Supporting Information

Acid-base responsive photoluminescence switching of CdSe/ZnS quantum dots coupled to plasmonic gold film using nanometer-thick poly[(2-diethylamino)ethyl methacrylate] layer

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Contents

1   Instrumentation

^{1}H NMR and spectra were obtained by a Bruker AC 300 MHz. Chemical shifts (δ) are expressed in parts per million relative to the solvent residual signal. ^{19}F NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer with a BBFO sample head and a $60 \times$ BACS automatic sample changer in CD_2Cl_2.

Size exclusion chromatography (SEC) was measured on an Agilent 1200 series system equipped with a PSS degasser, a G1310A pump, a G1362A refractive index detector and a PSS GRAM guard/30/10Å column running with DMAc (+ 0.21 wt% LiCl) as an eluent. The Techlab oven was set to 50 °C and the molar masses were calculated using (for Mowiols) and poly(methylmethacrylate) (PMMA) (for Pluronics and Tweens) calibration standards.

Spin coating of the synthesized copolymers was performed on a gold surface (RPM: 3000, 80 seconds and accelerating rate: 1000).

UV photo-crosslinking reactions of spin-coated films were performed through exposing the samples in an UV cube 100 equipped with a 100 W iron bulb (Dr. Hönle UV Technology, Germany) for 1.5 h. This UV source provides a significant broadband radiation spectrum in the UVA range, with a main peak at 360 nm.

Film thickness measurements was carried out using Atomic force microscopy (AFM) (NT-MDT, NTegra Aura) with commercial AFM tips (NT-MDT, NCS35/AIBS) in tapping mode. To this aim, first, the solution of the copolymer (**P1**) and terpolymer (**P2**) with specific concentrations (5, 10 and 15 mg/mL of **P1** and 5 mg/mL of **P2**) were prepared. Then each polymer solution was spin-coated onto a separate gold plate and the plates was placed into a thermal oven at 80 °C for 1 h to evaporate the residual solvent and to enhance the film homogeneity. Subsequently three scratches were made on each gold plate and AFM images of five different areas of the three scratches were recorded. Afterwards, the polymer film was washed away from the gold plate in hot ethanol and acetone and again the AFM images of the same areas before washing the film was recorded. Therefore, for each sample before and after washing of the polymer, five images were taken and in each images the scratch depth of 3 different areas were calculated and the average of them was obtained. Then, the thickness was calculated through subtracting the average depth of each image before and after washing. In total, we calculated 5 average thickness in each sample and the final thickness was reported as the average of 5 average thicknesses.

Photoluminescence (PL) microscopy and spectroscopy measurements were performed using a commercially available confocal laser-scanning microscope setup (PicoQuant, MicroTime200). For excitation, laser pulses (532 nm, repetition rate of 80 MHz, pulse lengths of 100 ps) were focused on the sample using a UPLSAPO60x/1.2 W objective the average laser power in front of the objective was approximately 5 µW. To measure the QDs' PL intensity at each pH value, 10 area of 80 µM×µM on the sample was scanned and the final results were obtained by averaging the respective 10 PL images. First a few drops of deionized water were added on top of the objective and the sample was scanned in aqueous environment. Afterwards, the sample was soaked in 25 mL solution at pH 5 for 15 min and meanwhile the objective was dried and some droplet of solution at pH 5 was poured on the objective and ten images were taken. After finishing the measurement, sample was taken out of the microscope, rinsed with distilled water and was soaked in 25 mL solution at pH 11. The objective was cleaned with distilled water and some droplet of the solution at pH 11 was poured onto the objective and again ten images were recorded. This procedure was continued to complete three cycles of pH variation. The measurement for the one by one increase of the pH value was performed in the same way, however, the immersion time of the samples was reduced to 3 minutes, as we could recognize PL changes in that time. Also, to accelerate the measurement, seven area of the sample (80 µM × 80µM) was scanned.

2   Synthesis and characterization

The following commercial reagents were used as received by the supplier: 4-((10-Mercaptodecyl)oxy)benzophenone (**BSH**) and methacryloyl benzophenone (**MAB**) monomer was used from our previous synthesis.[1] Pentafluorophenyl methacrylate (PFPMA), cysteamine, azobisisobutyronitrile (AIBN), 1,4-dioxane ($C_4H_8O_2$), deuterated dichloromethane (CD_2Cl_2) acetic acid (CH_3COOH) and sodium hydroxide (NaOH) (to prepare acidic and basic solutions). 2-(diethylamino)ethyl methacrylate monomer (DEAEMA) (Sigma-Aldrich) was stirred under the presence of an inhibitor remover resin (Sigma-Aldrich) for 30 min to eliminate inhibitor / stabilizing agents (i.e., hydroquinone or 4-*tert*-butylcatechol). Organic soluble CdSe/ZnS QDs (Qdot 800 ITK) was purchased from Invitrogen and used as received.

2.1   Preparation of poly[(2-diethylamino)ethyl methacrylate-*co*-methacryloyl benzophenone] p(DEAEMA-*co*-MAB$_{0.5}$)

p(DEAEMA-*co*-MAB$_{0.5}$) were synthesized through free radical polymerization as following: A 10 mL Schlenk tube was charged with DEAEMA (1.5 g, 8.1 mmol) which was already purified from inhibitor, methacryloyl benzophenone (10.7 mg, 0.040 mmol), AIBN (13.3 mg, 0.081 mmol) and dioxane (10 mL). The mixture was degassed by three times freeze-thaw cycles and was subsequently heated to 75 °C in an oil bath for four hours. The conversion was confirmed by ^{1}H NMR analysis (typically up to 90%) and the reaction was stopped and purified by dialysis in methanol for two days; M_n: 30,700 g/mol and Đ: 1.63 (PMMA calibration). The ^{1}H NMR spectrum of p(DEAEMA-*co*-MAB$_{0.5\%}$) was illustrated in **Figure. 1** (bottom)**.**

^{1}H NMR (CD2Cl2, 300 MHz) δ/ppm= 7.12-7.96 (Ar), 3.99 (CH2-C-O), 2.47-2.8 (CH$_2$-N), 1.64-2.16 (CH$_2$-C), 1.05(CH$_3$-CH$_2$-N), 0.91(CH$_3$-C). The MAB values in the copolymer were calculated from the proton signal areas: $(3.37/9)/(3.37/9 + 100/2) \times 100 = 0.74\%$

2.2   Preparation of poly[(2-diethylamino)ethylmethacrylate-*co*-methacryloyl benzophenone-*co*-pentafluorophenylmethacrylate] p(DEAEMA$_{80}$-*co*-PFPMA$_{20}$-*co*-MAB$_{0.5}$)

p(DEAEMA$_{80}$-*co*-PFPMA$_{20}$-*co*-MAB$_{0.5}$) were synthesized through free radical polymerization as following: A 10 mL Schlenk tube was charged with DEAEMA (2 g, 10.8 mmol) which was already purified from inhibitor, pentafluorophenylmethacrylate (0.54 g, 2.15 mmol), methacryloyl benzophenone (17.2 mg, 0.064 mmol), AIBN (21.3 mg, 0.13 mmol) and dioxane (10 mL). The mixture was degassed by three times freeze-thaw cycles and then was heated to 75 °C in an oil bath for four hours. The conversion was confirmed by ^{1}H NMR analysis (about 90%) and the reaction was stopped and purified by dialysis in methanol for two days; Mn: 25,300 g/mol and Đ: 1.76 (PMMA calibration). The ^{1}H NMR spectrum of p(DEAEMA$_{80}$-*co*-PFPMA$_{20}$-*co*-MAB$_{0.5}$) was illustrated in **Figure. 1** (top) which shows the successful incorporation of DEAEMA and MAB. Also, ^{19}F NMR spectroscopy revealed the pentafluorophenylmethacrylate moieties in the terpolymer.

^{1}H NMR (CD_2Cl_2, 300 MHz) δ/ppm= 7.12-7.96 (Ar), 3.99 (CH2-C-O), 2.47-2.8 (CH$_2$-N), 1.64-2.16 (CH$_2$-C), 1.05(CH$_3$-CH$_2$-N), 0.91(CH$_3$-C). The MAB/DEAEMA values in the copolymer were calculated from the proton signal areas: $(3.17/9)/ (100/2) \times 100 = 0.70\%$, which is in good agreement with pDEAEMA/MAB feed ratio (0.6).

FigureS1: ^{19}F NMR (CD_2Cl_2, 400 MHz,) δ/ppm: –163.2 (2F, meta), –158.9 (1F, para), –149.67 and 151.80 (2F, ortho).
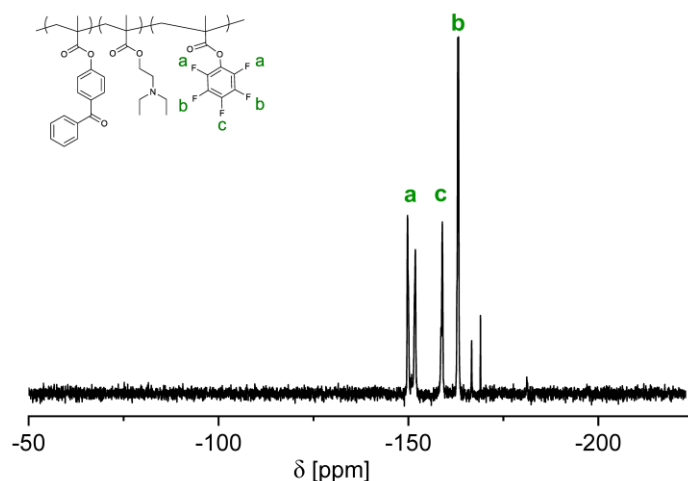
Figure S1. ^{19}F NMR spectrum (CD$_2$Cl$_2$, 400 MHz) of p(DEAEMA$_{80}$-*co*-PFPMA$_{20}$-*co*-MAB$_{0.5}$).

3   Sample fabrication method

Hybrid gold/pH-responsive film/QDs samples were prepared by the following steps: First, gold plates films (220 nm gold film prepared by thermal deposition) were pretreated through soaking in hot acetone for 30 min followed by oxygen plasma etching for 7 min. Then, the gold plates were immersed in a 0.01 M solution of BSH in ethanol for two days. Afterwards, the substrates were soaked in pure ethanol and stirred for 1 hour and rinsed several times to remove non-absorbed or physically absorbed BSH groups. Afterwards, the BSH-functionalized gold plates were spin-coated with p(DEAEMA-*co*-MAB$_{0.5\%}$) solutions with different concentrations (5, 10, 15 mg/mL in ethanol) using a spin coating rate of 3000 rpm for 80 seconds and then the plates were placed in oven at 80 °C for 1 h to evaporate the residual solvent and to enhance the film homogeneity. Afterwards, the films were exposed to UV irradiation for 1.5 h for the crosslinking reaction. Subsequently, the substrates were rinsed by ethanol to wash off any non-crosslinked polymers. The top layer was prepared *via* spin coating of p(DEAEMA$_{80\%}$-*co*-PFPMA$_{20\%}$-*co*-MAB$_{0.5\%}$) solution (5 mg/mL in toluene) on the primary layer using the same spin coating parameters (3000 rpm, 80 s) and curing condition (1 h in oven at 80 °C and UV irradiation for 1.5 h). Then, the samples were immersed in a cysteamine solution (0.06 M in toluene). The substitution reaction of fluorophenyl groups of the top layer with cysteamine was continued for 4 h at 52 °C. Subsequently, the samples were removed from the reaction solution and were rinsed several times with ethanol and toluene followed by soaking in 15 nM solution of CdSe/ZnS QDs in toluene for one day. Eventually, the samples were washed with toluene to remove non-attached QDs.

4   Acid-base PL switching behavior in samples containing a non-pH responsive top layer

The samples were prepared as explained in section 3, the only difference was spin coating of p(PFPMA$_{99.5}$-*co*-MAB$_{0.5}$) (5 mg/mL in toluene) as top layer. The results of QDs' PL switching in acidic and basic media was displayed in **Figure S2**. In general, pH-triggered PL switching trend could be detected in some samples, however it was not reproducible and the results showed large discrepancies and deviations. It can arise from PFPMA residual after substitution acting as a barrier against water and hydronium. As the substitution takes place randomly, in some of the samples there is some paths for the molecules diffusion and PL changes could be observed while in some other samples there was not such potential paths for pH-responsive film swelling and PL changes could not happen.
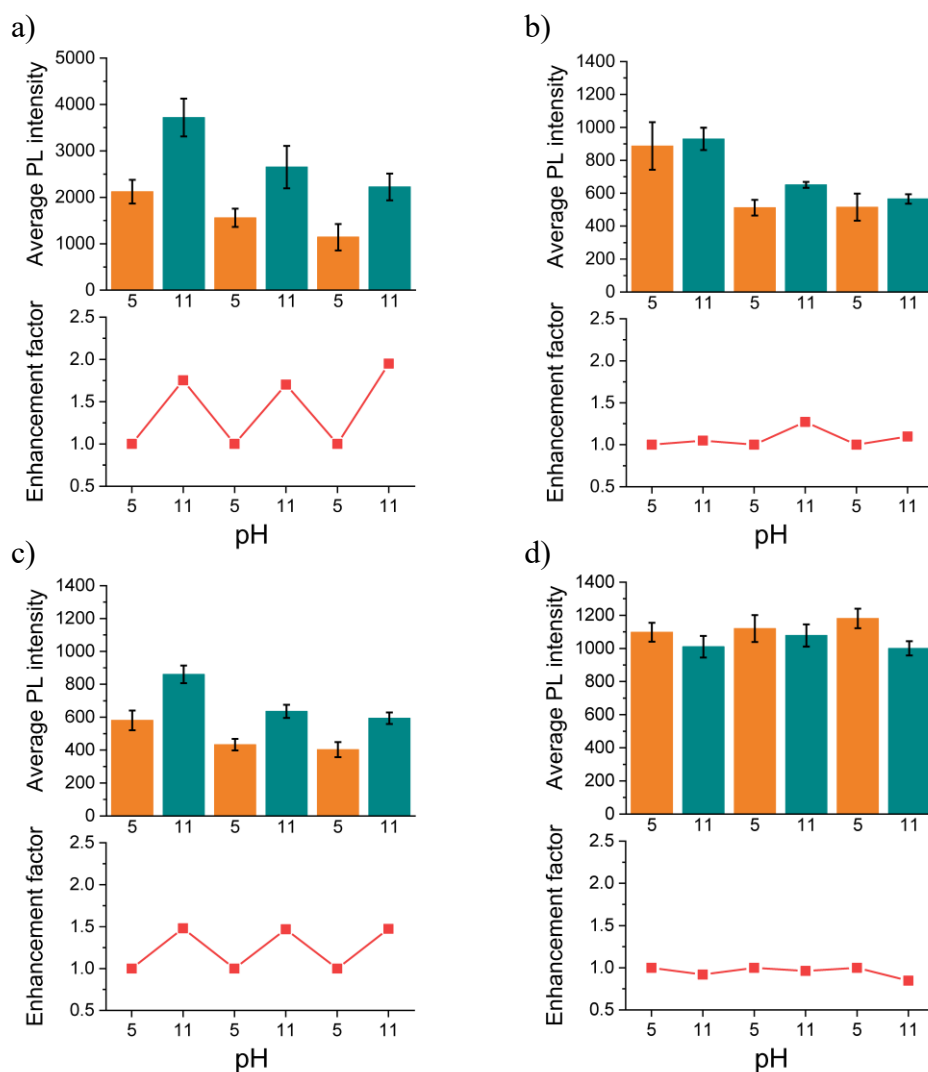
Figure S2. *a, b c and d) display reproducibility results of acid-base responsive PL switching behavior and the enhancement factor of samples containing gold/p(DEAEMA-co-MAB$_{0.5}$) (10mg/mL) as first layer and p(PFPMA$_{99.5}$-co-MAB$_{0.5}$) (5mg/mL) as top layer/QDs upon immersion of samples in solutions with pH 5 and 11, measured by confocal scanning microscopy.*

5 Film thickness measurements by AFM

Figure **Figure S3** demonstrates AFM images and height profile of the scratch on gold plate in two steps; **Figure S3a and c**, the scratch with polymer film on the gold plate and **Figure S3b and d**, the scratch after washing the polymer film from gold plate. The represented figures are related to sample B and the same calculations were applied for the film thickness estimation of sample A and C and also the top layer. In general, we did the AFM analysis for 4 samples including sample 5, 10, 15 mg/mL of P1 and one sample of 5mg/mL of **P2.** Then we added P2 thickness value to **P1** of watch sample to estimate the whole double layer thickness**.** The summary of the obtained thicknesses presented in **Table S1**. Please note that the depth was measured independently and that the values were estimated.
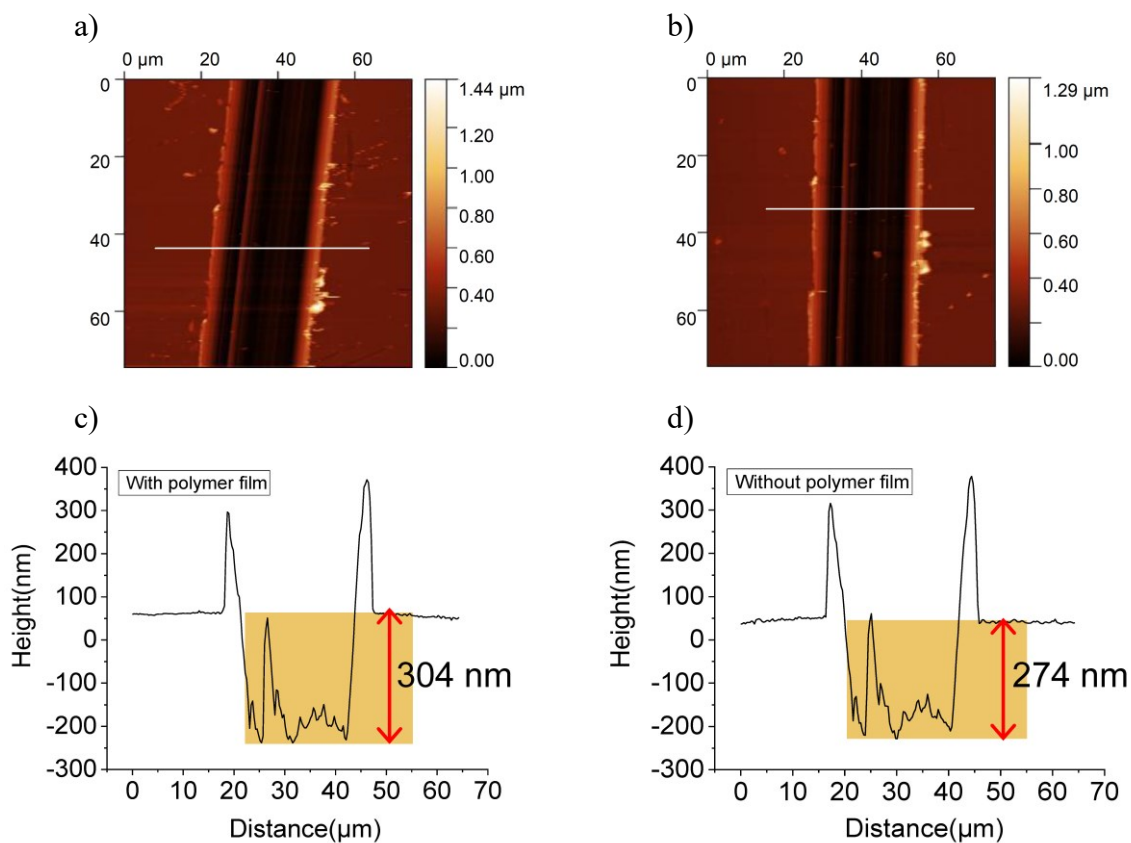
Figure S3. *AFM images and height profile of scratched gold plate with 10 mg/mL non-UV crosslinked **P1** layer on the gold plate (a and c), and after washing the **P1** layer from the same plate (b and d). Note that the height profiles include also the scratching of the gold film to the bottom support and thus exceed the numbers in Table S1.*

Table S1. *Thicknesses of **P1** and **P2** layer of samples A, B and C measured by AFM.*

Samples	**P1**[*] layer thickness (nm)	**P2**[*] layer thickness (nm)	Total layer thickness (nm)
A	24 ± 3	15 ± 2	39
B	31 ± 4	15 ± 2	46
C	59 ± 6	15 ± 2	74

[*]**P1**: p(DEAEMA-*co*-MAB$_{0.5}$) and **P2**: p(DEAEMA$_{80}$-*co*-PFPMA$_{20}$-*co*-MAB$_{0.5}$)

6   Reproducibility investigation of acid-base responsive PL switching
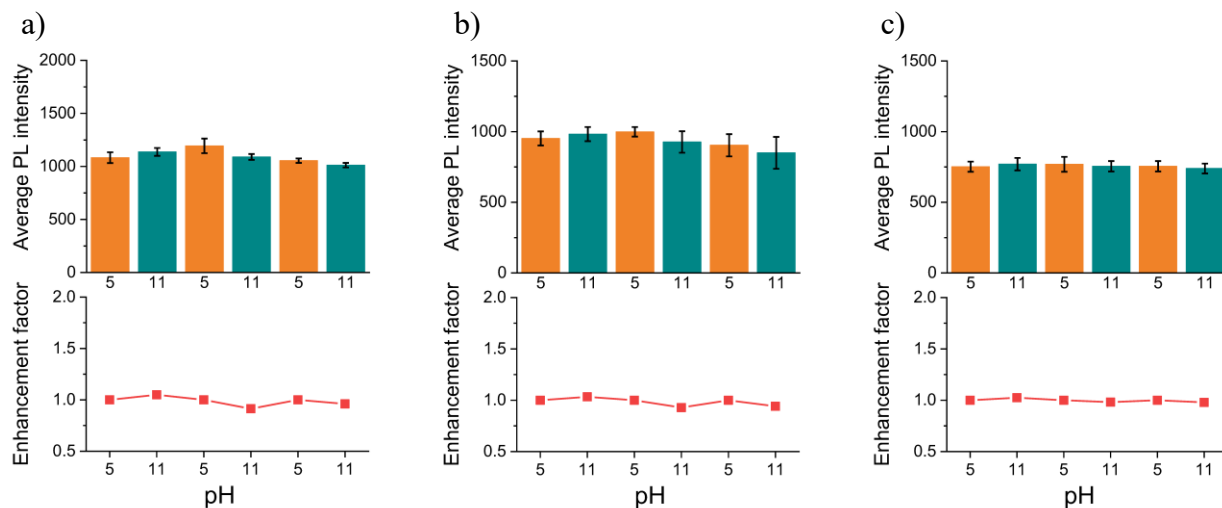

Figure S4. *a, b and c) display reproducibility results of acid-base responsive PL switching behavior and the enhancement factor of sample A: gold/p(DEAEMA-co-MAB$_{0.5}$)/QDs with the film thickness of 39 nm, upon immersion of samples in solutions with pH 5 and 11, measured by confocal scanning microscopy. Note* **Figure S2a** *is the same* **Figure 3c.**
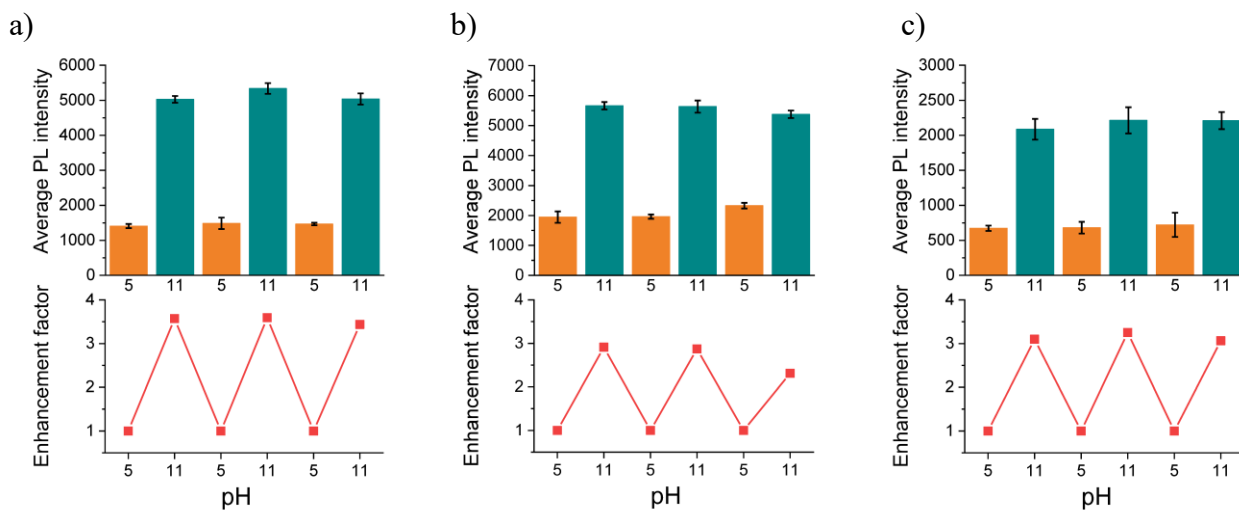

Figure S5. *a, b and c) show reproducibility results of acid-base responsive PL switching behavior and the enhancement factor of sample B: gold/p(DEAEMA-co-MAB$_{0.5}$)/QDs with the film thickness of 46 nm, upon immersion of samples in solutions with pH 5 and 11, measured by confocal scanning microscopy. Note* **Figure S3a** *is the same* **Figure 3d.**
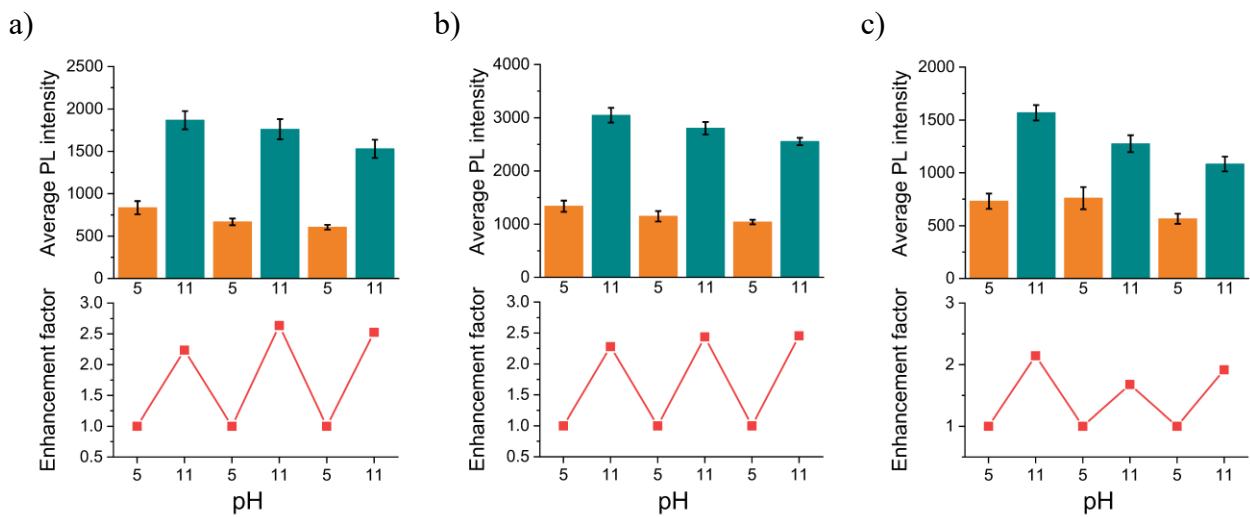
Figure S6. *a, b and c) show reproducibility results of acid-base responsive PL switching behavior and the enhancement factor of sample C: gold/p(DEAEMA-co-MAB$_{0.5}$)/QDs with the film thickness of 74 nm, upon immersion of samples in solutions with pH 5 and 11, measured by confocal scanning microscopy. Note* **Figure S4a** *is the same* **Figure 3e.**
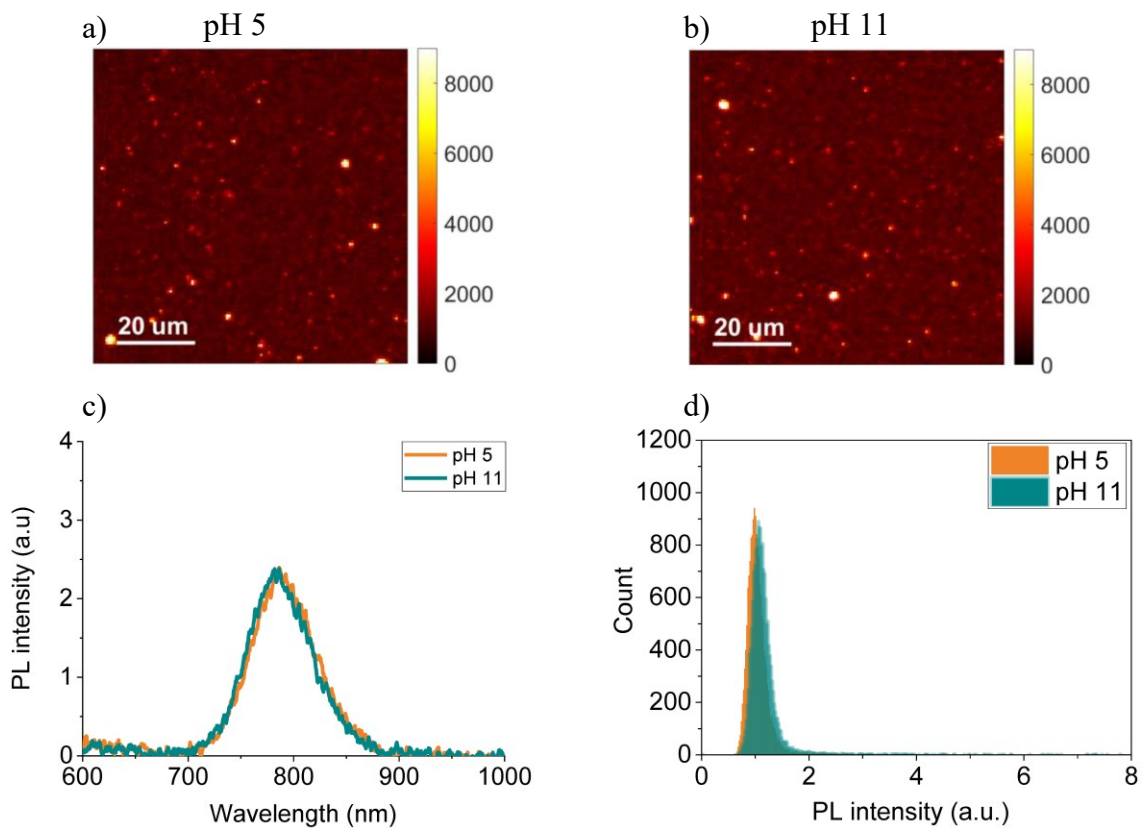

Figure S7. *Confocal scanning microscopy images of sample A showing the spatially resolved PL intensity at (a) pH 5 and (b) pH 11, as well as the corresponding (c) histogram. (d) PL spectra taken at different at pH 5 and 11.*
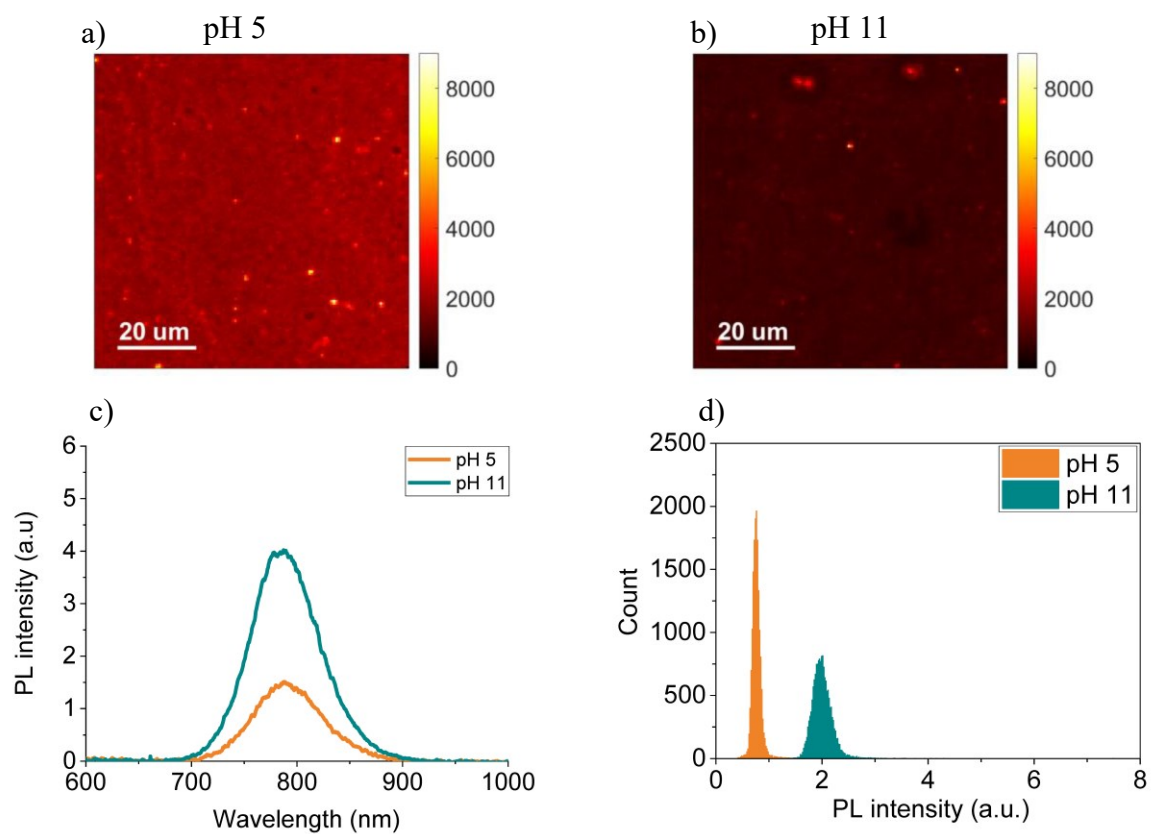
Figure S8. *Confocal scanning microscopy images of sample B showing the spatially resolved PL intensity at (a) pH 5 and (b) pH 11, as well as the corresponding (c) histogram. (d) PL spectra taken at different at pH 5 and 11.*

7   References

1.   M. Moradi, A. Vaskin, I. Staude, M. Jäger, J. Elbert and U. S. Schubert, *ACS Appl. Nano Mater*, 2021, **4**, 2386-2394.