heterometallic cubane {M_xM_{4-x}O₄} containing POMs have been previously found.³² For instance, in 1999, Kortz et al communicated an interesting ferromagnetic mono-{Ni₄O₄}-cubane-capped Keggin phosphotungstate [H₂PW₉Ni₄O₃₄(OH)₃(H₂O)₆]²⁻.^{32a} In the same year, Coronado's group discovered a ferromagnetic mono-{Ni₃WO₄}-cubane substituted Keggin phosphotungstate species [Ni₃(H₂O)₃(PW₁₀O₃₉)H₂O]⁷⁻.^{32b} In 2009, three 3d–4f heterometallic cubane {RECu₃(OH)₃O} (RE = La³⁺, Gd³⁺, Eu³⁺) inserted Keggin silicotungstates were obtained by Mialane and co-workers.^{32c} In 2010, Fang et al reported a mixed-valence cubane {Mn^{III}₃Mn^{IV}O₄} embedded Dawson phosphotungstate [(α-P₂W₁₅O₅₆)Mn^{III}₃Mn^{IV}O₃(CH₃COO)₃]⁸⁻ that exhibits a single-molecule magnet behavior.^{32d} Furthermore, multi-{M₄O₄} cubane encapsulated POM oligomers were also made. In 2007, Yang et al communicated a mixed-valence tetrameric phosphotungstate aggregate [{Fe^{II}_{1.5}Fe^{III}]₁₂(μ₃-OH)₁₂(μ₄-PO₄)₄}(B-α-PW₉O₃₄)₄]²⁰⁻ containing one {Fe^{II}O₄} and four {Fe^{III}₃Fe^{II}O(OH)₃} cubane units, which illustrates the antiferromagnetic coupling interactions within magnetic centers.^{32e} Later, multi-{Ni₄O₄}, multi-{Mn₄O₄} and multi-{Co₄O₄} cubane-unit encapsulated POMs were consecutively found by Wang's group.^{32f-h}

4. IR spectra

IR spectra of **1–13** have been investigated between 4000 and 400 cm⁻¹ on a Nicolet 170 SXFT-IR spectrometer by utilizing KBr pellets (Fig. S1 in ESI). Their IR spectra show similar characteristic peaks for the skeletal vibrations in the region between 400 and 1000 cm⁻¹, indicating that **1–13** contain the same polyoxoanion skeleton, which is in good agreement with the results of single-crystal X-ray diffraction analysis. In **1–3**, the intense absorption bands at 941–939 cm⁻¹ and 901–900 cm⁻¹ correspond to the ν(Mo–O_t) stretching vibration, those at 681–680 cm⁻¹ and 595–593 cm⁻¹ are assigned to the ν(Mo–O_b–Mo) stretching vibration and the absorption band appearing at 543–542 cm⁻¹ is attributed to the Mn–O stretching vibration.^{1,2} Correspondingly, these characteristic peaks are observed at 936–933 cm⁻¹ and 905–900 cm⁻¹; 685–682 cm⁻¹, 595–593 cm⁻¹; and 543–540 cm⁻¹ in **4–13**. Furthermore, the ν(Mo–O_t) absorption vibration bands of **1–13** show the bathochromic shift red-shifts in comparison with the ν(Mo–O_t) absorption vibration band (927, 881 cm⁻¹) of K_{1.5}(NH₄)_{4.5}[MnMo₉O₃₂]·4.2H₂O,^{2b} the probable reason for which may be that there are comparatively stronger interactions between the {[RE(Hina)(ina)(H₂O)₂]₂}⁴⁺ or [RE(Hina)₂(H₂O)₆]³⁺ cations and the terminal oxygen atoms of the [MnMo₉O₃₂]⁶⁻ polyoxoanions, whittling the Mo–O_t bonds, reducing the Mo–O_t bond force constant, and leading to the diminishing in the Mo–O_t vibration frequency.³ In addition, the strong broad band at around 3400 cm⁻¹ is assigned to the stretching vibration mode of coordinate and lattice water molecules. As a rule, the carboxylic group is anticipated to show very intense absorption bands from asymmetric (1500–1630 cm⁻¹) and symmetric (1350–1460 cm⁻¹) stretching vibration.^{4a,b} Apparently, the absorption bands observed at 1642–1637 cm⁻¹, 1592–1590 cm⁻¹ and 1404–1402 cm⁻¹ for **1–3** and 1613–1608 cm⁻¹ and 1397–1393 cm⁻¹ for **4–13** are attributed to the asymmetric [ν_{as}(CO₂⁻)] and symmetric [ν_{sy}(CO₂⁻)] stretching vibrations of carboxylic groups of the ina ligands, respectively.^{4b,c} In general, the separation (Δν) between ν_{as}(CO₂⁻) and ν_{sy}(CO₂⁻) in the IR spectrum has been effectively used to obtain information concerning bonding modes of carboxylic groups.^{4a-c} If Δν is larger than 200 cm⁻¹, the carboxylic group employs the monodentate coordination mode, in contrast, if Δν is smaller than 200 cm⁻¹, the carboxylic group utilizes the chelating coordination pattern.^{4d} Therefore, the occurrence of Δν of 240–233 cm⁻¹ and 190–186 cm⁻¹ for **1–3** illustrates the coexistence of monodentate and chelating coordination modes of the carboxylic groups in **1–3** while Δν of 220–211 cm⁻¹ for **4–13** indicates the monodentate coordination mode of the carboxylic groups in **4–13**. These results are consistent with their crystal structures. The signal appearing at 3164–3153 cm⁻¹ for **1–13** is attributable to the ν(N–H) stretching vibration of NH₄⁺.² In a word, the results of IR spectra coincide with those

from the X-ray single-crystal structural analysis.

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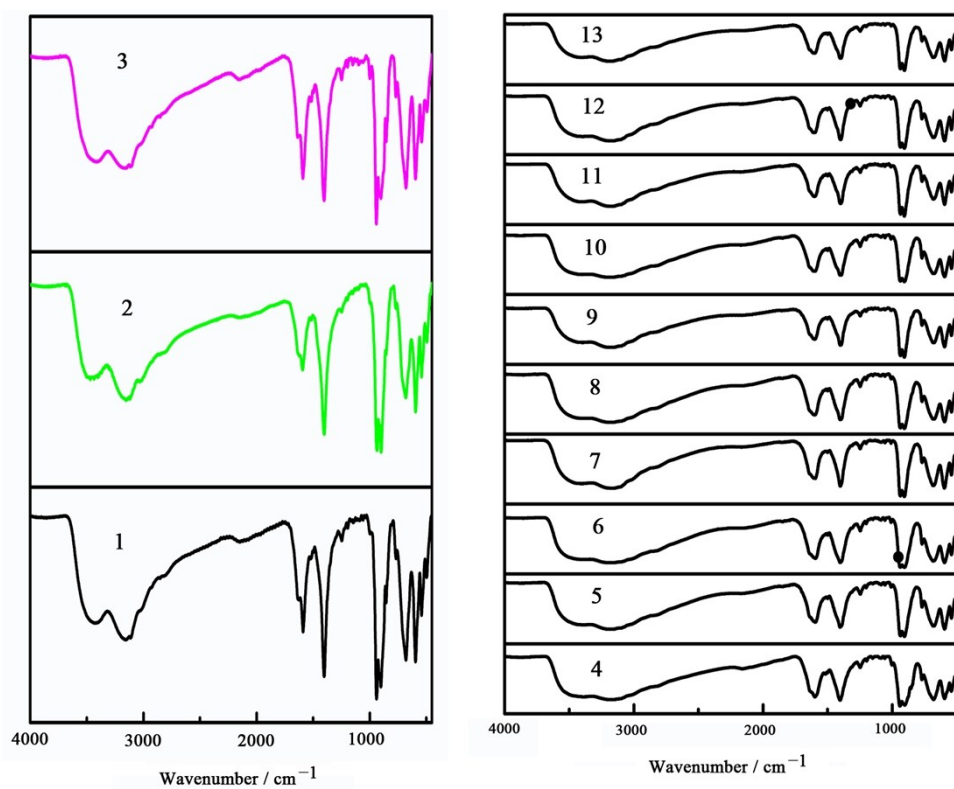


Fig. S1 IR spectra of 1–13.

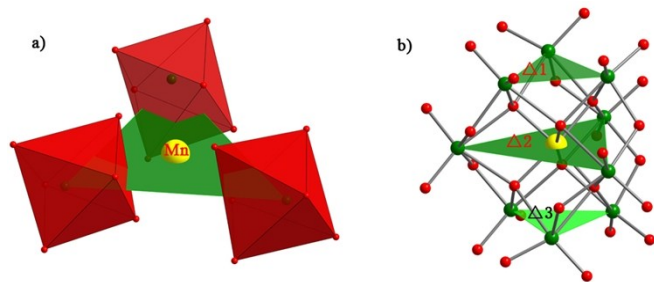


Fig. S2 a) The Mn-centered triangular $\{\text{MnMo}_3\text{O}_{18}\}$ cluster; b) Three triangles ($\Delta 1$, $\Delta 2$, $\Delta 3$) in the $[\text{MnMo}_9\text{O}_{32}]^{6-}$ polyoxoanion.

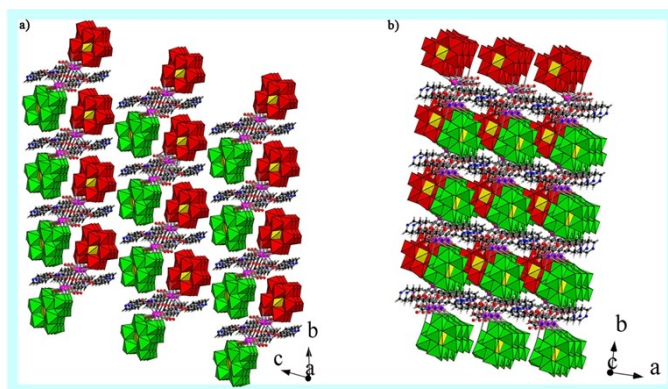


Fig. S3 a) The 3-D supramolecular packing of **1** viewed along the a axis; b) The 3-D supramolecular packing of **1** viewed along the c axis.

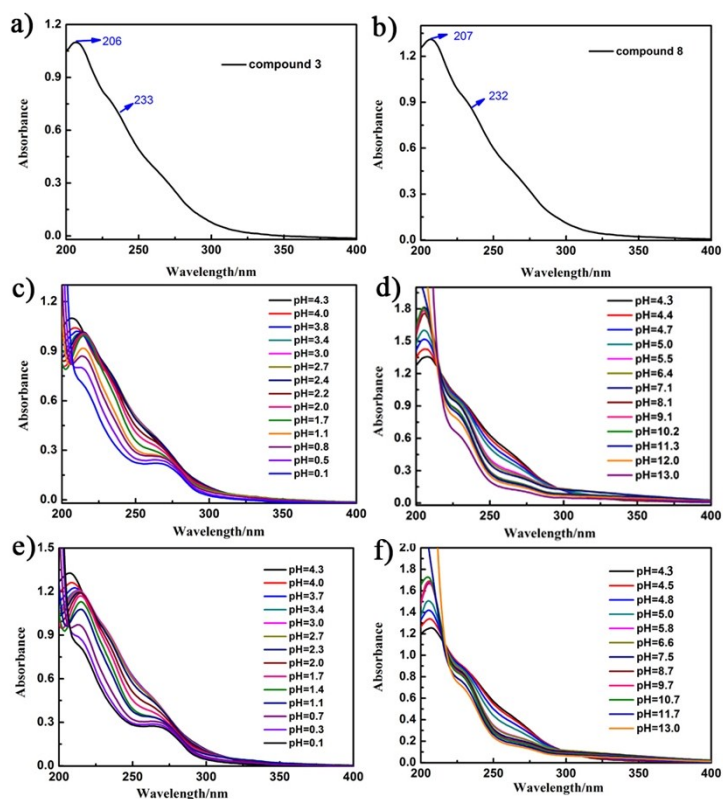


Fig. S4 (a) The UV spectrum of **3** in the range of 400–200 nm. (b) The UV spectrum of **8** in the range of 400–200 nm. (c) The UV spectral evolution of **3** in the acidic region. (d) The UV spectral evolution of **3** in the alkaline region. (e) The UV spectral evolution of **8** in the acidic region. (f) The UV spectral evolution of **8** in the alkaline region.

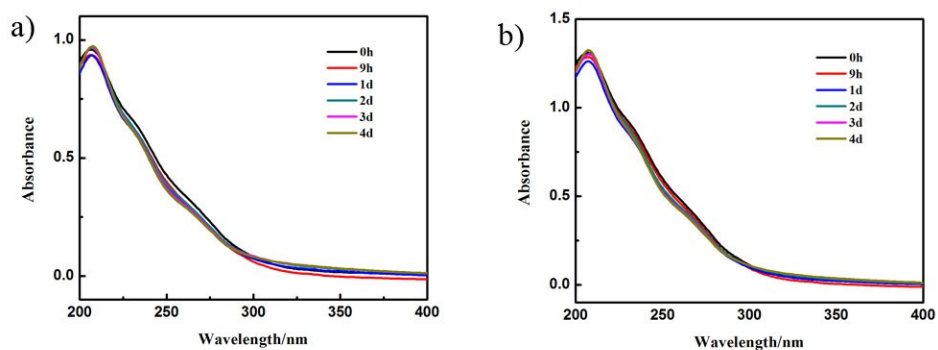


Fig. S5 a) The UV spectral evolution of **3** in aqueous solution with time; b) The UV spectral evolution of **8** in aqueous solution with time.

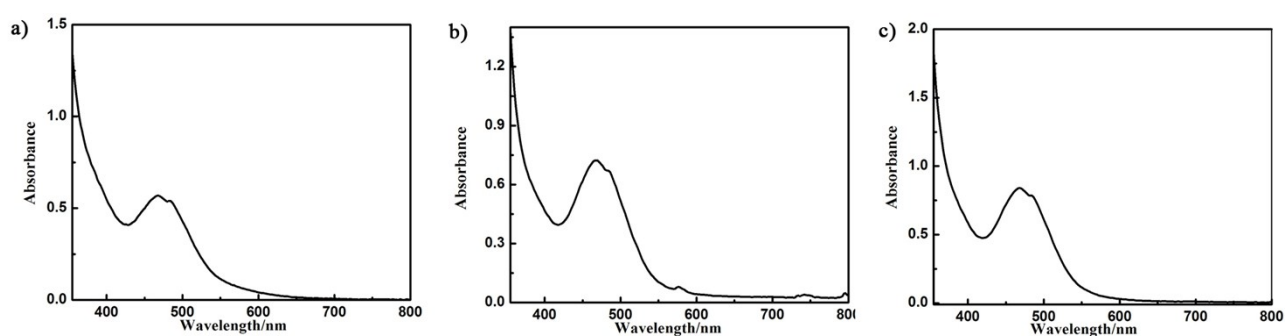


Fig. S6 a) The visible spectrum of $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$ in aqueous solution; b) The visible spectrum of **3** in aqueous solution; c) The visible spectrum of **8** in aqueous solution.

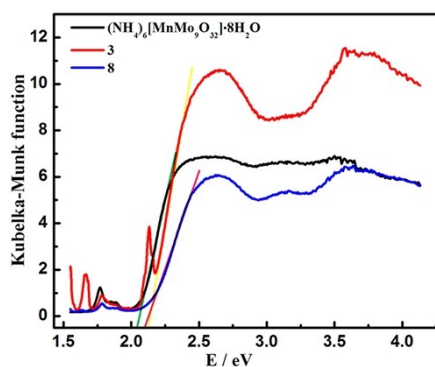


Fig. S7 Plots of Kubelka-Munk function versus energy E (eV) for **3**, **8** and $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$.

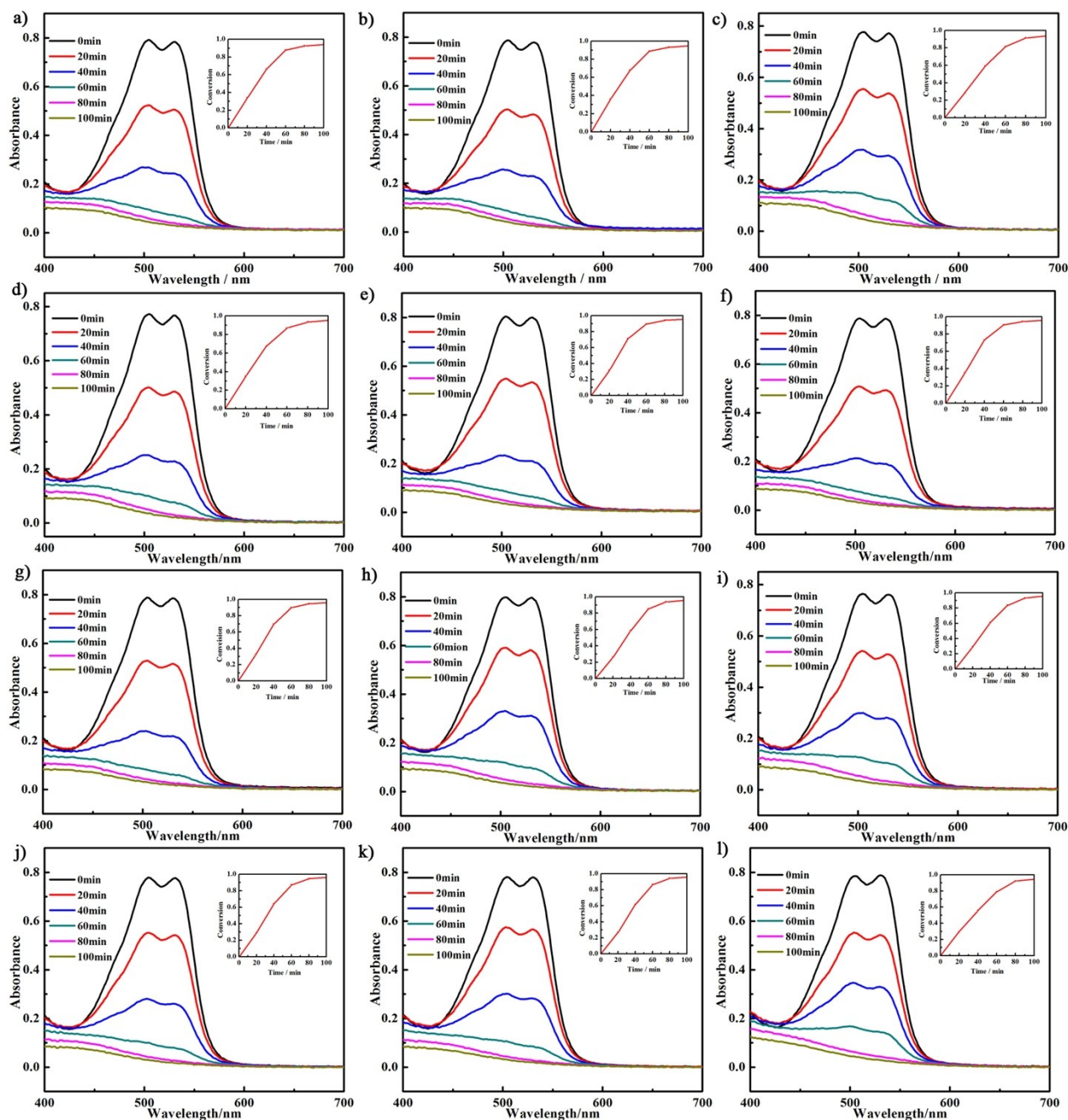


Fig. S8 UV-visible absorption spectral changes for the azophloxine solutions at various irradiation times: a) in the presence of **1** (19.9 mg); b) in the presence of **2** (19.9 mg); c) in the presence of **4** (20.7 mg); d) in the presence of **5** (20.7 mg); e) in the presence of **6** (20.8 mg); f) in the presence of **7** (20.8 mg); g) in the presence of **9** (20.9 mg); h) in the presence of **10** (20.9 mg); i) in the presence of **11** (20.9 mg); j) in the presence of **12** (21 mg); k) in the presence of **13** (20.1 mg); l) in the presence of (NH₄)₆[MnMo₉O₃₂]·8H₂O. Inset: the conversion of azophloxine (y) with reaction time (t). Experimental conditions: the initial concentration of azophloxine: $6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$; the dye solution volume: 50 mL; the catalyst amount: $9.8 \times 10^{-6} \text{ mol}$ (based on [MnMo₉O₃₂]⁶⁻); pH = 2.6.

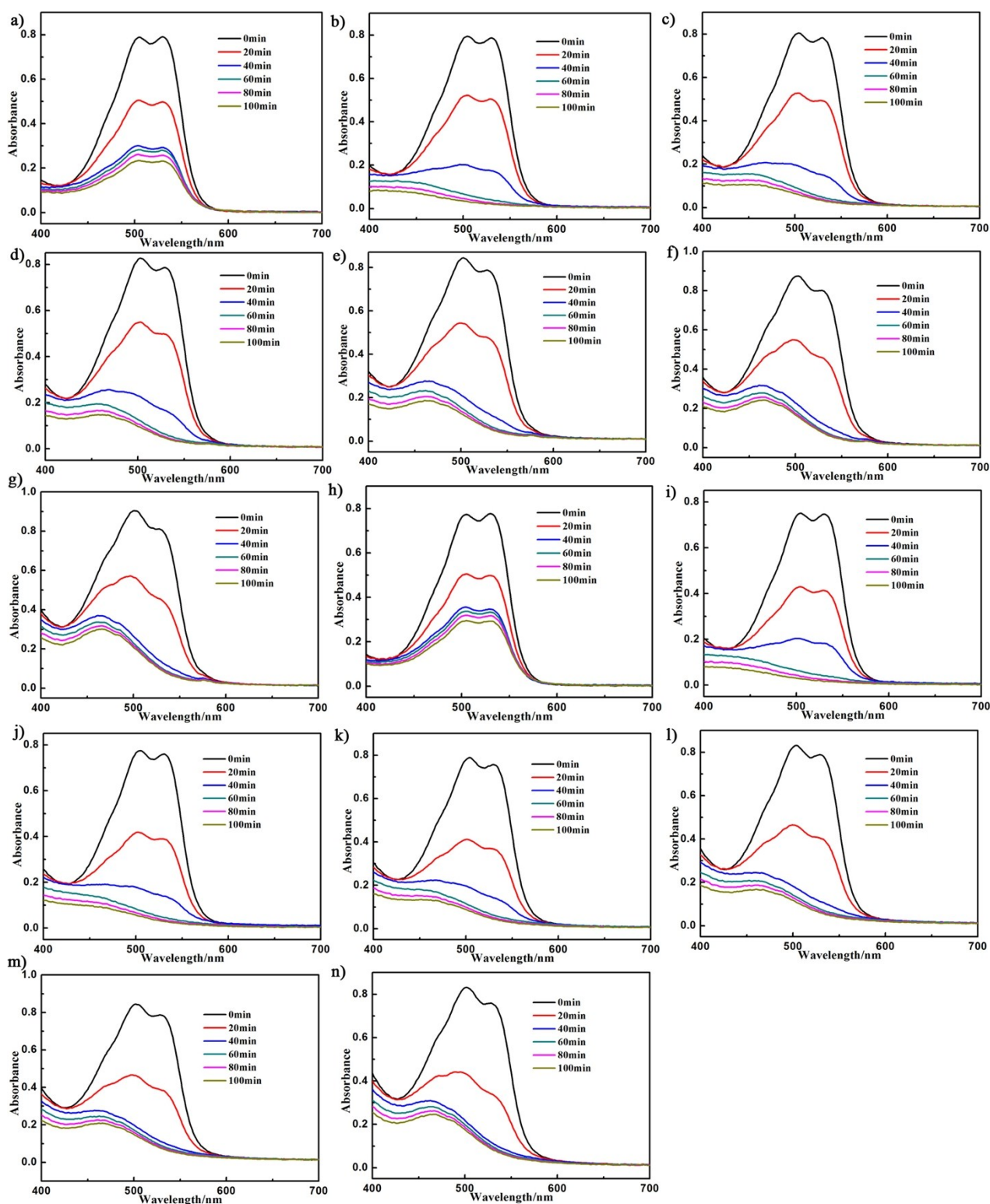


Fig. S9 UV-visible absorption spectral changes for the azophloxine solutions at various catalyst dosages of **3**: a) 2.46×10^{-6} mol (5 mg); b) 9.82×10^{-6} mol (20 mg); c) 1.72×10^{-5} mol (35 mg); d) 2.46×10^{-5} mol (50 mg); e) 3.19×10^{-5} mol (65 mg); f) 3.93×10^{-5} mol (80 mg); g) 4.66×10^{-5} mol (95 mg), and **8**: h) 2.46×10^{-6} mol (5.2 mg); i) 9.82×10^{-6} mol (20.9 mg); j) 1.72×10^{-5} mol (36.6 mg); k) 2.46×10^{-5} mol (52.3 mg); l) 3.19×10^{-5} mol (67.9 mg); m) 3.93×10^{-5} mol (83.6 mg); n) 4.66×10^{-5} mol (99.1 mg). Experimental conditions: the initial concentration of azophloxine: 6×10^{-5} mol·L⁻¹, the dye solution volume: 50 mL, pH = 2.6.

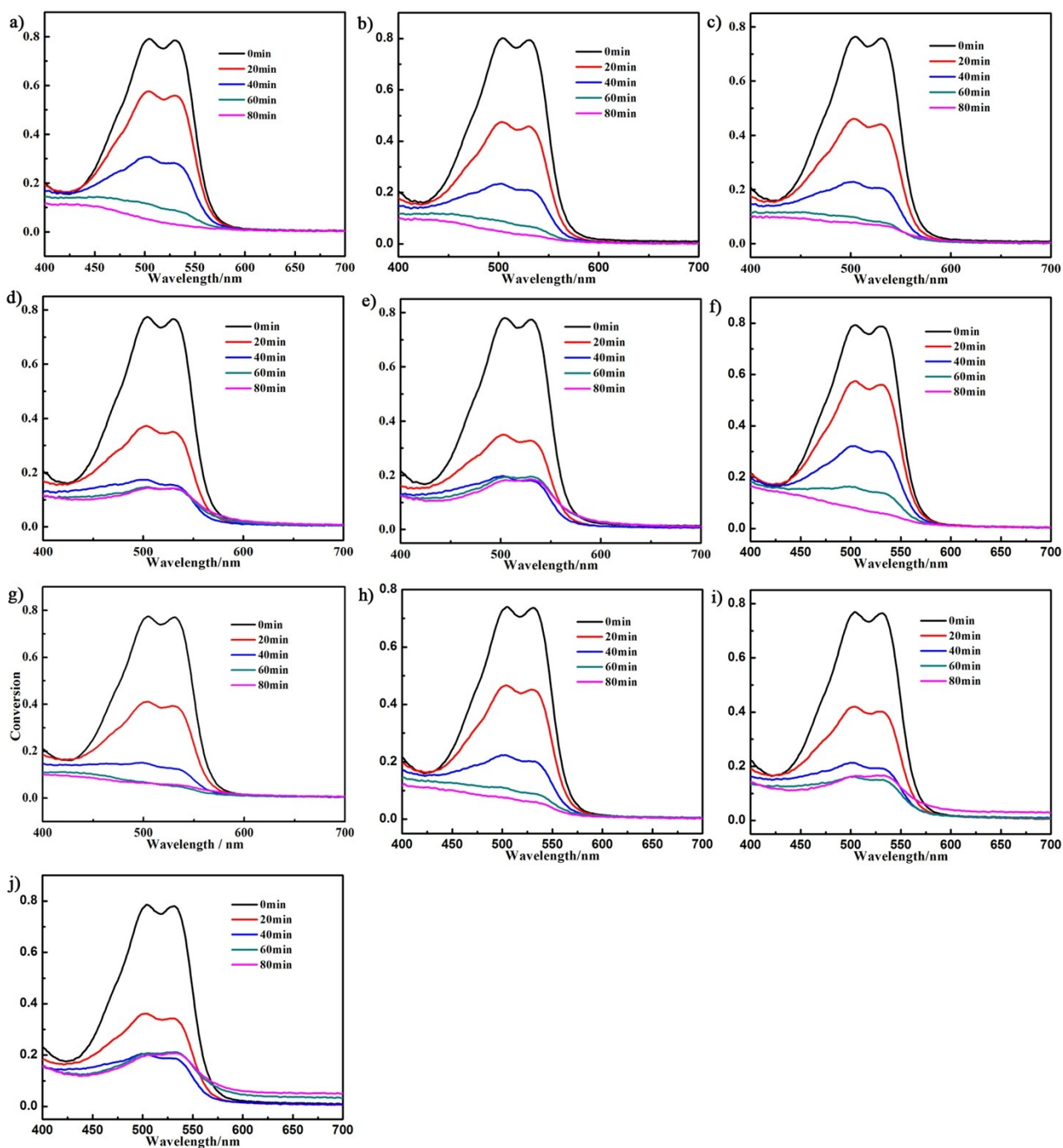


Fig. S10 The effect of the molar ratio of the doped VK-TA18-TiO₂ : **3** on the degradation of azophloxine: a) 0, b) 1:2, c) 1:1, d) 2:1, e) 4:1; The effect of the molar ratio of the doped VK-TA18-TiO₂ : **8** on the degradation of azophloxine: f) 0, g) 1:2, h) 1:1, i) 2:1, j) 4:1. Experimental conditions: the initial concentration of azophloxine: $6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, the dye solution volume: 50 mL, pH = 2.6.

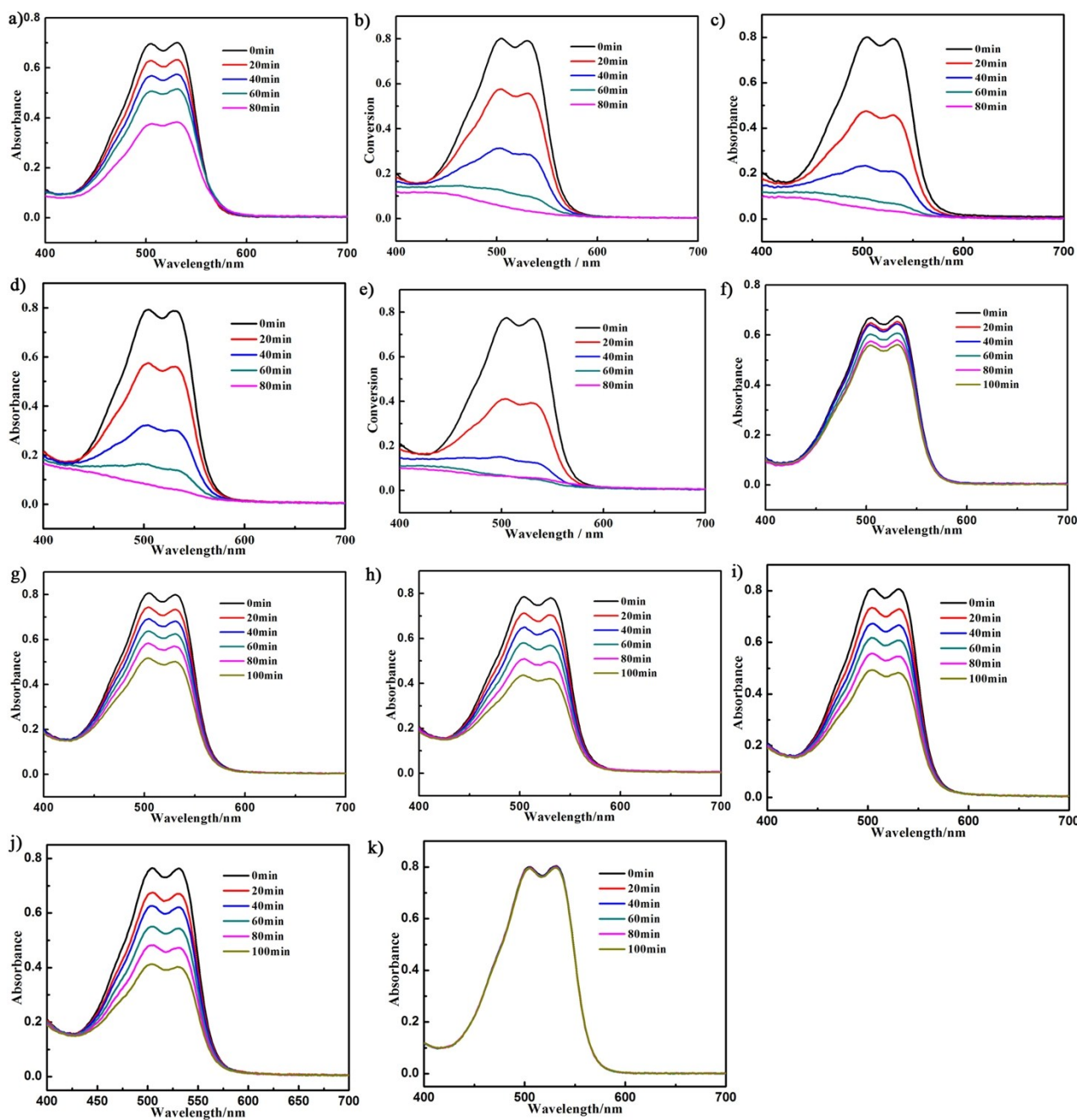


Fig. S11 Effect of different light intensities and different catalysts on the azophloxine degradation: Under UV light: a) 0.4 mg VK-TA18-TiO₂; b) 20 mg-**3**; c) VK-TA18-TiO₂-TiO₂:**3** (mole ratio) = 1:2 (20 mg **3** and 0.4 mg VK-TA18-TiO₂-TiO₂); d) 20.9 mg-**8**; e) VK-TA18-TiO₂-TiO₂:**8** (mole ratio) = 1:2 (20.9 mg **8** and 0.4 mg VK-TA18-TiO₂-TiO₂). Under visible light: f) 0.4 mg VK-TA18-TiO₂; g) 20 mg-**3**; h) VK-TA18-TiO₂-TiO₂:**3** (mole ratio) = 1:2 (20 mg **3** and 0.4 mg VK-TA18-TiO₂-TiO₂); i) 20.9 mg-**8**; j) VK-TA18-TiO₂-TiO₂:**8** (mole ratio) = 1:2 (20.9 mg **8** and 0.4 mg VK-TA18-TiO₂-TiO₂); k) without any catalyst. Experimental conditions: Initial concentration of azophloxine: $6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, Volume: 50 mL, pH = 2.6.

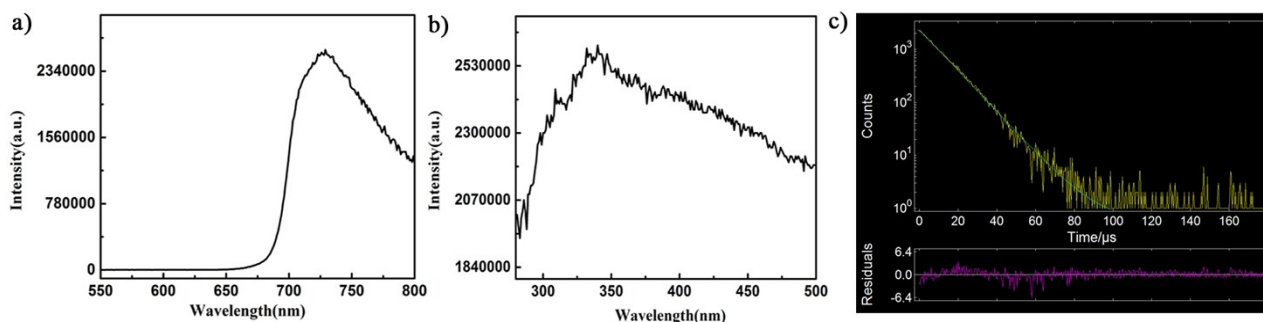


Fig. S12 (a) The emission spectrum of $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$ under excitation at 340 nm at room temperature; (b) The excitation spectrum of $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$ obtained by monitoring the emission at 705 nm; (c) The luminescence decay curve of $(\text{NH}_4)_6[\text{MnMo}_9\text{O}_{32}] \cdot 8\text{H}_2\text{O}$.

Table S1 Bond valence sum (BVS) parameters for the La1, Mn1, Mo1 and Mo2 in **1**.

Bond	Bond length	Bond valence	Bond valence sum
La1-O34	2.491(8)	0.42	$\Sigma(\text{La1}) = 2.95$
La1-O36	2.495(7)	0.42	
La1-O23	2.517(6)	0.39	
La1-O35#1	2.540(7)	0.37	
La1-O26	2.541(6)	0.37	
La1-O2W	2.553(8)	0.36	
La1-O1W	2.592(9)	0.32	
La1-O19	2.614(6)	0.30	
Mn1-O21	1.872(6)	0.73	$\Sigma(\text{Mn1}) = 4.18$
Mn1-O5	1.887(6)	0.70	
Mn1-O28	1.890(6)	0.69	
Mn1-O14	1.891(6)	0.69	
Mn1-O10	1.891(6)	0.69	
Mn1-O4	1.896(6)	0.68	
Mo1-O1	1.688(7)	1.81	$\Sigma(\text{Mo1}) = 6.06$
Mo1-O2	1.694(7)	1.78	
Mo1-O6	1.964(7)	0.86	
Mo1-O3	1.965(7)	0.86	
Mo1-O4	2.250(6)	0.40	
Mo1-O5	2.291(6)	0.35	
Mo2-O7	1.704(6)	1.73	$\Sigma(\text{Mo2}) = 5.98$
Mo2-O8	1.712(7)	1.69	
Mo2-O6	1.874(6)	1.09	
Mo2-O9	2.074(6)	0.64	
Mo2-O5	2.204(6)	0.45	
Mo2-O10	2.263(6)	0.38	

Table S2 Summary of RE³⁺ ionic radii, RE–O bond lengths, RE–O Average bond length and RE³⁺ coordination numbers of **1–13**.

Compound	RE ³⁺	RE ³⁺ ionic radii (Å)	RE–O bond lengths (Å)	RE–O average bond lengths (Å)	RE ³⁺ coordination number
1	La ³⁺	1.061	La(1)–O(34) 2.491(8) La(1)–O(36) 2.495(7) La(1)–O(23) 2.517(6) La(1)–O(35)#1 2.540(7) La(1)–O(26) 2.541(6) La(1)–O(2W) 2.553(8) La(1)–O(1W) 2.592(9) La(1)–O(19) 2.614(6) La(1)–O(35) 2.963(7)	2.590	9
2	Pr ³⁺	1.013	Pr(1)–O(34) 2.425(5) Pr(1)–O(36) 2.465(4) Pr(1)–O(1W) 2.465(5) Pr(1)–O(35)#1 2.473(4) Pr(1)–O(26) 2.483(4) Pr(1)–O(23) 2.485(4) Pr(1)–O(2W) 2.516(4) Pr(1)–O(19) 2.574(4) Pr(1)–O(35) 3.045(4)	2.548	9
3	Nd ³⁺	0.995	Nd(1)–O(34) 2.416(5) Nd(1)–O(35)#1 2.444(5) Nd(1)–O(36) 2.447(5) Nd(1)–O(1W) 2.459(6) Nd(1)–O(26) 2.465(5) Nd(1)–O(23) 2.472(5) Nd(1)–O(2W) 2.505(5) Nd(1)–O(19) 2.556(5) Nd(1)–O(35) 3.081(4)	2.538	9
4	Sm ³⁺	0.964	Sm(1)–O(33) 2.319(4) Sm(1)–O(35) 2.364(3) Sm(1)–O(6W) 2.406(3) Sm(1)–O(1W) 2.428(4) Sm(1)–O(2W) 2.446(4) Sm(1)–O(4W) 2.453(3) Sm(1)–O(3W) 2.471(4) Sm(1)–O(5W) 2.483(4)	2.421	8
5	Eu ³⁺	0.950	Eu(1)–O(33) 2.300(5) Eu(1)–O(35) 2.349(4) Eu(1)–O(6W) 2.392(4) Eu(1)–O(1W) 2.407(5)	2.403	8

			Eu(1)–O(2W) 2.433(5) Eu(1)–O(4W) 2.435(4) Eu(1)–O(3W) 2.449(6) Eu(1)–O(5W) 2.462(5)		
6	Gd ³⁺	0.938	Gd(1)–O(33) 2.303(5) Gd(1)–O(35) 2.344(4) Gd(1)–O(6W) 2.383(4) Gd(1)–O(1W) 2.412(5) Gd(1)–O(4W) 2.426(4) Gd(1)–O(2W) 2.428(5) Gd(1)–O(3W) 2.440(5) Gd(1)–O(5W) 2.454(5)	2.399	8
7	Tb ³⁺	0.923	Tb(1)–O(33) 2.277(5) Tb(1)–O(35) 2.322(4) Tb(1)–O(6W) 2.375(4) Tb(1)–O(1W) 2.386(5) Tb(1)–O(2W) 2.409(4) Tb(1)–O(4W) 2.413(4) Tb(1)–O(3W) 2.430(5) Tb(1)–O(5W) 2.434(4)	2.381	8
8	Dy ³⁺	0.908	Dy1–O(33) 2.273(6) Dy1–O(35) 2.310(5) Dy1–O(6W) 2.351(5) Dy1–O(1W) 2.382(6) Dy1–O(4W) 2.397(5) Dy1–O(2W) 2.398(5) Dy1–O(3W) 2.415(6) Dy1–O(5W) 2.422(5)	2.369	8
9	Ho ³⁺	0.894	Ho(1)–O(33) 2.259(7) Ho(1)–O(35) 2.306(6) Ho(1)–O(6W) 2.351(6) Ho(1)–O(1W) 2.377(7) Ho(1)–O(2W) 2.391(6) Ho(1)–O(4W) 2.394(6) Ho(1)–O(3W) 2.402(7) Ho(1)–O(5W) 2.408(6)	2.361	8
10	Er ³⁺	0.881	Er(1)–O(33) 2.267(6) Er(1)–O(35) 2.320(5) Er(1)–O(6W) 2.347(6) Er(1)–O(1W) 2.384(6) Er(1)–O(4W) 2.398(5) Er(1)–O(2W) 2.401(6) Er(1)–O(5W) 2.406(6) Er(1)–O(3W) 2.410(7)	2.367	8

11	Tm ³⁺	0.870	Tm(1)–O(33) 2.267(5) Tm(1)–O(35) 2.315(4) Tm(1)–O(6W) 2.347(4) Tm(1)–O(1W) 2.378(5) Tm(1)–O(2W) 2.390(5) Tm(1)–O(4W) 2.394(4) Tm(1)–O(3W) 2.398(5) Tm(1)–O(5W) 2.412(4)	2.363	8
12	Yb ³⁺	0.858	Yb(1)–O(33) 2.226(5) Yb(1)–O(35) 2.285(4) Yb(1)–O(6W) 2.316(5) Yb(1)–O(1W) 2.344(5) Yb(1)–O(3W) 2.354(6) Yb(1)–O(4W) 2.359(4) Yb(1)–O(2W) 2.360(5) Yb(1)–O(5W) 2.374(5)	2.327	8
13	Y ³⁺	0.893	Y(1)–O(33) 2.261(5) Y(1)–O(35) 2.315(4) Y(1)–O(6W) 2.340(4) Y(1)–O(1W) 2.384(5) Y(1)–O(3W) 2.385(5) Y(1)–O(2W) 2.387(4) Y(1)–O(4W) 2.395(4) Y(1)–O(5W) 2.409(4)	2.360	8