Supporting Information

Room Temperature Synthesis of pH-switchable Polyaniline Quantum Dots as a Turn-on Fluorescent Probe for Acidic Biotarget Labeling

Yanfeng Liu, Yin Ding, Huilin Gou, Xin Huang, Guiyang Zhang, Qi Zhang, Yunzhong Liu, Zhen Meng, Kai Xi, and Xudong Jia**

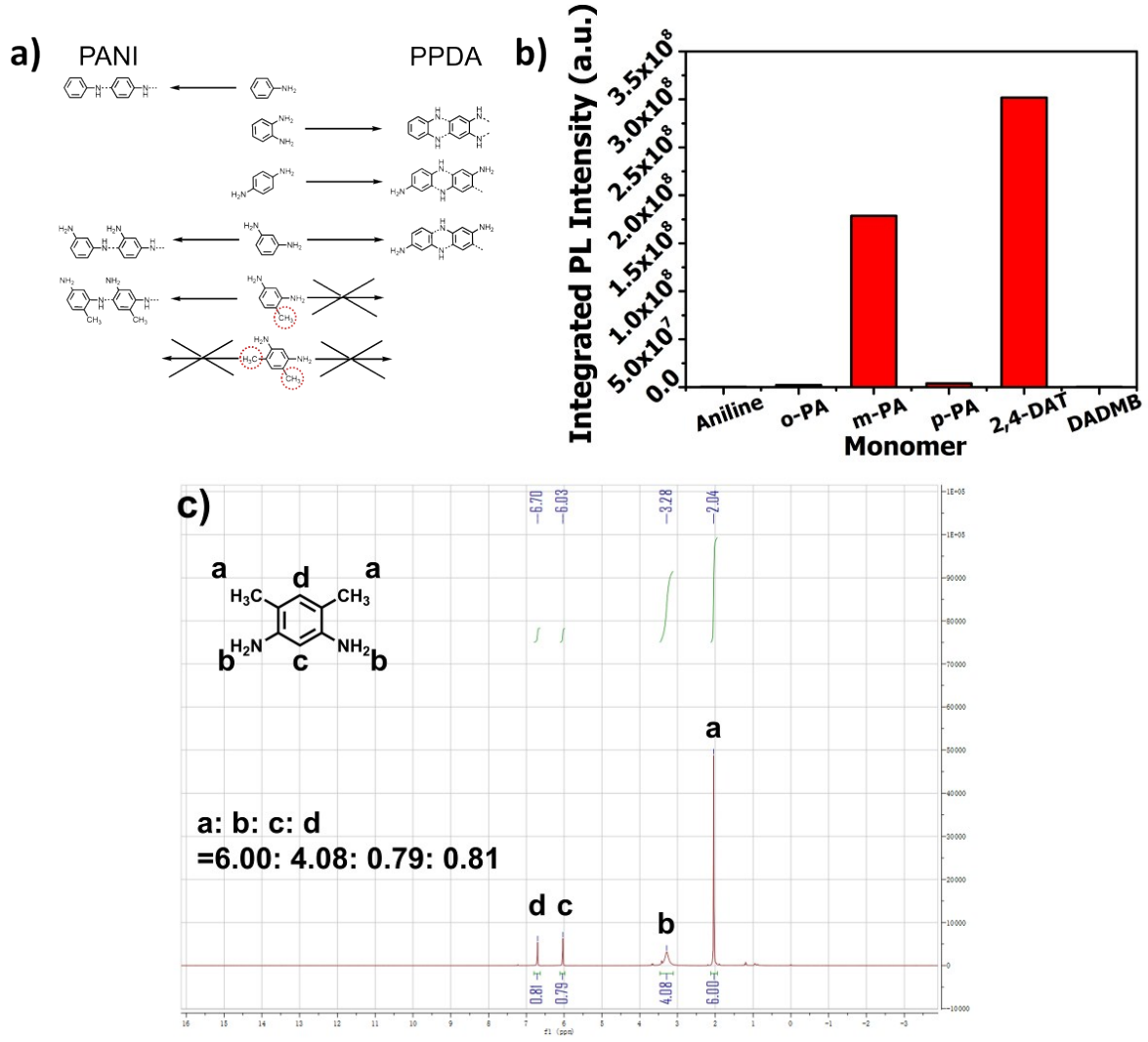


Figure S1. (a) Illustration of the coupling patterns of the different monomers. The phenylenediamine structures (ortha, meta and para) may yield poly(phenylenediamine) (PPDA) structure[s1] besides PANI structure. However, by introducing methyl group, the

generation of PPDA structure can be sterically avoided, producing well-defined PAQD24 with highest PL intensity. Also, when two methyl groups are introduce (the case of DADMB), both amino groups are sterically blocked and no coupling reaction goes on. (b) PL intensities of different aniline derivatives after treatment with auto-oxidized THF and HCl. c) the 1H-NMR spectrum of synthesized DADMB (400 MHz, CDCl3, 298 K, TMS): δ_a = 2.04 ppm (s, 6 H; CH_3); δ_b= 3.28 (s, 4 H; NH_2); δ_c = 6.03 (s, 1 H; benzene); δ_d = 6.70 (s, 1 H; benzene).

Table S1. Quantitation of THF-HPO in auto-oxidized THF by titration.

Experiment	mTHF [g]	ΔV [mL]	ΔV_b [mL] [a)]	ΔV_c [mL] [b)]	M($Na_2S_2O_3$) [mol·L^{-1}]	m(THF-HPO) [g]	M(THF-HPO) [mol·L^{-1}] [c)]
I	25.16	9.15	3.02	6.13	$2.018x10^{-2}$	$6.44x10^{-3}$	$3.26x10^{-3}$
II	24.98	9.10	3.00	6.10	$2.018x10^{-2}$	$6.39x10^{-3}$	$3.27x10^{-3}$

[a)] Volume of sodium thiosulfate used to titrate same amount of freshly distilled THF (blank);

[b)] Corrected volume of sodium thiosulfate used to titrate oxidized THF;

[c)] Molar concentration of THF-HPO, the molecular weight of THF-HPO is 104 g mol^{-1}.

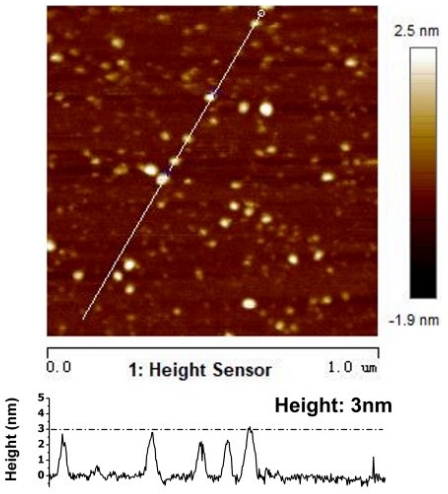


Figure S2. AFM image of PAQD24 with typical height of 3 nm.

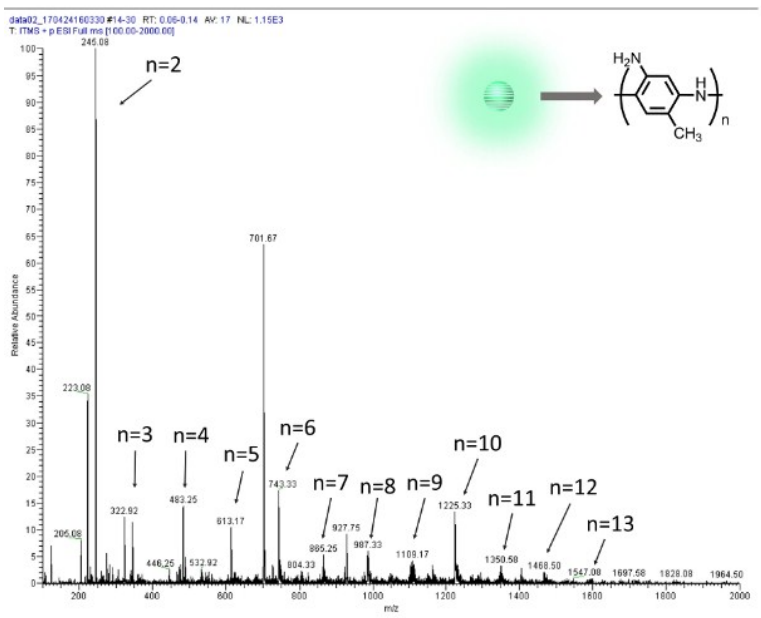


Figure S3. ESI mass spectrum of as-prepared PAQD24.

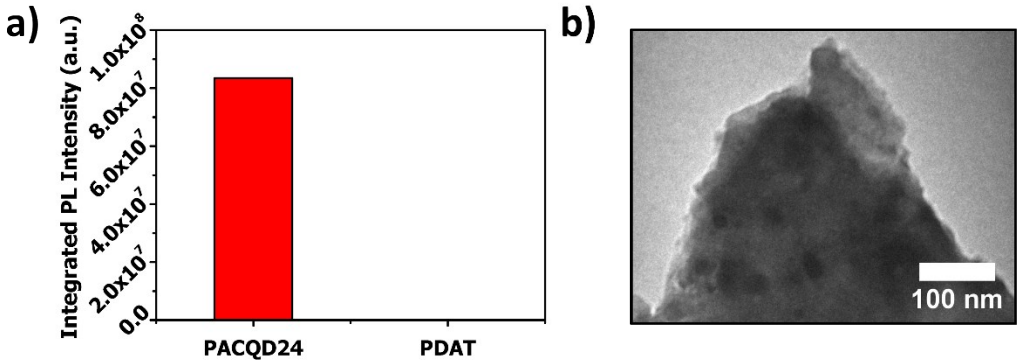


Figure S4. (a) PL intensities PAQD24 and PDAT at same concentration (20μg mL^{-1}) under 365 nm excitation. (b) TEM image of PDAT

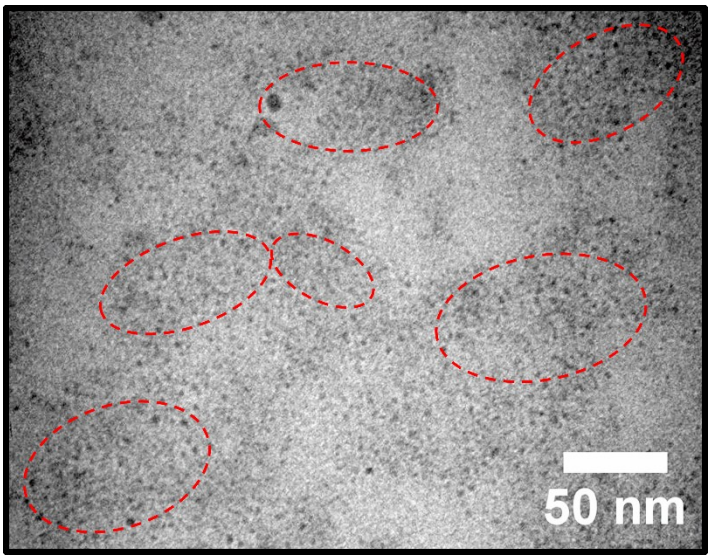
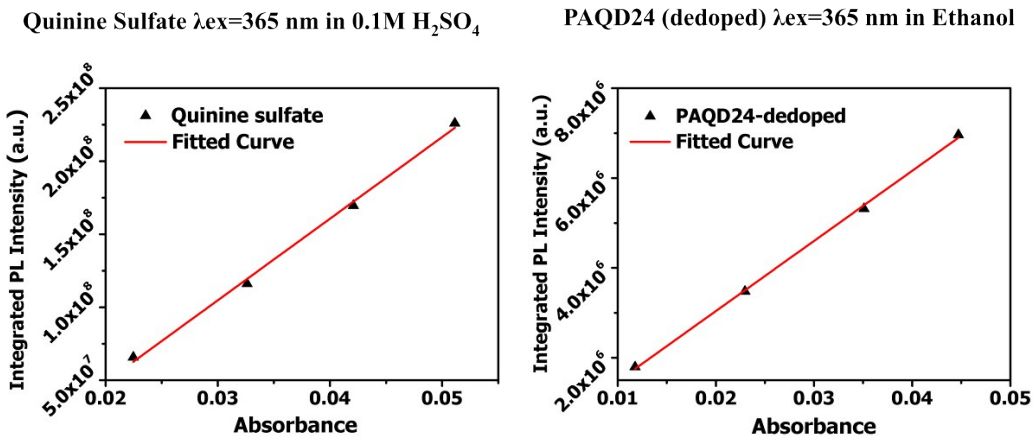
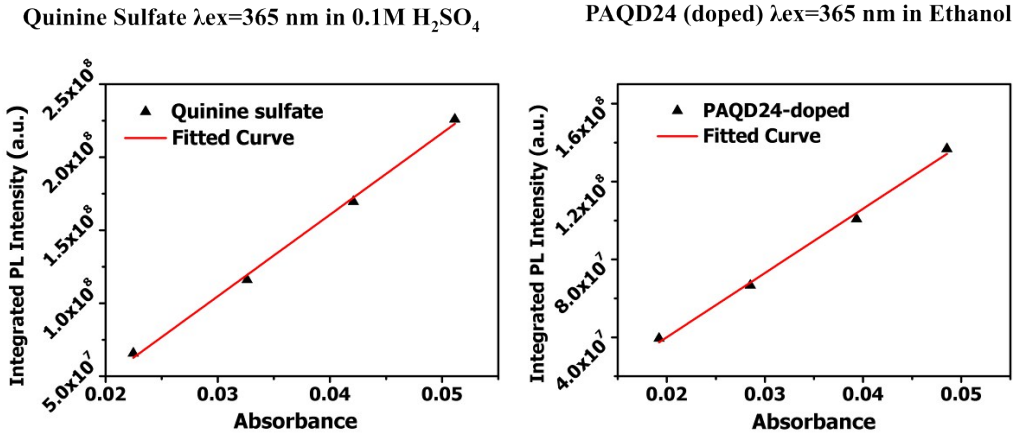


Figure S5. TEM image of the aggregated dedoped PAQD24 in aqueous solution.



	Quinine Sulfate				PAQD24-dedoped			
Abs	2.25×10^{-2}	3.26×10^{-2}	4.21×10^{-2}	5.11×10^{-2}	2.30×10^{-2}	3.51×10^{-2}	4.47×10^{-2}	5.62×10^{-2}
FL Intensity	6.57×10^{7}	1.16×10^{8}	1.70×10^{8}	2.26×10^{8}	3.48×10^{6}	5.32×10^{6}	6.96×10^{6}	8.48×10^{6}
Slope	5.59×10^{9}				1.56×10^{8}			
QY	55.0%				1.54%			

Figure S6-1. QY assessment of dedoped PAQD24 by plotting of the integrated PL intensity against absorbance at 365 nm. Quinine sulfate (QY = 55%) is used as a reference dye.



	Quinine Sulfate				PAQD24-doped			
Abs	2.25×10^{-2}	3.26×10^{-2}	4.21×10^{-2}	5.11×10^{-2}	1.92×10^{-2}	2.85×10^{-2}	3.93×10^{-2}	4.85×10^{-2}
FL Intensity	6.57×10^{7}	1.16×10^{8}	1.70×10^{8}	2.26×10^{8}	3.94×10^{7}	6.67×10^{7}	1.01×10^{8}	1.37×10^{8}
Slope	5.59×10^{9}				3.30×10^{9}			
QY	55.0%				32.5%			

Figure S6-2. QY assessment of doped PAQD24 by plotting of the integrated PL intensity against absorbance at 365 nm. Quinine sulfate (QY = 55%) is used as a reference dye.

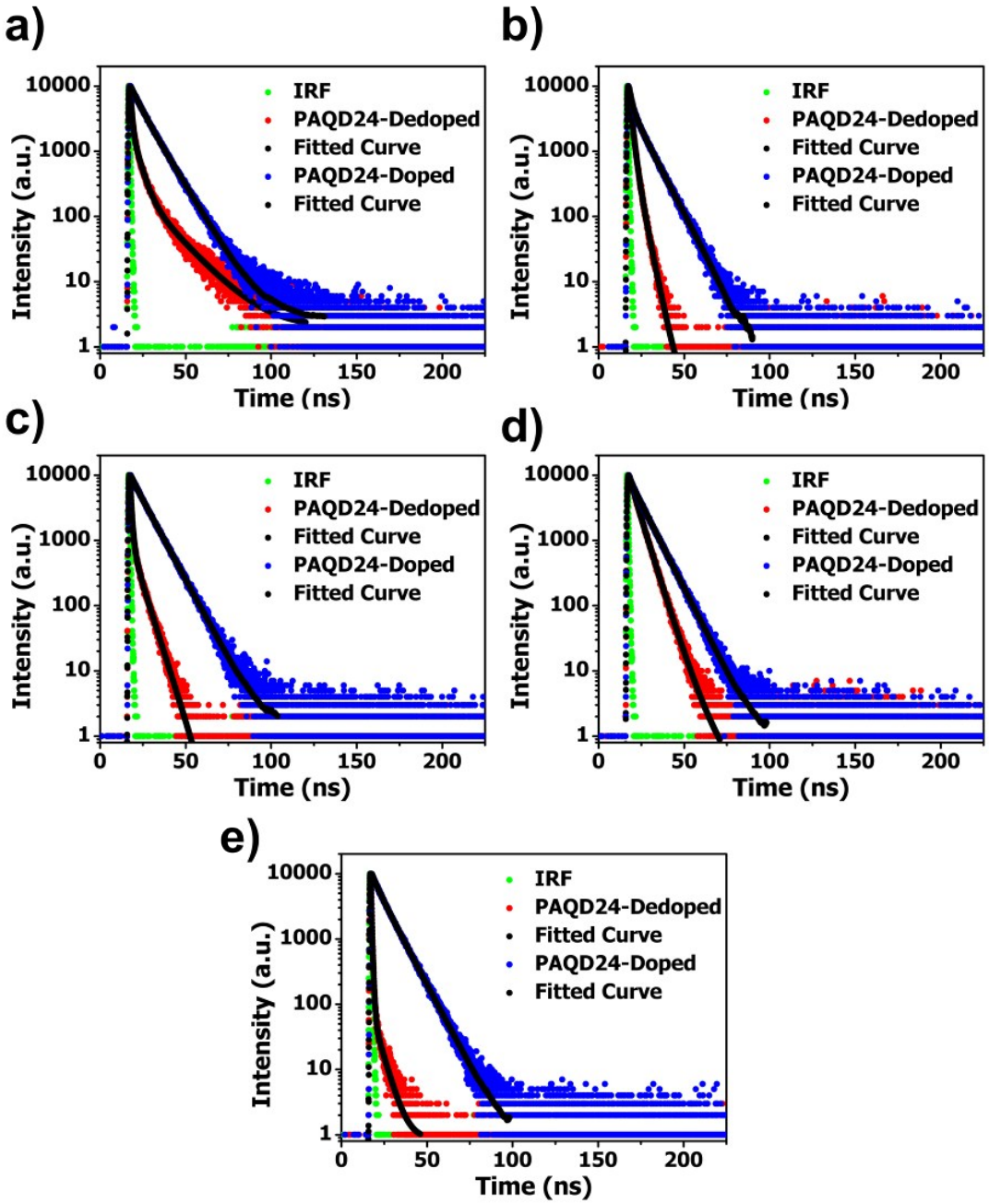


Figure S7. PL lifetimes of PAQD24 in different solvents: a) BuOH, b) DCM, c) EtOH, d) THF and e) water. Blue dots stand for the plot of doped PAQD24, red dots stand for the dedoped ones, green dots stand for the instrument response function (IRF) and black lines stand for the fitted curves.

Table S2. Detailed PL decay properties of doped and dedoped PAQD24 in different solvents.

State/ solvent	T_1 [ns]	B_1	T_2 [ns]	B_2	T_3 [ns]	B_3	T_{avg} [ns]
Dedoped/ BuOH	3.85	36.97%	15.44	16.84%	0.78	46.19%	4.38
Doped/ BuOH	3.41	9.65%	9.77	90.35%	-----	-----	9.16
Dedoped/ DCM	0.94	16.40%	1.59	59.27%	3.45	24.34%	1.94
Doped/ DCM	1.61	22.53%	8.48	77.47%	-----	-----	6.93
Dedoped/ EtOH	1.21	26.60%	0.46	48.23%	5.25	25.17%	1.87
Doped/ EtOH	2.23	3.19%	8.94	96.81%	-----	-----	8.73
Dedoped/ THF	2.46	10.11%	5.16	88.91%	3.40	0.98%	4.87
Doped/ THF	1.08	4.38%	8.38	95.62%	-----	-----	8.06
Dedoped/ H_2O	0.15	85.92%	0.68	11.09%	4.68	2.99%	0.34
Doped/ H_2O	2.57	8.59%	8.70	91.41%	-----	-----	8.17

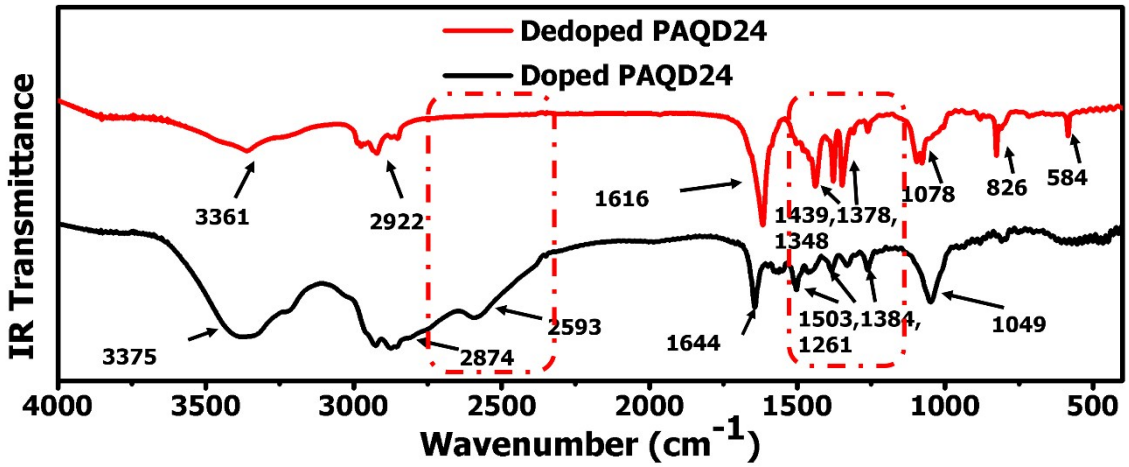


Figure S8. FT-IR spectra of dedoped (red) and doped (black) PAQD24. The benzenoid-NH^+=quinoid vibration blueshifted from 1078 cm^{-1} to 1049 cm^{-1} upon doping, as reported for polyaniline. The peak at 1616 cm^{-1} for dedoped PAQD24 and at 1644 cm^{-1} for doped PAQD24 should be assigned to benzenoid structure, while the multiple peaks between 1300

cm^{-1} and 1500 cm^{-1} are related to quinoid structure and weakened after proton doping, as the doped emeraldine structure contains less quinoid component. Peaks at 3361 cm-1 for the dedoped PAQD24 and 3375 cm^{-1} for the doped PAQD24 should be assigned to the N-H vibration, while the peaks at 2922 cm^{-1} for the dedoped and 2874 cm^{-1} for the doped PAQD24 are contributed by the C-H vibration. Both of the above peaks enhanced upon proton doping. Notably, a broad peak centered at 2593 cm^{-1} appears in the spectrum of doped PAQD24, while is totally missing in the dedoped ones. The origination of this peak is related to the increased intra-chain free carrier upon doping.

Table S3. Plotting details of pH value/ Nromalized PL Intensity

pH value	Normalized PL Intensity
12.95	$6.14x10^{-4}$
12.25	$1.26x10^{-3}$
11.08	$3.16x10^{-3}$
10.15	$3.68x10^{-3}$
9.22	$1.26x10^{-2}$
8.33	$3.74x10^{-2}$
7.83	$8.61x10^{-2}$
7.54	$1.32x10^{-1}$
7.05	$2.66x10^{-1}$
6.66	$3.99x10^{-1}$
6.2	$6.56x10^{-1}$
5.47	$8.93x10^{-1}$
4.01	$9.67x10^{-1}$
3.17	1.00
1.94	$9.55x10^{-1}$
1.23	$9.66x10^{-1}$

Table S4. Fitting details of pH-PL plot

I_{max}	I_{min}	pKa (calculated)	Standard Error	R^2
1.00	6.14×10^{-4}	6.52207	0.02987	0.99601

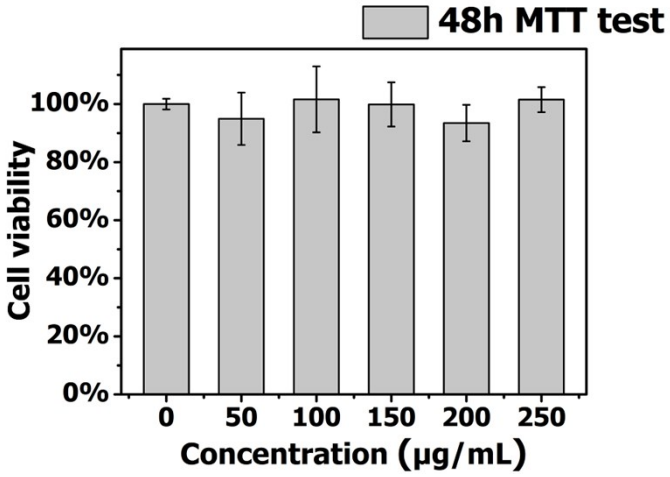


Figure S9. Cytotoxicity assessment of PAQD24 by a standard MTT array.

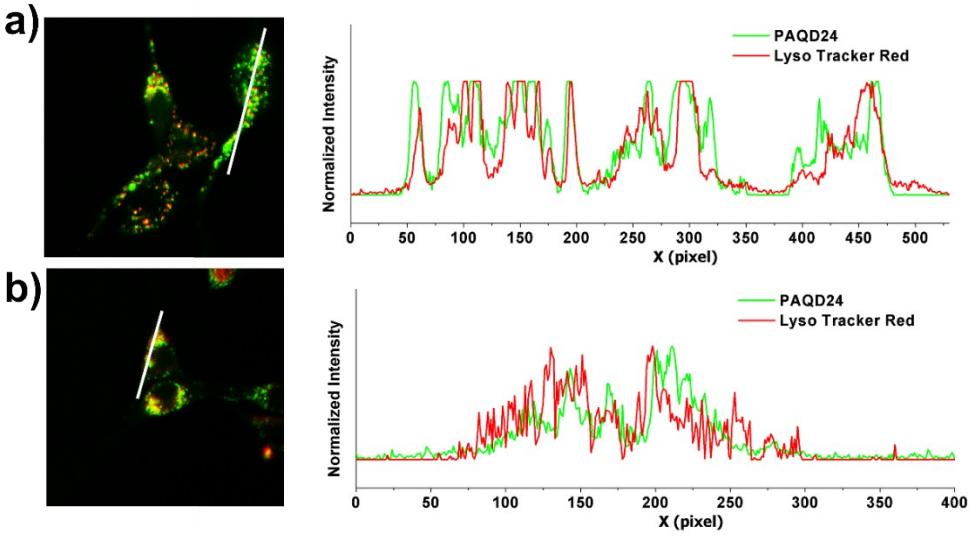


Figure S10. Overlapping analysis of PAQD24 and Lyso Tracker Red after a) 1h and b) 12 h cultivation.

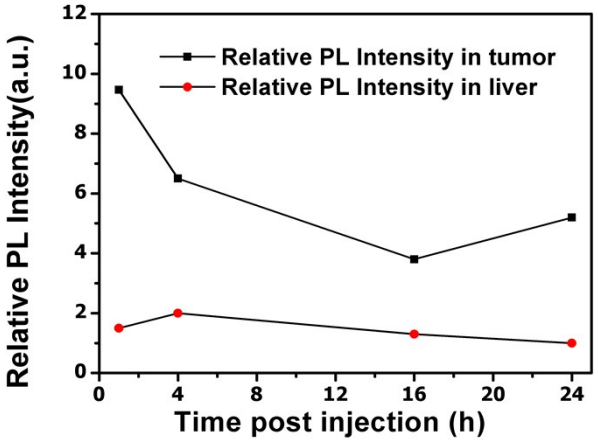


Figure S11. PL intensity in tumor sites and livers plotted against post injection time.

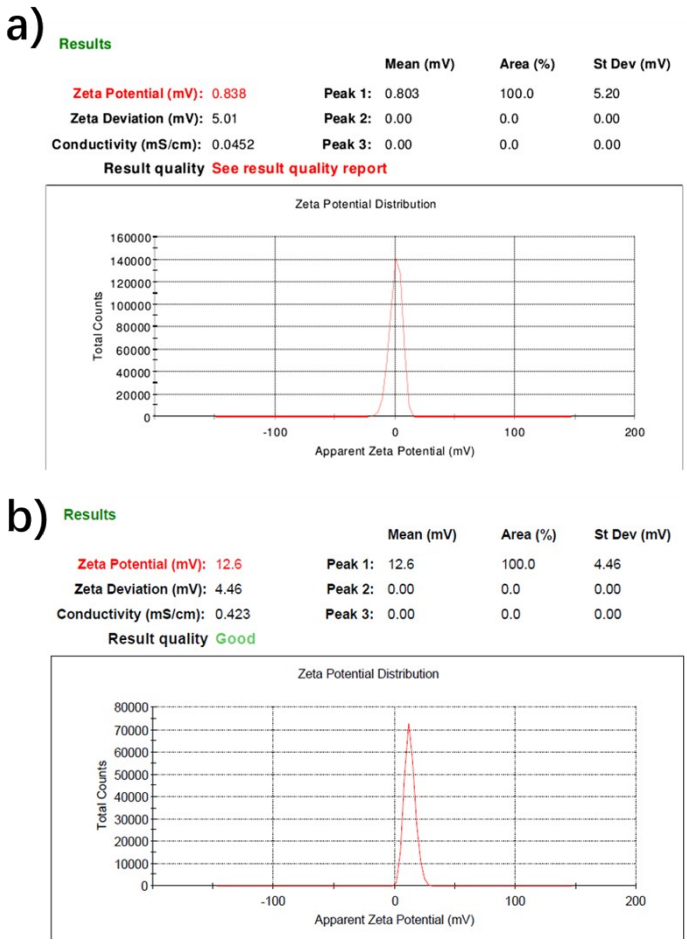


Figure S12. Zeta potential of (a) dedoped PAQD24 (pH = 6.0) and (b) doped PAQD24(pH = 7.4)

[s1] T. Sulimenko, J. Stejskal, J. Prokeš, *J. Colloid Interface Sci.* **2001**, *236*, 328.