

Electronic Supplementary Information

Tuning oxygen-sensing behaviour of porous coordination framework by guest fluorophore

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Calculation of photoluminescence quenching

GCMC simulations

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Calculation of photoluminescence quenching. In common luminescent oxygen sensing systems, the bimolecular collision luminescence quenching can be described by the Stern-Volmer equation [ref. 55]

$$I_0 / I = \tau_0 / \tau = 1 + \frac{4}{1000} \pi \sigma \alpha N_A \tau_0 (D_{O_2} S_{O_2}) p_{O_2} = 1 + K_{sv} p_{O_2}$$

where I_0/τ_0 and I/τ are the luminescent intensity/lifetime in the absence and presence of quencher, respectively, σ is the collision radius of the oxygen-sensing dye, α represents the probability that a collision leads to quenching, N_A is Avogadro's number, D_{O_2} is the diffusion coefficients of oxygen, S_{O_2} is the oxygen solubility, p_{O_2} is the oxygen pressure, and K_{sv} is a combinational constant describing the quenching efficiency of the system. The product of D_{O_2} and S_{O_2} is the oxygen permeability ($P_{O_2} = D_{O_2} S_{O_2}$).

GCMC simulations. All the GCMC simulations were performed in the MS modeling 5.0 package [Accelrys, Materials Studio Getting Started, release 5.0, Accelrys Software, Inc., San Diego, CA, 2009]. The framework and the individual AlQ₃ molecules were considered to be rigid. Partial charges for atoms of MAF-X10 were derived from QEq method and QEq_neutral1.0 parameters. The simulations were carried out at 298 K, adopting the Fixed Loading task, Metropolis method in Sorption module and the universal forcefield (UFF). The interaction energy between AlQ₃ and framework were computed through the Coulomb and Lennard-Jones 6-12 (LJ) potentials. The cutoff radius was chosen as 15.5 Å for the LJ potential and the long-range electrostatic interactions were handled using the Ewald & Group summation method. The loading steps and the equilibration steps were 2×10^6 , the production steps were 5×10^6 .

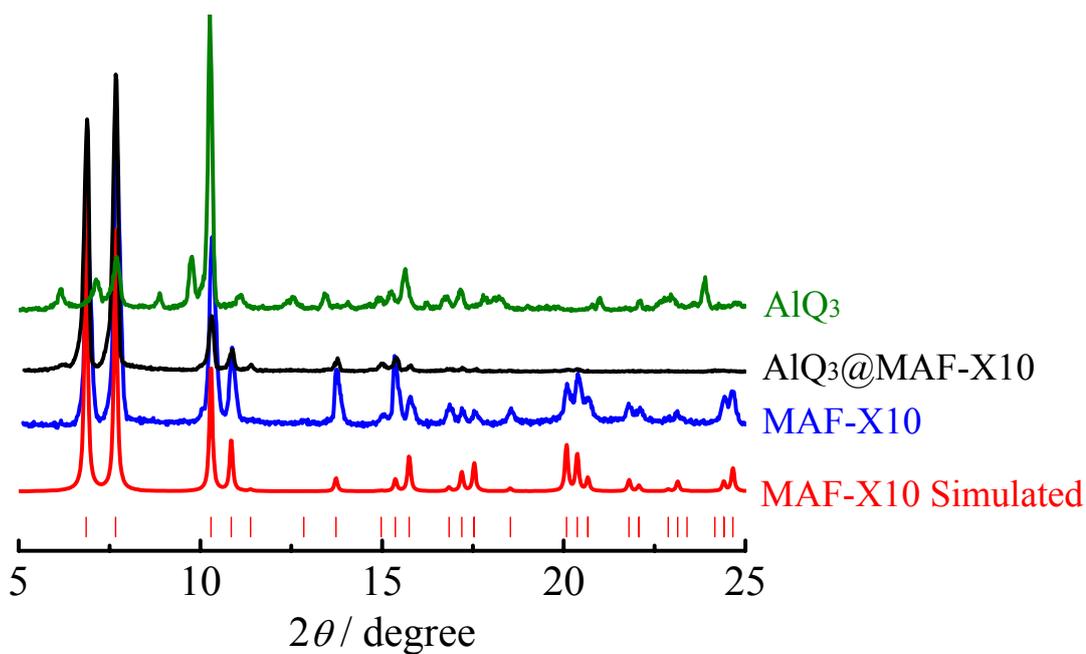


Figure S1. PXRD patterns of $MAF-X10$ and $\text{AlQ}_3@MAF-X10$.

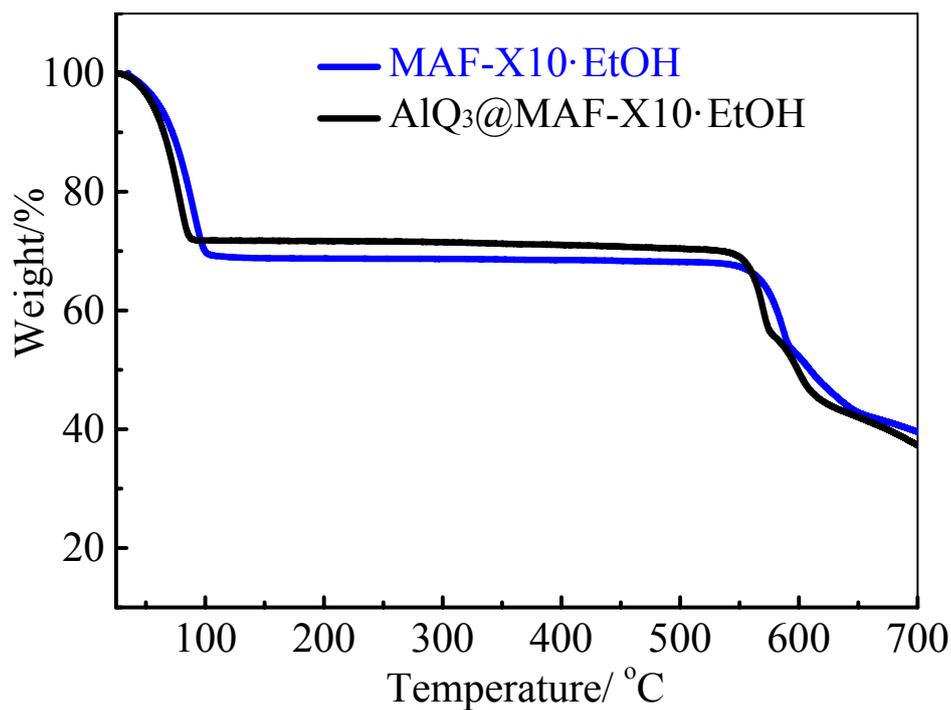


Figure S2. Thermogravimetry curves of $MAF-X10 \cdot EtOH$ and $\text{AlQ}_3@MAF-X10 \cdot EtOH$.

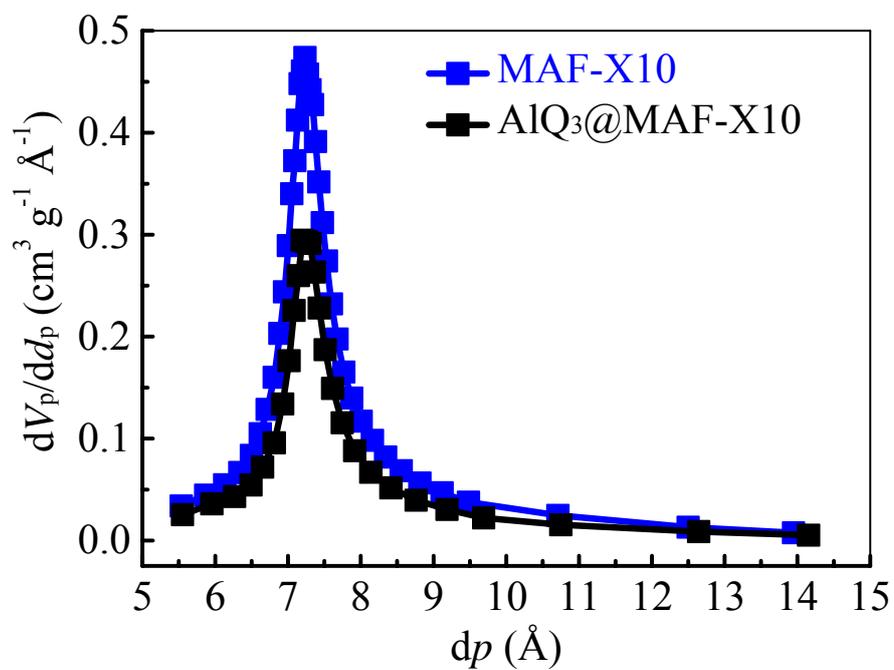


Figure S3. Pore size distribution (Horvath–Kawazoe model) of MAF-X10 and AlQ₃@MAF-X10 calculated from the N₂ adsorption isotherms.

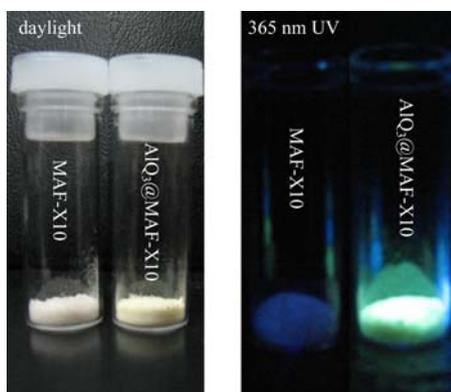


Figure S4. Photographs under daylight and 365 nm UV light for MAF-X10·EtOH and AlQ₃@MAF-X10·EtOH.

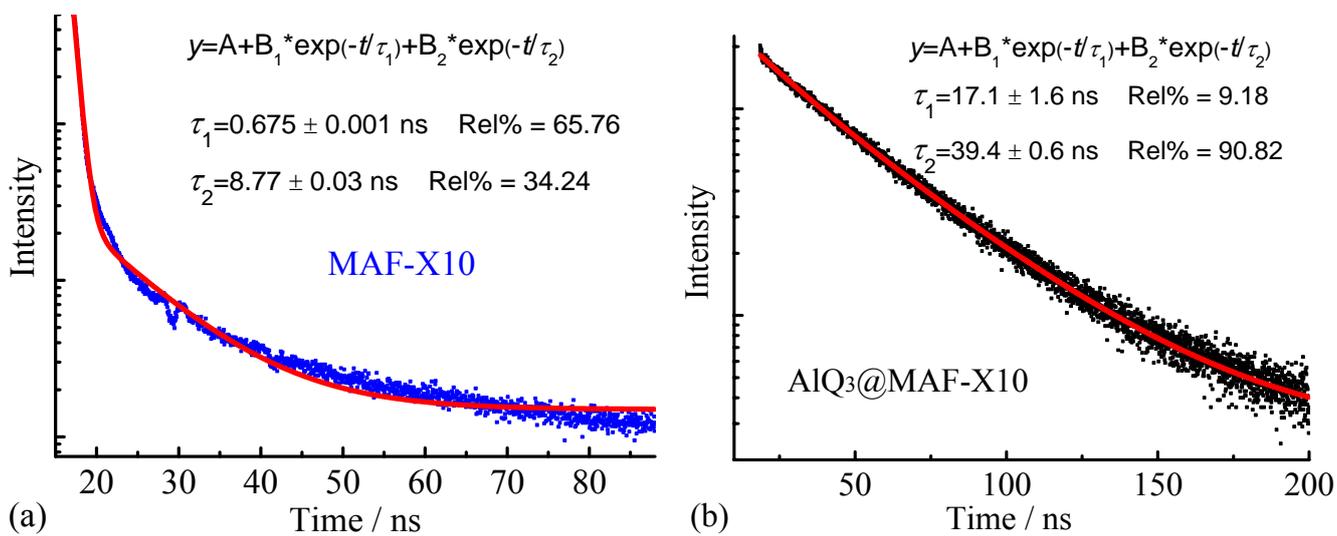


Figure S5. Luminescence decay profiles and reconvolution fitting.

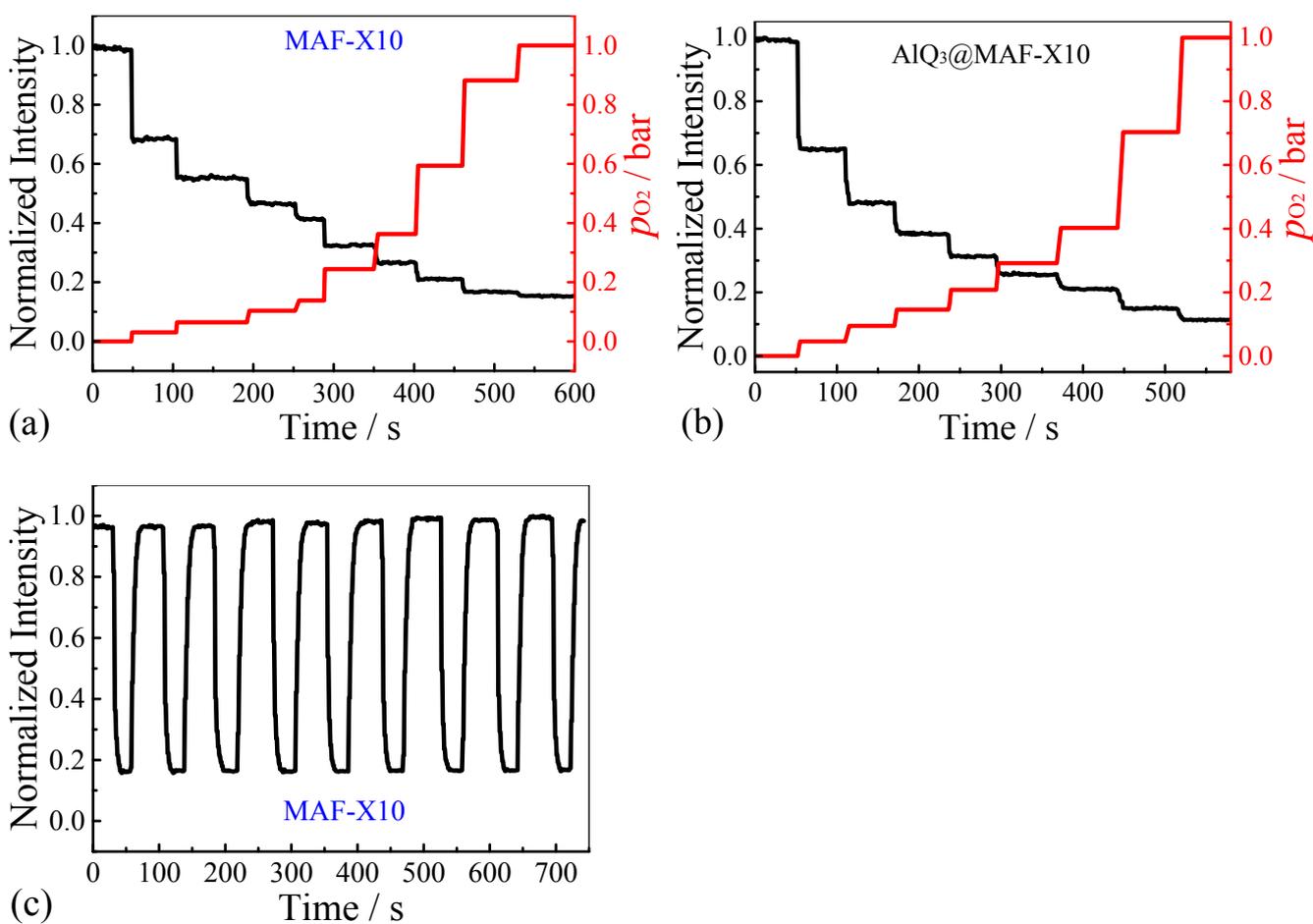


Figure S6. (a), (b) Changes in luminescence intensity from vacuum to 1.0 bar of O₂, and (c) reversible quenching/recovery of luminescence upon alternating exposure to O₂ and vacuum.

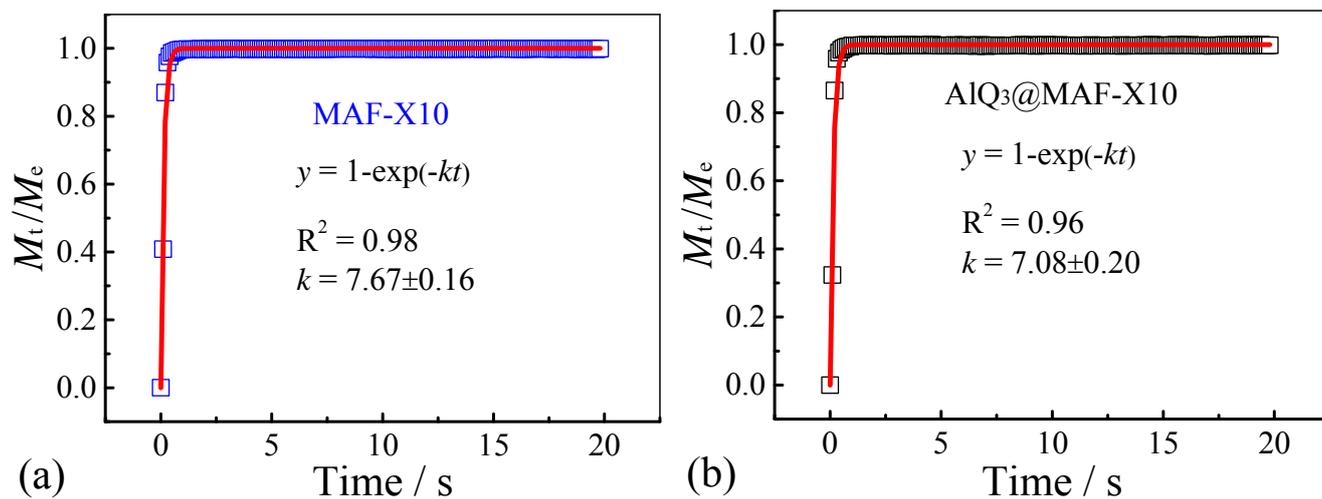


Figure S7. Exponential fitting of the kinetic profiles of O₂ adsorption at 298 K for (a) MAF-X10 and (b) AlQ₃@MAF-X10, respectively (lines represent the exponential fitting).

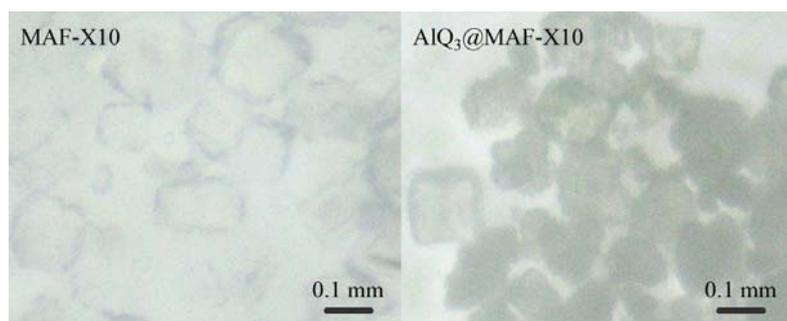


Figure S8. Optical images of MAF-X10 and AlQ₃@MAF-X10 (the average particles radii are estimated to be *ca.* 0.007 cm). The diffusion coefficient $D_{O_2} = k \cdot r_c^2 / 15 = 7.67 \text{ s}^{-1} \times (0.007 \text{ cm})^2 \div 15 = 2.5 \times 10^{-5} \text{ cm}^2/\text{s}$ for MAF-X10, while $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$ for AlQ₃@MAF-X10, respectively.