Supporting Information

Experimental Procedure

Solvent-free syntheses of supermicroporous silicas (SMPSs)

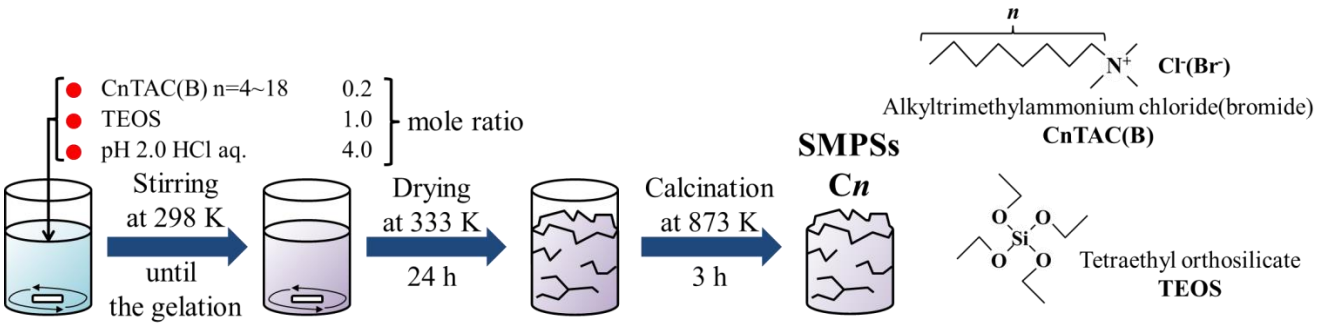

Figure S1. Solvent-free syntheses of supermicroporous silicas (SMPSs)

Alkyltrimethylanmonium chloride (bromide) (CnTAC(B)), n=4-18, n: carbon number of alkyl chain), tetraethyl orthosilicate (TEOS), and pH 2.0 HCl aq. were mixed with 0.2: 1.0: 4.0 mole ratio, respectively. After stirring the mixture at 298 K until the gelation, the products were dried at 333 K for 24 h and calcined at 873 K for 3 h.

Preparation of aqueous solution of peroxotungstic acid (WO_3 precursor solution)

A powder of 2.0 g of tungsten acid (H_2WO_4) was suspended in the mixture of 20 mL of H_2O and 20 mL of 17.5% H_2O_2 aqueous solution. The suspension was stirred for 1 week at R. T. to obtain a colorless clear solution of peroxotungstic acid [$WO_2(O_2)H_2O$].

Preparation of WO_3-QDs

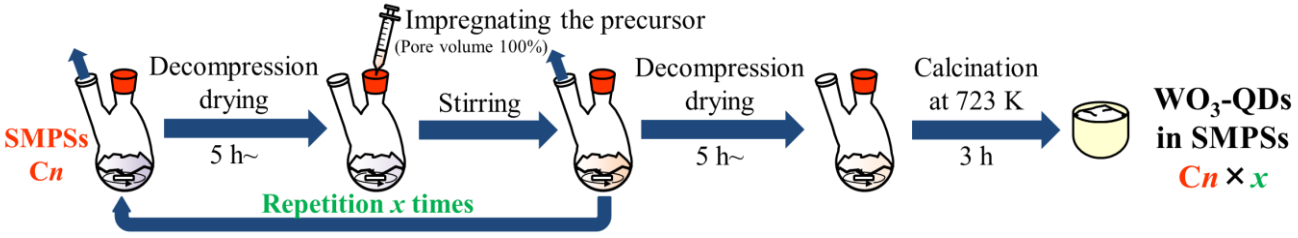

Figure S2. Preparation of WO_3-QDs.

WO_3-QDs were prepared in decompression dried SMPSs by impregnating peroxotungstic acid aq. (0.20 mol/dm^3, the volume of impregnation is equal to the pore volume of SMPSs). And then, the powder was stirred and decompression dried. This procedure was repeated several times. After stirring and decompression drying the powder, they were calcined at 723 K for 3 h. The products are denoted as Cn×m (n=4-18, n: carbon number of alkyl chain of CnTAC(B) in preparation of SMPSs; m=1-10, m: the amount of the precursor solution of the WO_3-QDs impregnated into SMPSs). The amounts of WO_3 in SMPSs were estimated by ICP-AES.

Composite with phenol

Cn×m was added to the melted phenol at 318 K. The mixture was decompression dried to volatilize the extra phenol. The products are denoted as Cn×m/phenol.

Photoreduction of proton by WO_3-QDs

Cn×m (the amount of WO_3: 5 mg), H2O 40 cm^2 and ethanol 10 cm^3 were mixed under Ar bubbling for 30 min. After Ar bubbling, this system was closed. Then, H2 in this system was detected per 90 min for 270 min under UV irradiation (290-350 nm) by GC-TCD. Although Ar bubbling was done, O2 and N2 were remained in this system.

Photoreduction of molecular oxygen by WO_3-QDs

Cn×m (the amount of WO_3: 1 mg), ethanol 4 cm^3 and 5, 5-dimethyl-1-pyrroline-N-oxide (DMPO) 18 mm^3 were mixed. After UV irradiation (290-350 nm) for 60 min at 297 K, the DMPO-OOH radicals as the spin adducts in the solution were detected by electron spin resonance (ESR) technology.

Characterization of WO_3-QDs

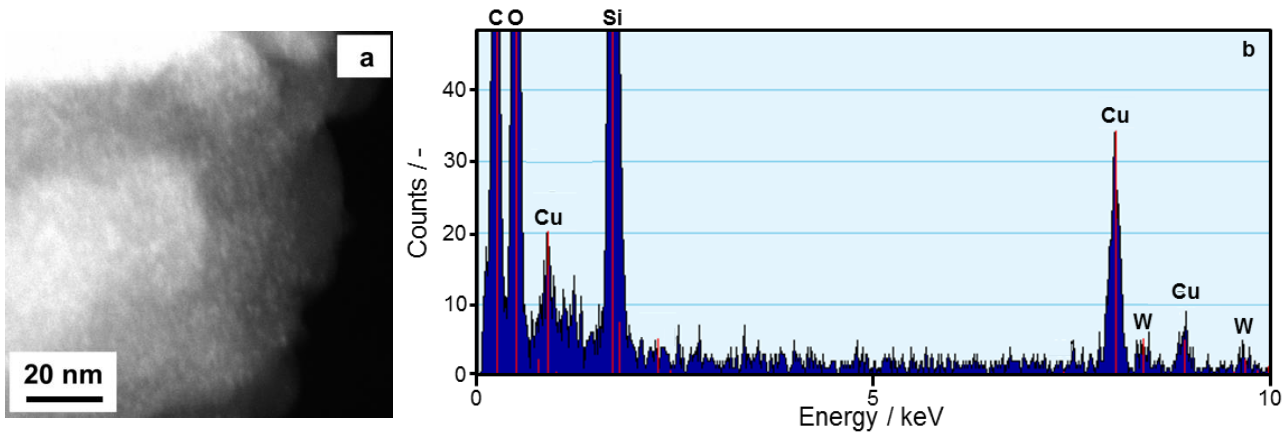

Figure S3. a) HAADF-STEM (High-Angle Annular Dark Field Scanning TEM) image of WO_3-QDs (C6×2). b) EDX spectrum of C6×2.

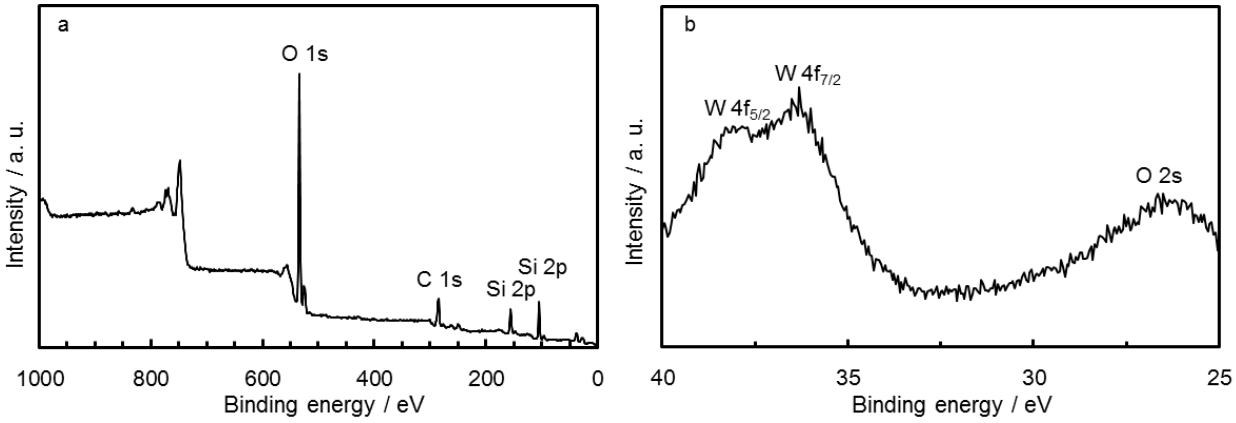

Figure S4. XPS spectrum of WO_3-QDs (C16×1). a) wide scan. b) narrow scan. XPS spectrum were measured JPS-9000MX (JEOL).

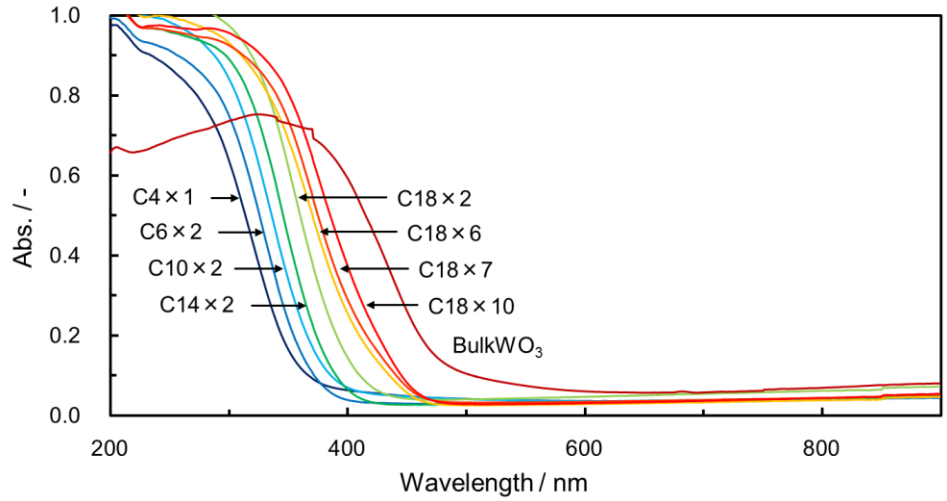

Figure S5. UV-vis spectra of WO_3-QDs (Cn×m).

Size control of WO_3-QDs

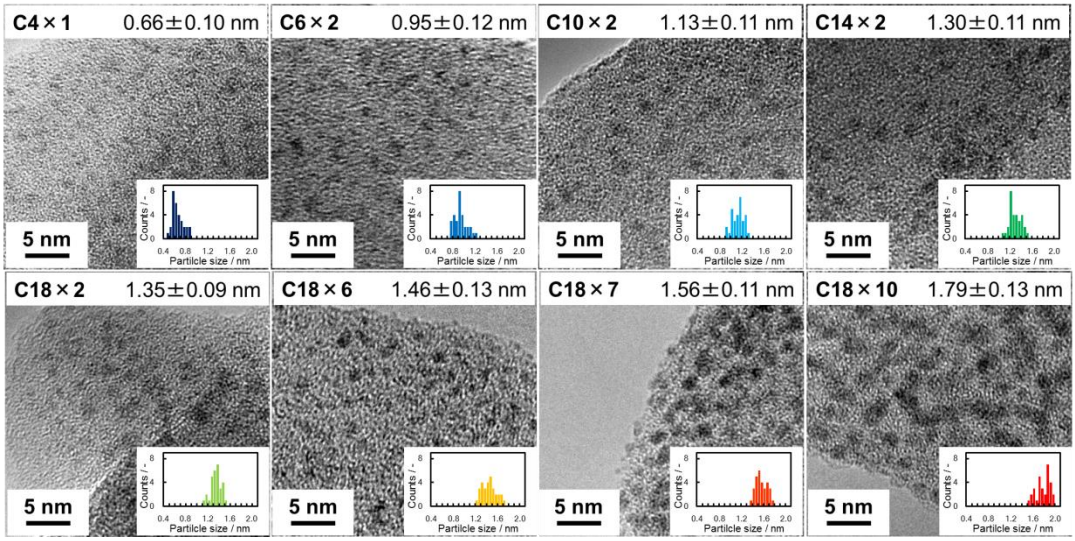

Figure S6. FE-TEM image of WO_3-QDs (Cn×m). Top images show tuning of the size of WO_3-QDs by changing the pore size of SMPSs. Bottom images show tuning of the WO_3-QDs by changing the impregnation of the precursor solution of WO_3-QDs. TEM images were obtained using TECNAI F20 (FEI).

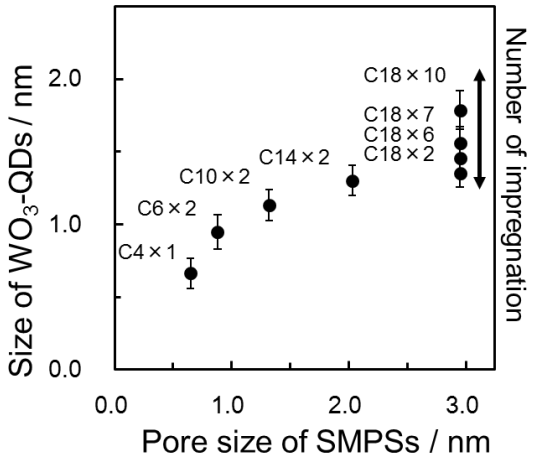

Figure S7. The relationship between the size of WO_3-QDs, the pore size of SMPSs, and the number of impregnation of the precursor solution of WO_3-QDs.

Optical properties of WO_3-QDs

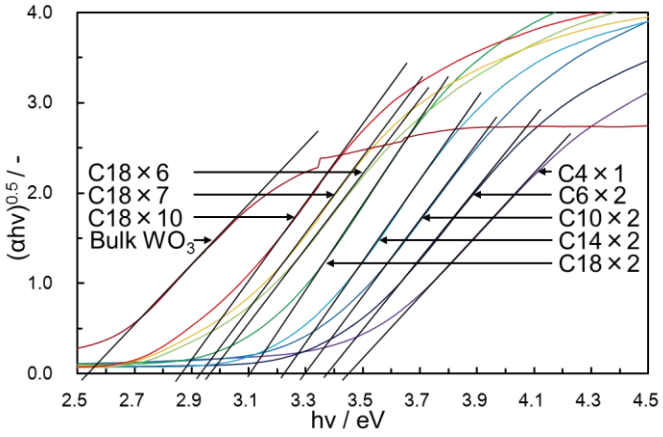

Figure S8. Tauc plot of WO_3-QDs (Cn×m). Tauc plot were obtained using V-670ST (JASCO).

Effective mass approximation (EMA) theory

The relationship between band-gap energy $\boldsymbol{E_g}$ and the particle radius $\boldsymbol{R}$ of semiconductor is described by Brus as follow equation.

$$\boldsymbol{E_g = E_{g(\mathrm{Bulk})} + \frac{\hbar^2\pi^2}{2R^2}\frac{1}{\mu} - \frac{1.8e^2}{\varepsilon R} + smaller\ terms}$$

Brus equation was deformed to follow equation. For narrow gap semiconductors, the contribution of the Coulomb term (the 3rd term) is far smaller than that of the quantum localization term (the 2nd term).

$$\boldsymbol{R\left(E_g - E_{g(\mathrm{Bulk})}\right) = \frac{\hbar^2\pi^2}{2\mu}\frac{1}{R}}$$

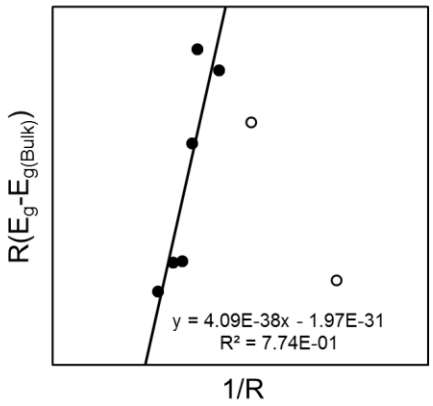

Figure S9. The relationship between $R\left(E_g - E_{g(\mathrm{Bulk})}\right)$ and $1/R$. The value of μ was calculated to be $1.47m_0$ from the slope of the approximation straight line above 1.1 nm in the size of WO_3-QDs.

Conduction band edge of WO_3-QDs

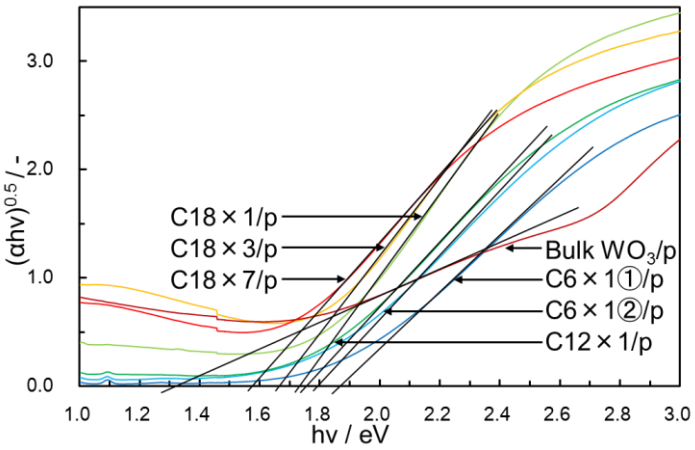

Figure S10. Tauc plot of WO_3-QDs/phenol (Cn×m/p).

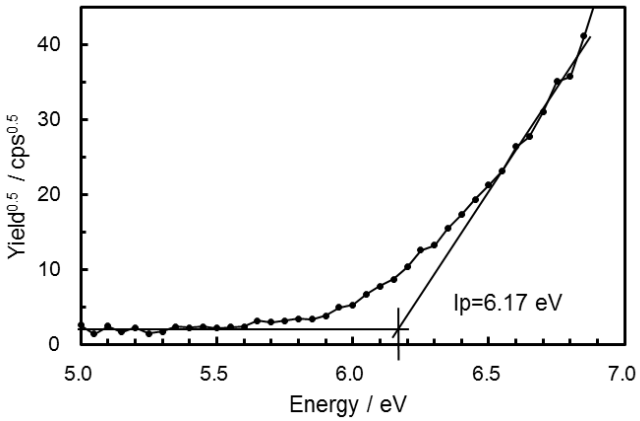

Figure S11. Estimation of HOMO level of phenol in SMPSs. The ionization potential (Ip) of phenol is 6.17 eV. Thus, HOMO level of phenol is 1.73 V vs. SHE. HOMO level of phenol was evaluated with photoemission yield spectroscopy in air (PYSA, AC-3 (RIKEN KEIKI))

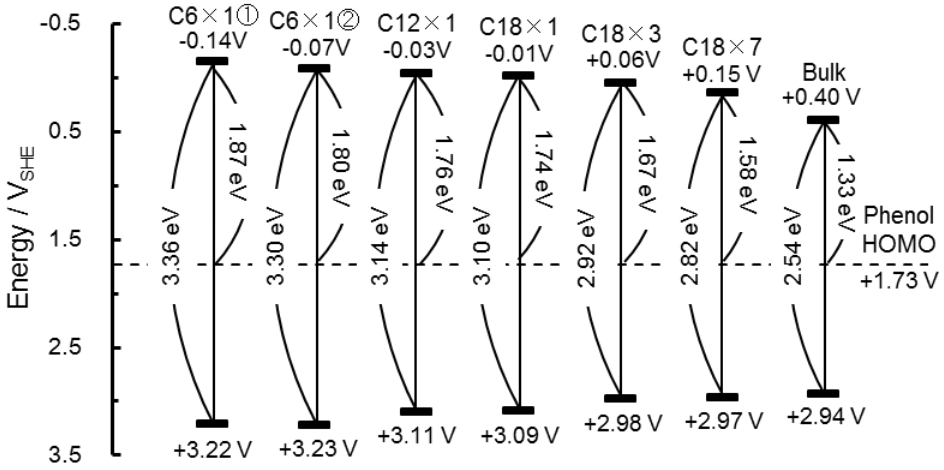

Figure S12. Calculation of the conduction band edge (CBE) of WO_3-QDs. $E_{CB} = E_{HOMO\,phenol} - E_{CT}$.

Calculation of the conduction band edge and the valence band edge by using EMA theory

The relationship between quantum confinement energy $\boldsymbol{E_{e/h}}$ and the particle radius $\boldsymbol{R}$ of semiconductor is calculated by using following equation.

$$\boldsymbol{E_{e/h} = \frac{\hbar^2 \pi^2}{2 m_{e/h} R^2}}$$

The relation between effective mass of electron $\boldsymbol{m_e}$, effective mass of hole $\boldsymbol{m_h}$ and their reduced mass $\boldsymbol{\mu}$ is shown by following equation.

$$\boldsymbol{\frac{1}{\mu} = \left(\frac{1}{m_e} + \frac{1}{m_h}\right)}$$

From the slope value (Figure 2 b)) and $\boldsymbol{\mu}$=1.47$\boldsymbol{m_0}$, $\boldsymbol{m_e}$ and $\boldsymbol{m_h}$ are calculated to be 2.39$\boldsymbol{m_0}$ and 3.83$\boldsymbol{m_0}$, respectively.

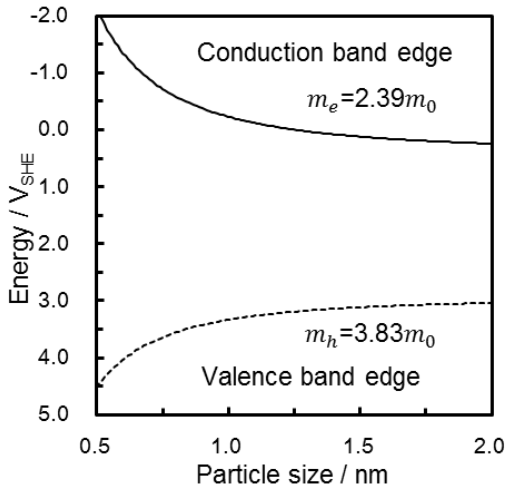

Figure S13. Correlation between the conduction band edge, the valence band edge and the particle size of WO_3-QDs. The up-shift of the conduction band edge is larger than the downshift of the valence band edge.

Photoreduction of O_2 by WO_3-QDS

Table S1. **Concentration of WO_3-QDs in SMPSs (Photoreduction of proton)**

Sample	Amount of Si / mg dm^{-3}	Amount of W / mg dm^{-3}	Concentration of WO_3 in SMPSs / wt%
C6×1	9.88	0.192	1.13
C12×1	9.97	0.382	2.21
C18×1	8.60	0.494	3.27
C18×3	6.44	1.26	10.34
C18×5	6.36	2.23	17.12
C18×7	4.55	4.75	38.09

Amounts of Si and W in Cn×m were estimated by using Inductively Coupled Plasma Atomic emission spectroscopy (ICP-AES, ICPE-9000 (SHIMADZU)).

Table S2. **Concentration of WO_3-QDs in SMPSs (Photoredution of molecular oxygen)**

Sample	Amount of Si / mg dm^{-3}	Amount of W / mg dm^{-3}	Concentration of WO_3 in SMPSs / wt%
C6×1	8.89	0.126	0.83
C12×1	10.1	0.349	2.00
C18×1	7.76	0.460	3.38
C18×3	7.23	1.21	8.98
C18×5	7.50	2.09	14.1
C18×10	6.62	4.60	29.1

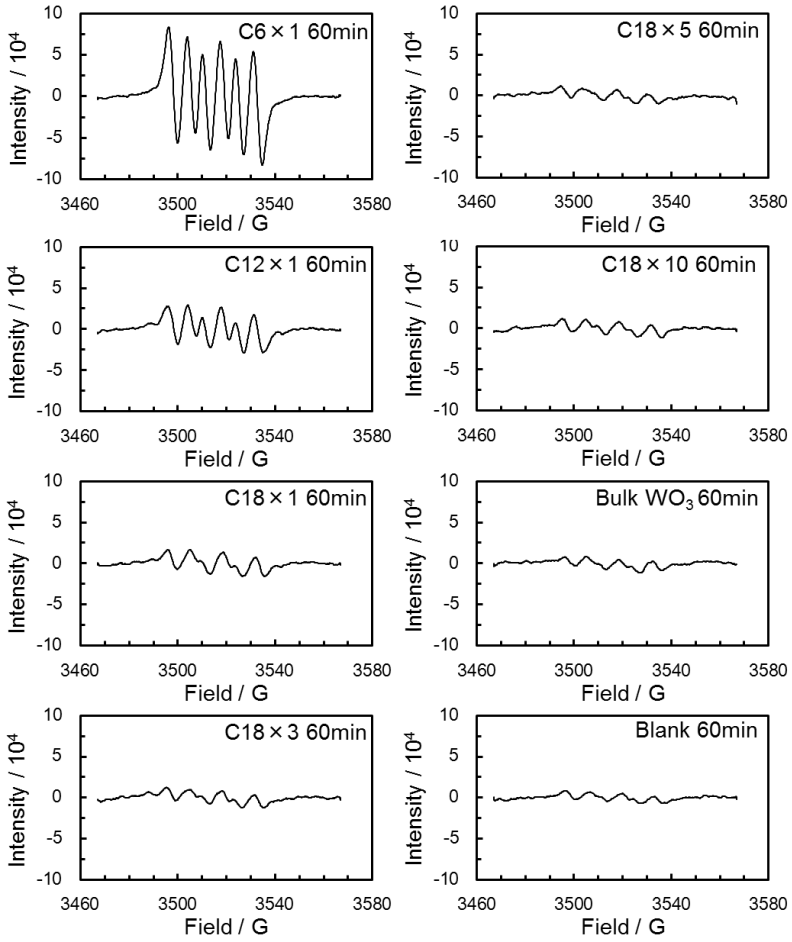

Figure S14. ESR spectra of DMPO-OOH photogenerated by WO_3-QDs (Cn×m). ESR spectra were measured with ELEXSYS E500 (Bruker BioSpin).