Electronic Supplementary Information

Facile and rapid synthesis of color-tunable molybdenum oxide quantum dots as a versatile probe for fluorescence imaging and environmental monitoring

Haiyan Cao, [*a#] Mingjie Tang, [b#] Xin Wang [c] and Wenbing Shi [a]

[a] *The Key Laboratory of Chongqing Inorganic Special Functional Materials; College of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, China.*

[b] *Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing 400714, China.*

[c] *College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China.*

*Corresponding authors. Tel./Fax: +86-23-72793565 (H. Cao).

[#] Contributed equally to this work.

E-mail addresses: *caohaiyan@yznu.edu.cn* (H. Cao)

Table S1. Photoelectron binding energies of Mo 3d level XPS spectra in different pH.

Sample	Ration of Mo^{6+} to Mo^{5+}	Mo $3d_{5/2}$		Mo $3d_{3/2}$	
		Centre (eV)	Area	Centre (eV)	Area
MoO_x (pH 9.0)	1.6588	232.6 (+6)	8923.8	235.7 (+6)	4923.8
		231.4 (+5)	4723.8	234.5 (+5)	3623.8
MoO_x (pH 5.0)	1.5134	232.6 (+6)	10814.3	235.7 (+6)	7087.2
		231.4 (+5)	7814.3	234.5 (+5)	4014.3
MoO_x (pH 2.0)	0.9149	232.6 (+6)	4965.1	235.7 (+6)	3204.8
		231.4 (+5)	5165.1	234.5 (+5)	3765.1

Table S2. Photoelectron binding energies of P 2p level XPS spectra in different pH.

Sample	P $2p_{3/2}$		P $2p_{1/2}$	
	Centre (eV)	Area	Centre (eV)	Area
MoO_x (pH 9.0)	129.3 (Mo-P)	108.8	131.5 (Mo-P)	67.8
	132.6 (oxygenated P)	73.8	133.7 (oxygenated P)	194.0
MoO_x (pH 5.0)	129.3 (Mo-P)	14.1	131.5 (Mo-P)	32.3
	132.6 (oxygenated P)	199.3	133.7 (oxygenated P)	418.3

Table S3. Fluorescence lifetimes obtained with two-exponential fit of the fluorescence decay curves of the N,P-MoO_x QDs in pH 9.0, 2.0, respectively.

Samples	**τ_1/ns**	**A_1**	**τ_2/ns**	**A_2**	**τ_3/ns**	**A_3**	**τ/ns**
N,P-MoO_x (pH 9.0)	0.1642	-166.0675	0.5092	386.7519	3.4454	91.5874	2.4382
N,P-MoO_x (pH 2.0)	0.7175	264.4625	4.2277	45.0684	/	/	2.4762

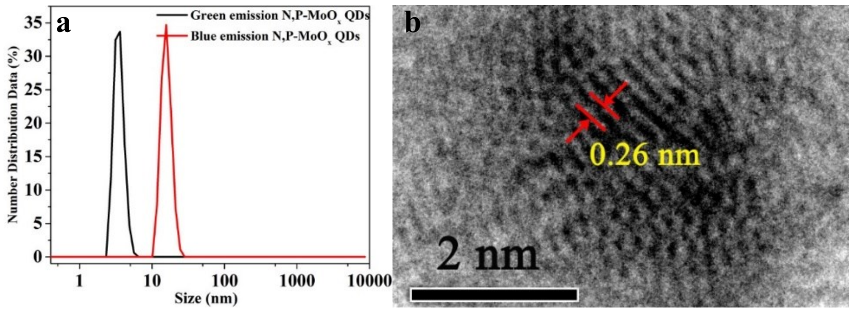

Fig. S1 (a) DLS spectra of green emission N,P-MoO_x QDs solution (black line) and blue emission N,P-MoO_x QDs; (b) HRTEM image of green emission N,P-MoO_x QDs.

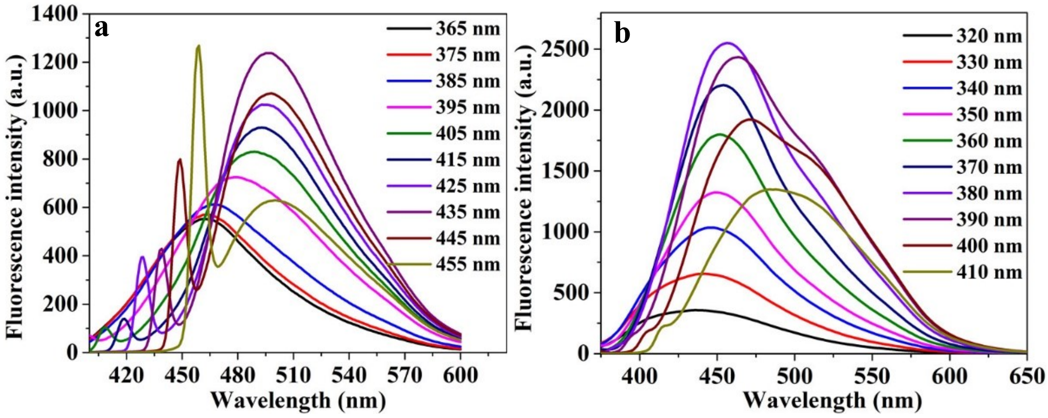

Fig. S2 (a) Emission spectra of green emission N,P-MoO_x QDs at excitation wavelengths from 365 to 455 nm; (b) Emission spectra of blue emission N,P-MoO_x QDs at excitation wavelengths from 320 to 410 nm.

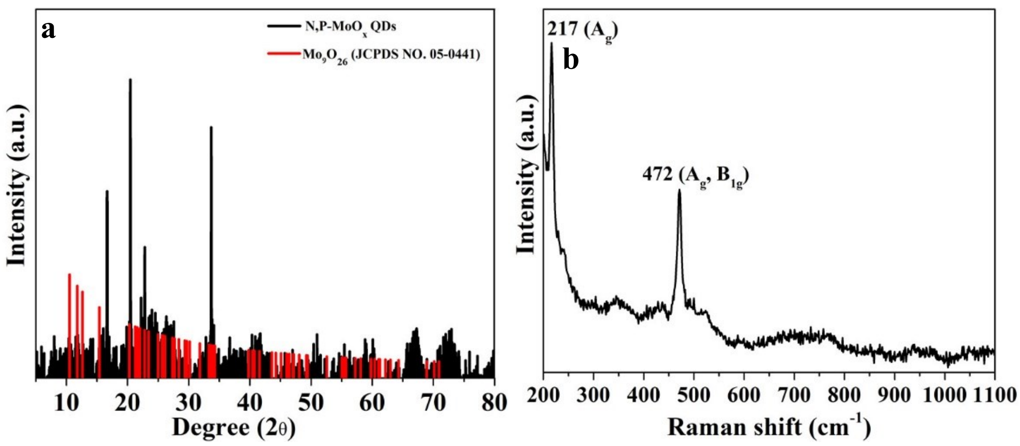

Fig. S3 (a) XRD patterns of N,P-MoO_x QDs. XRD patterns at the bottom show Mo_9O_{26} (JCPDS NO. 05-0441). (b) Raman spectrum of N,P-MoO_x QDs.

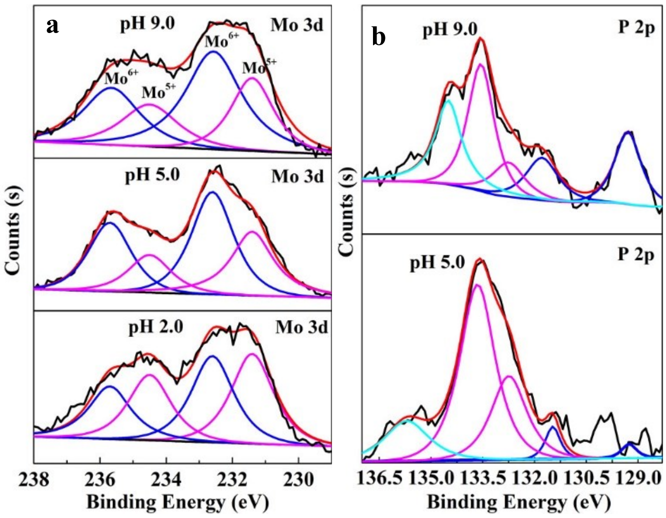

Fig. S4 XPS spectra in the Mo 3d (a) and P 2p (b) regions under different pH conditions.

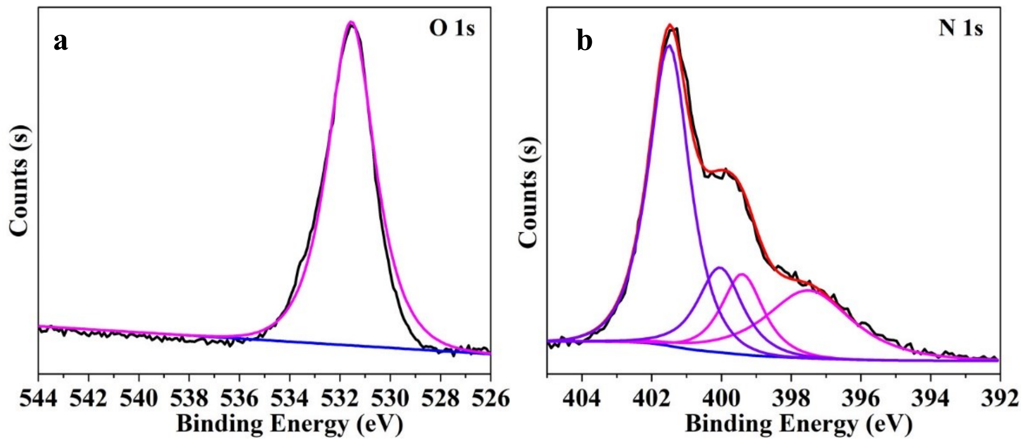

Fig. S5 XPS spectrum in the O 1s (a) and N 1s (b) region of N,P-MoO_x QDs.

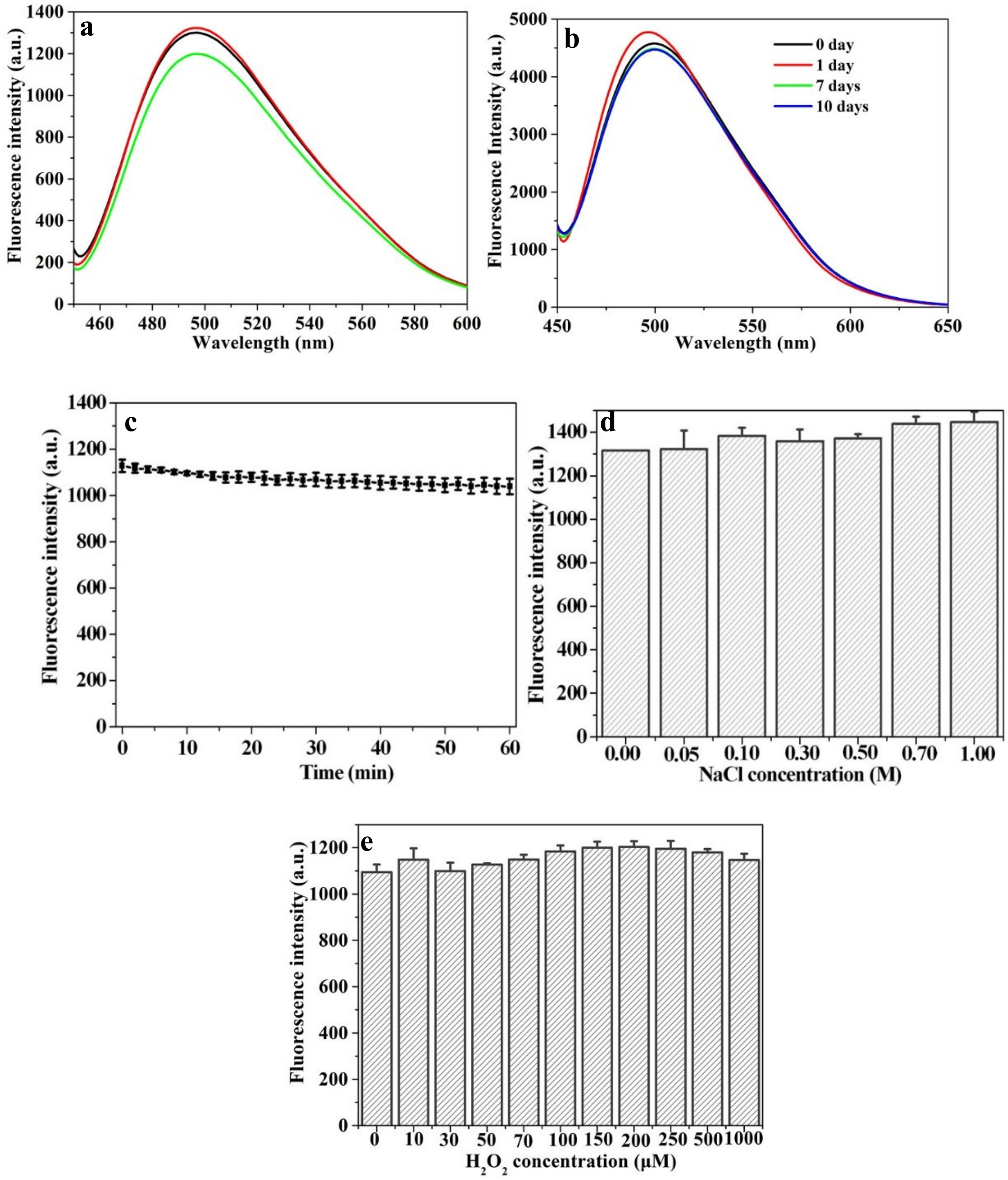

Fig. S6 The fluorescence spectra of N,P-MoO_x QDs (a) from different batches prepared in the same condition, (b) with different storage time (0-10 day), (c) with different illumination time (0-60 min), (d) with different concentrations of NaCl (0-1 M), (e) with different concentrations of H_2O_2 (0-1000 μM).

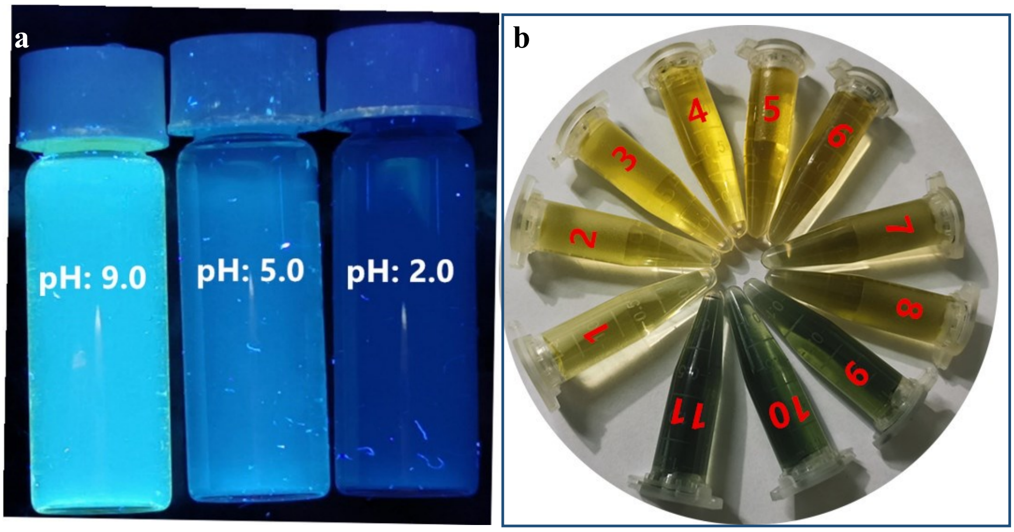

Fig. S7 (a) The color of N,P-MoO_x QDs solutions in different pH condition under the irradiation of 365 nm UV lamp; (b)The color of N,P-MoO_x QDs solutions in different pH condition: 1-pH 9.0; 2-pH 8.0; 3-pH 7.0; 4-pH 6.0; 5-pH 5.0; 6-pH 4.5; 7-pH 4.0; 8-pH 3.5; 9-pH 3.0; 10-pH 2.5; 11-pH 2.0.

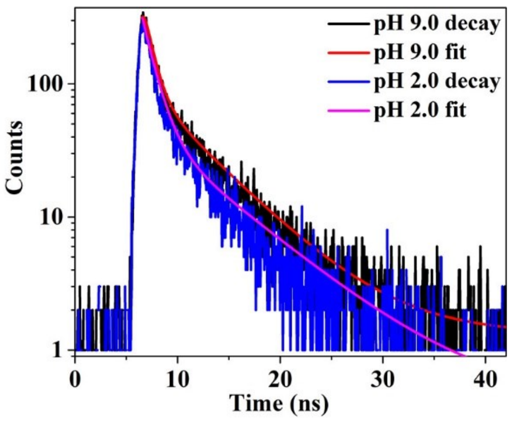

Fig. S8 Fluorescence lifetimes of N,P-MoO_x QDs in different pH condition.

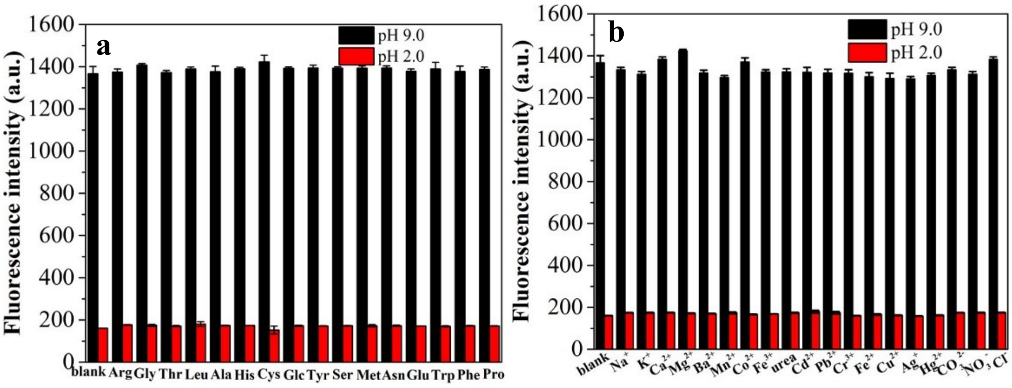

Fig. S9 Fluorescence intensity at 500 nm of the probe at pH 2.0 and 9.0 in the presence of (a) metal ions: 100 mM Na^{+} and K^{+} , 1 mM $Ca^{2+}$and Mn^{2+}, 0.5 mM Mg^{2+} , urea and Ba^{2+}, 0.25 mM Cr^{3+}, 0.1 mM Co^{2+} and Fe^{3+}, 0.05 mM Cd^{2+} and Fe^{2+}, 0.01 mM Cu^{2+}, 0.005 mM Pb^{2+}, Ag^{+} and Hg^{2+}, 100 mM NO_3^{-}, 50 mM CO_3^{2-}, 2 mM Cl^{-} ; (b) biomolecules: 1 mM Arg, Gly, Thr, Leu, Ala, His, Cys, Glc, Tyr, Ser, Met, Asn, Glu, Trp, Phe and Pro.

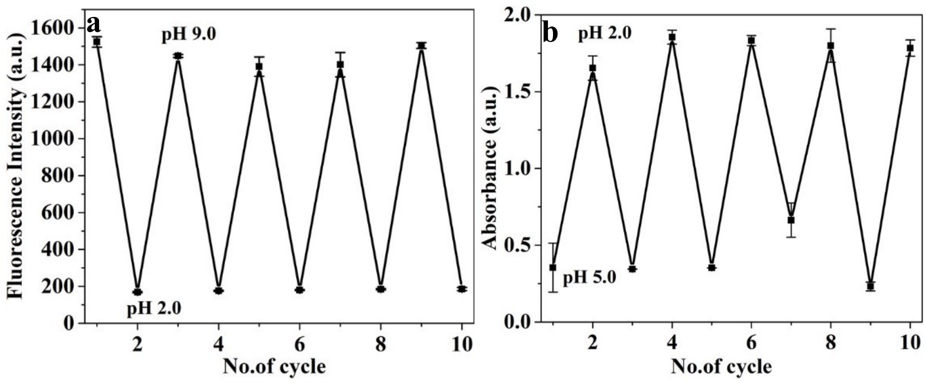

Fig.S10 Reversibility of N,P-MoO_x QDs in different pH values. (A) the fluorescence intensity of N,P-MoO_x QDs reversibly decreased and then increased by alternating the pH value of the system from pH 9.0 to 2.0 and then from 2.0 to 9.0. (B) the absorbance intensity of N,P-MoO_x QDs reversibly increased and then decreased by alternating the pH value of the system from pH 5.0 to 2.0 and then from 2.0 to 5.0.

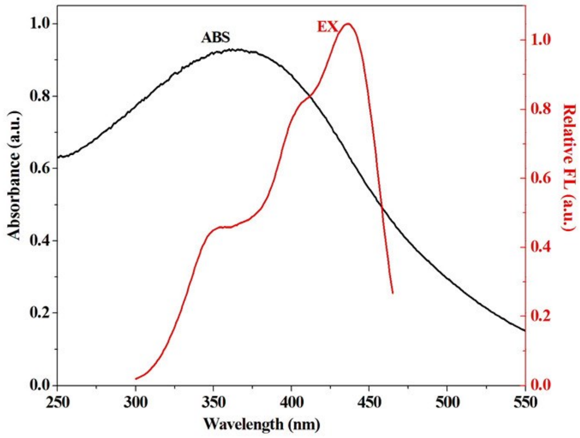

Fig. S11 The UV absorption spectrum of MnO_4^- and excitation spectum of N,P-MoO_x QDs.

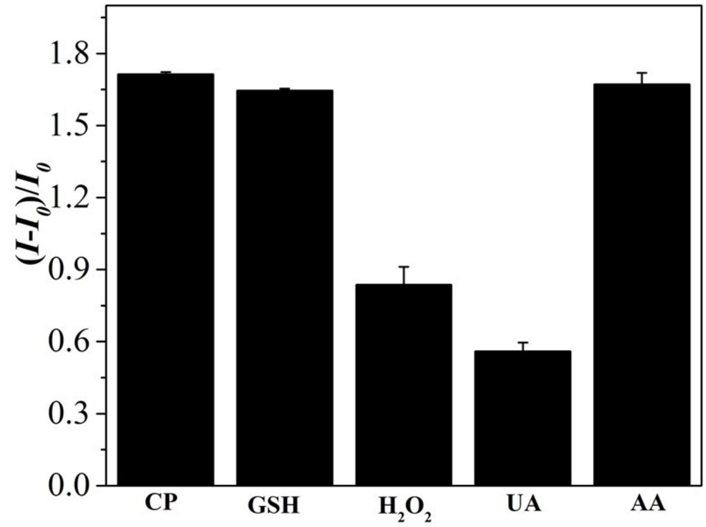

Fig. S12 The relative fluorescence intensities ([$(I\text{-}I_0)/I_0$]) at 510 nm of N,P-MoO_X QDs-MnO_4^- after the addition of 31 μM CP or 31 μM other reducing substances, including GSH, H_2O_2, UA and AA, respectively.

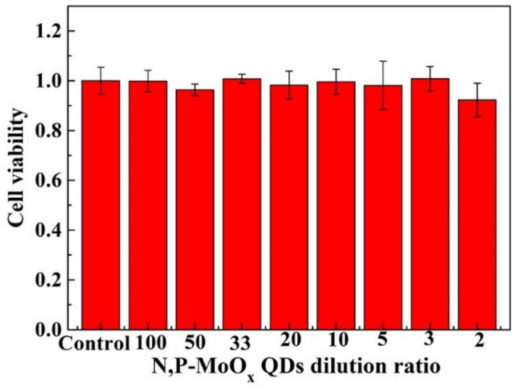

Fig. S13 The viability of HEB cell after being incubated with N,P-MoO_x QDs in the dilution ratio range from 2 to 100. The error bars represent standard deviations based on three independent measurements.