Supporting information

Facile synthesis of optically pH-sensitive molybdenum disulfide quantum dots

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Experimental section

Chemicals and materials: Bulk MoS_2 powder (<2 μm) and alkali metals Na, K were obtained from Aladdin. Bulk WS_2 (2 μm) and BN (98%) powder were purchased from Sigma-Aldrich (USA). 1,2-Dimethoxyethane was purchased from Sinopharm Chemical Reagent (Shanghai, China). Water was purified by Millipore system (18.2 MΩ •cm^{-1}).

Methods and Characterization: The preparation of TEM sample was conducted by drop-casting MoS_2, WS_2 and BN QDs suspension on the copper grid and then drying overnight at room temperature. TEM and HRTEM measurements were taken from a JEM-2100F high-resolution transmission electron microscope (Netherlands) which was operated at 200 kV. AFM measurements were collected on Veeco nanoscope in tapping mode. The MoS_2 QDs powder was dissolved in acetone in order to remove residual alkali metal species like sodium hydroxide/ potassium hydroxide. The acetone suspension was deposited on mica substrate by spin-coating. The XPS measurements were obtained on an ESCALAB-MKII 250 photoelectron spectrometer (VG Co.) using Al Kα radiation. The XRD was performed on D8 ADVANCE (Bruker) with Cu Kα X-ray radiation (λ= 0.15406 nm). Raman spectra were made on LabRAM HR Evolution (HORIBA Scientific). UV-vis absorption spectra were collected on Cary 50 Scan UV-visible spectrophotometer (Varian, USA). Fluorescence spectra were measured on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon Inc. France). The fluorescence decay profile was taken on a FLS920 spectrofluorometer (Edinburgh Instruments, UK) with EPL375 pulsed laser diode.

The concentration of MoS_2 QDs suspension was determined by ICP-OES. According to the ICP-OES result, the concentration of Mo and S was 1315 ppm and 905.6 ppm, respectively, which confirmed that the ratio of Mo:S was actual 1:2.06. In addition, the MoS_2 QDs yield (wt %) was calculated to be 2.24%.

Preparation of MoS_2 , WS_2 and BN QDs: Typically, 1.0625 g Na, 1.0213 g K and 200 mL 1,2-dimethoxyethane (DME) were bubbled with nitrogen for 10 min to remove dissolved oxygen, and then stirred for 7 h at room temperature until the color of the mixture turned blue. Bulk MoS_2 powder (1.2134 g) was added to the mixture, and then kept stirring for another 36 h to obtain a dark suspension. Afterwards, the dispersion was centrifuged at 8000 rpm to recycle DME. 150 mL water was carefully added to the sample dropwise to gain a homogeneous suspension, and was then vacuum filtered with mixed cellulose ester membrane (0.2 μm). The obtained pale yellow solution was put through dialysis to further purify. The procedures were applicable for single alkali metal Na or K. Intercalation and exfoliation process for WS_2 and BN was similar except that 1.5021 g of WS_2 was required for the same amount of reagent above. **Caution**: The reaction between alkali metal and water is violent which may cause fire or even explosion if not carefully operated. Therefore, the experiment must be conducted away from water, and in last step, water must be slowly added dropwise to intercalated sample to avoid fire.

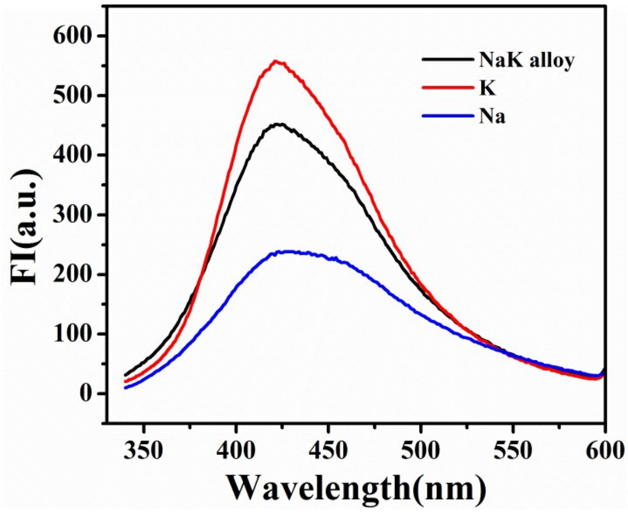

Figure S1. The fluorescence spectra of MoS_2 exfoliated by Na, K and NaK alloy.

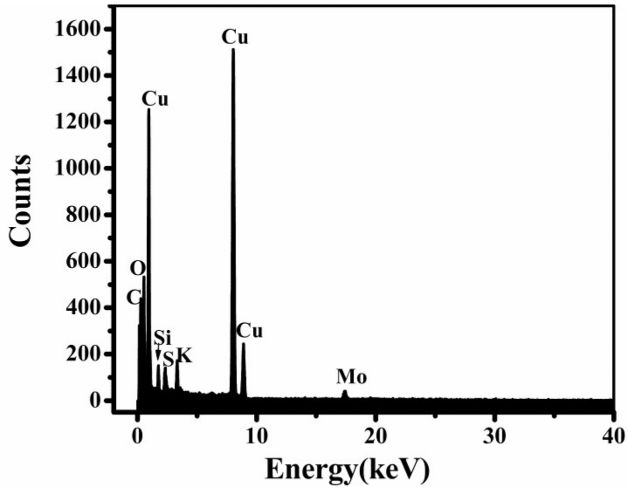

Figure S2. TEM-EDX pattern of MoS_2 QDs, showing the presence of Mo and S, including elements of Cu, Si, partial C and O, which is rooted in the support grid[1] and residual element K.

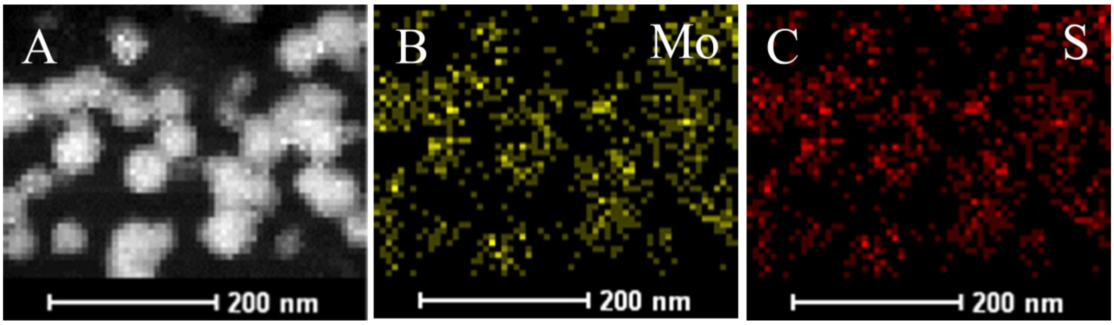

Figure S3. (A) STEM of obtained MoS_2 QDs and corresponding elemental mapping of (B) Mo and (C) S.

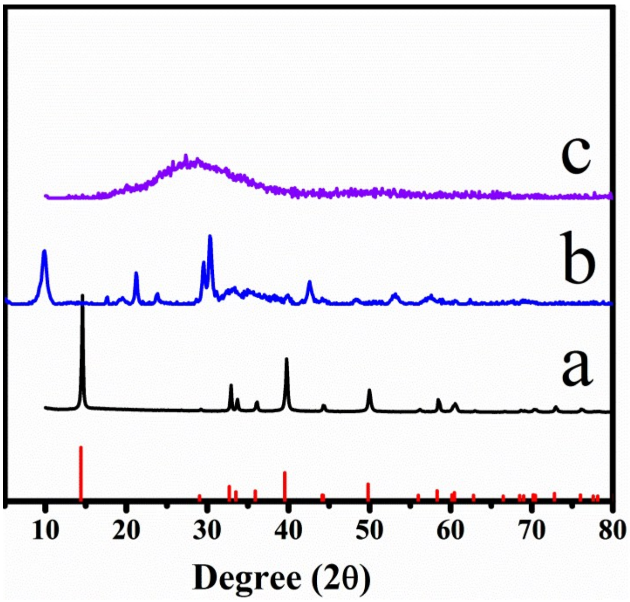

Figure S4. XRD patterns of a) bulk MoS_2 powder, b) intermediate product (Na, K)$_x$$MoS_2$ after intercalation, and c) MoS_2 QDs.

It can be easily observed from Figure S4-a that the bulk powder was identified as 2H phase with an conspicuous peak at 14.4°, which is distributed to the (002) face (JCPDF 65-1951). Upon Na/K intercalation, the (002) peak shifted drastically to 9.83° (Figure S4-b), indicating the alkali metals were indeed inserted into the layer of bulk powder, thus resulting in the enlargement of layer spacing.

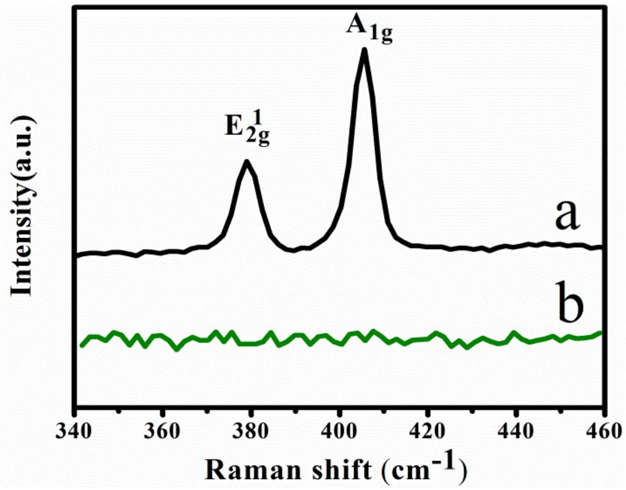

Figure S5. Raman spectra of a) bulk MoS_2 powder and b) MoS_2 QDs.

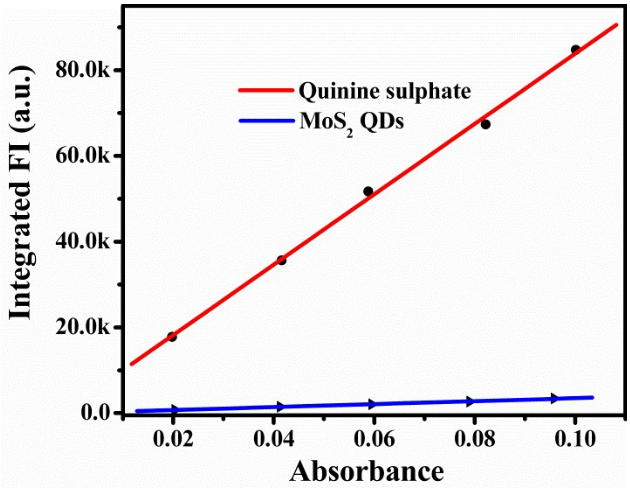

Figure S6. Linear plots for quinine sulphate and MoS_2 QDs.

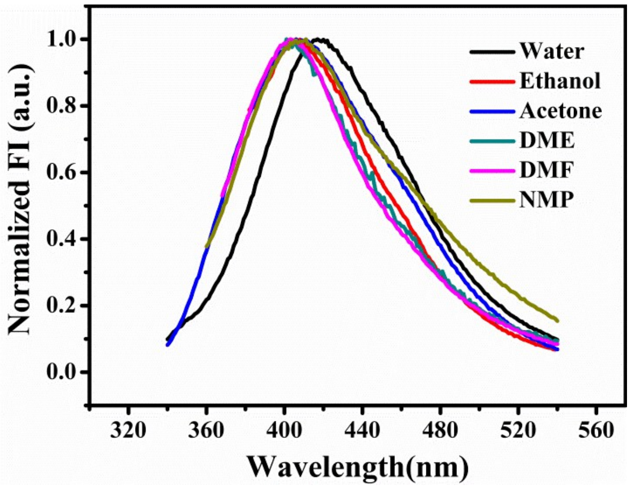

Figure S7. Normalized fluorescence intensity of MoS_2 QDs in various solvents.

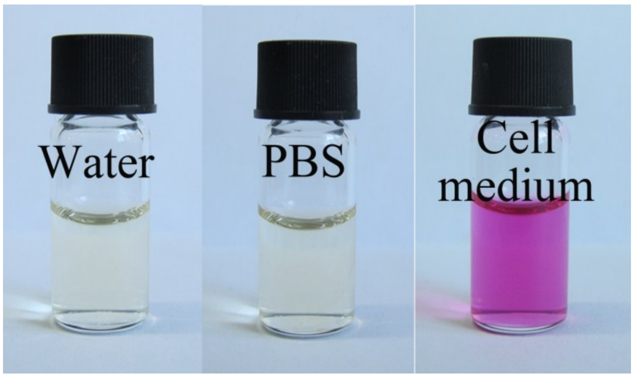

Figure S8. Photographs of MoS_2 QDs dissolved in water, phosphate buffered saline (PBS) and cell culture medium (DMEM), respectively.

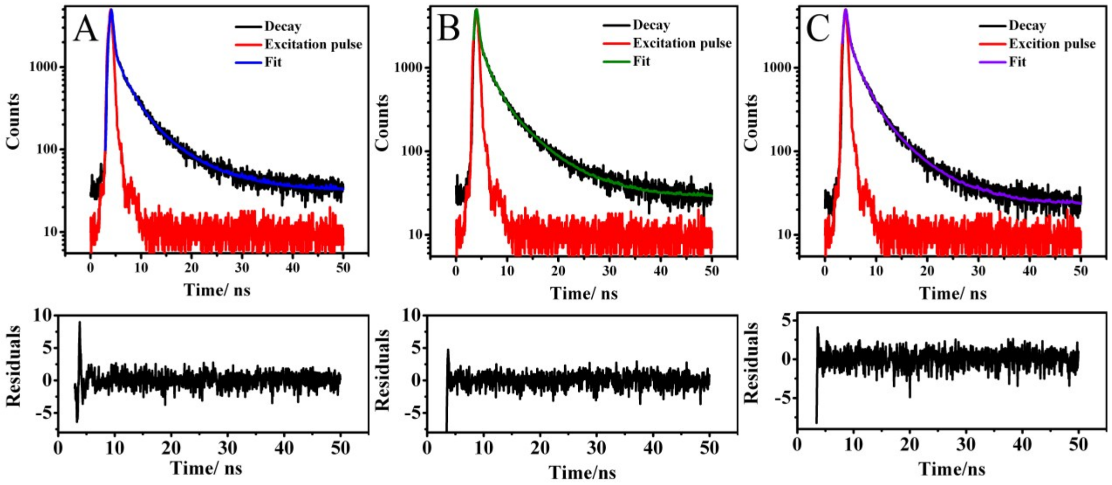

Figure S9. Fluorescence decay profiles of MoS_2 QDs at different pH values. A: pH=11.44, B: pH=7.32, C: pH=5.33.

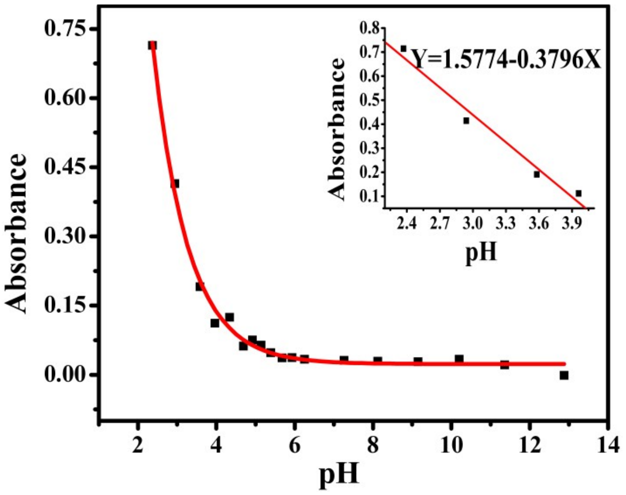

Figure S10. The plot of absorbance at 680 nm versus pH values. The inset shows linear relationship between absorbance at 680 nm and pH values from 2.37 to 3.96.

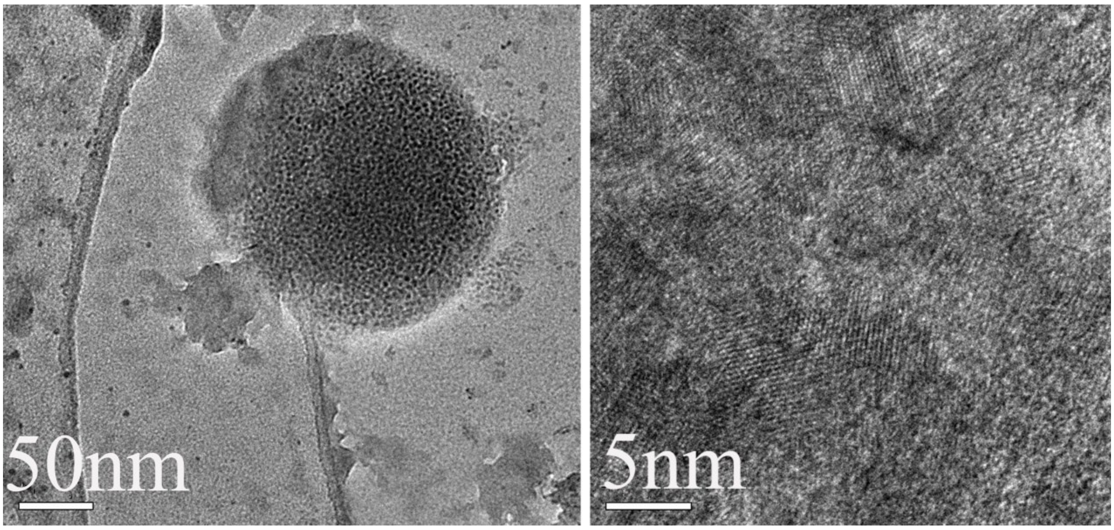

Figure S11. TEM and HRTEM images of MoS_2 QDs aggregates in acidic condition (pH~3).

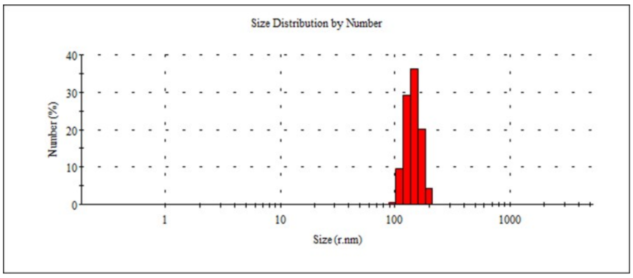

Figure S12. DLS spectra of MoS_2 QDs aggregates in acidic condition.

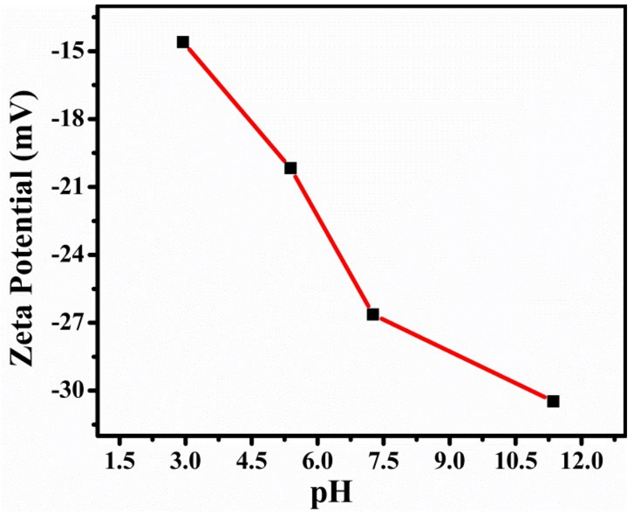

Figure S13. Representative Zeta potential of MoS_2 QDs at various pH values.

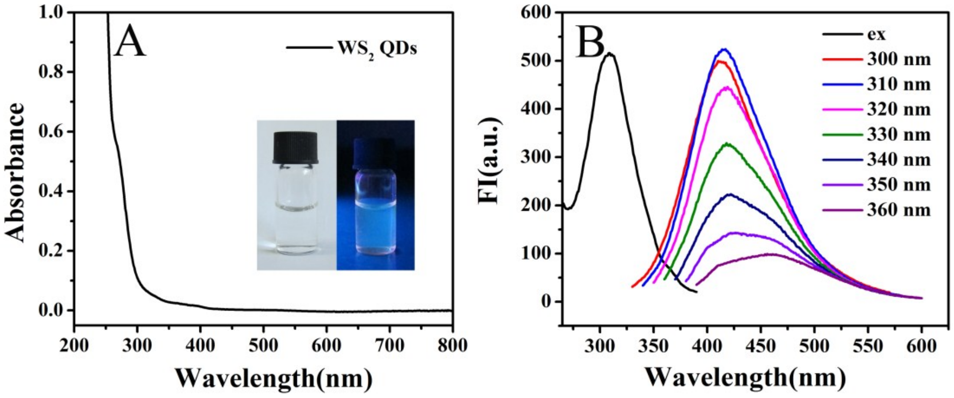

Figure S14. (A) UV-vis absorption spectra of the WS_2 QDs solution. The inset showed the photographs of corresponding WS_2 QDs solution under room (left) and 365 nm irradiation light (right). (B) Fluorescence excitation and emission spectra of WS_2 QDs with progressively increasing excitation wavelengths from 300 to 360 nm.

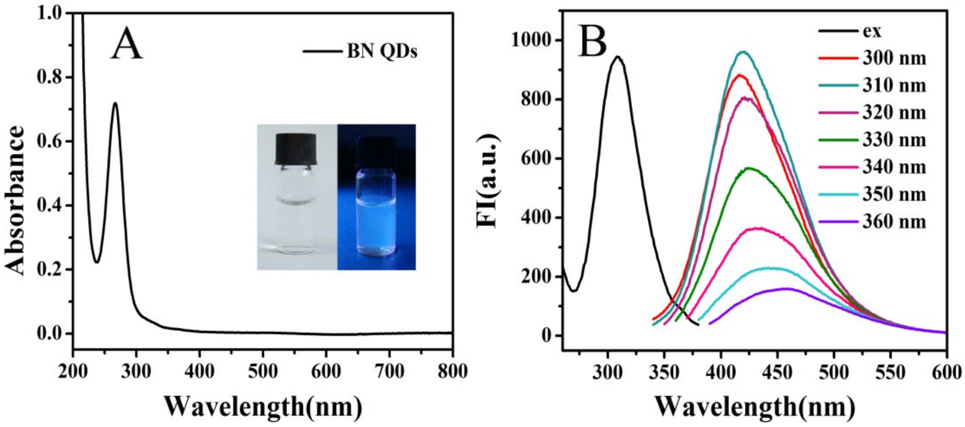

Figure S15. (A) UV-vis absorption spectra of the BN QDs solution. The inset showed the photographs of corresponding BN QDs solution under room (left) and 365 nm irradiation light (right). (B) Fluorescence excitation and emission spectra of BN QDs with progressively increasing excitation wavelengths from 300 to 360 nm.

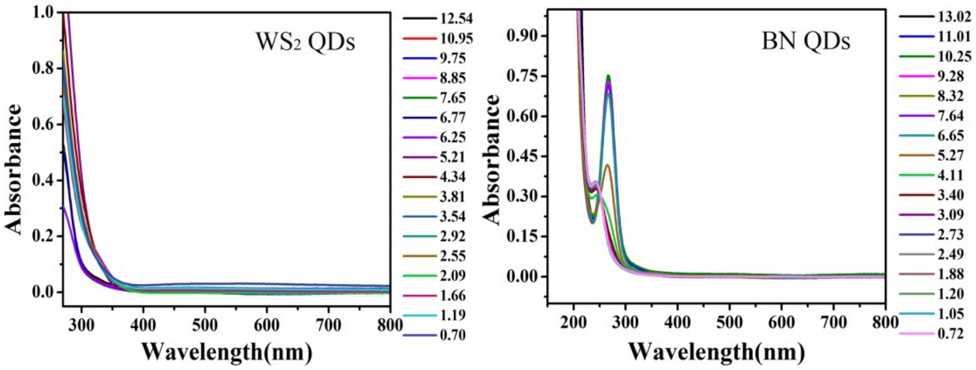

Figure S16. UV-vis absorption spectra of as-prepared WS_2 and BN QDs at different pH values.

Table S1. Element ratio obtained by XPS.

	Mo3d	S2p
Peak/eV	232.35	167.97
FWHM/eV	1.93	1.4
Area (P) CPS.eV	2592.78	1919.43
At. %	27.3	67. 8

Table S2.The fluorescence quantum yield of MoS_2 QDs.

Sample	K	η	ϕ
MoS_2 QDs	34787.36	1.33	0.023[a]
Quinine sulphate	832743.87	1.33	0.546(known)

a: $\phi_x = \phi_s \left(\frac{K_x}{K_s}\right)\left(\frac{\eta_x}{\eta_s}\right)^2$,where ϕ is the fluorescence quantum yield, K is the gradient from the plot of integrated fluorescence intensity versus absorbance, which is obtained from Figure S6, and η is the refractive index of the solvent.

Table S3. Fluorescence lifetime of MoS_2 QDs at different pH values.

pH	11.44	7.32	5.33
τ_1	0.02 ns	0.11 ns	0.15 ns
τ_2	2.49 ns	2.01 ns	2.10 ns
τ_3	7.57 ns	6.77 ns	6.54 ns
A_1 [a]	33.68%	34.18%	33.33%
A_2	31.49%	30.07%	37.48%
A_3	34.83%	35.75%	29.18%
τ_{ave} [b]	3.43 ns	3.06 ns	2.75 ns

a: $A_i = \alpha_i\tau_i / \sum \alpha_j\tau_j$, α_i and τ_i represent the amplitudes and decay time of the component at t=0, respectively. b: $\tau_{ave} = \sum A_i\tau_i$

1. H. Huang, C. Du, H. Shi, X. Feng, J. Li, Y. Tan and W. Song, *Part. Part. Syst. Charact.*, 2015, **32**, 72-79.