

Supplementary Information

Highly Efficient Visible Blue-emitting Black Phosphorus Quantum Dot: Mussel-inspired Surface Functionalization for Bioapplications

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Lot#	Name	Molecular weight (g/mol)	Surface tension (dynes/cm)	Solvent exfoliation ^a	Emission ^b
1	Water	18.02	72.7 ¹	decomposed	n. a.
2	Diethylene glycol	106.12	55.1 ¹	poor	n. a.
3	Ethylene glycol	62.07	48.4 ¹	poor	n. a.
4	<i>N</i> -Methyl-2-pyrrolidone	99.13	44.6 ¹	excellent	n. a.
5	Polyethylene glycol (<i>M_n</i> 200 Da)	200	43.50 ²	good	n. a.
6	Aniline	93.13	43.40 ²	good	n. a.
7	Propylene carbonate	102.09	40.9 ¹	excellent	n. a.
8	Benzyl ether	198.26	40.44 ⁴	excellent	Weak blue (A)
9	Benzaldehyde	106.12	38.3 ¹	poor	n. a.
10	Pyridine	79.10	36.7 ¹	good	Weak blue (B)
11	<i>N,N</i> -Dimethyl acetamide	87.12	36.70 ²	excellent	Medium greenish blue (C)
12	γ -Butyrolactone	86.09	35.4 ⁵	excellent	n. a.
13	<i>N,N</i> -Dimethyl formamide	73.09	34.4 ¹	good	n. a.
14	Chlorobenzene	112.56	33.60 ²	good	n. a.
15	1,4-Dioxane	88.11	32.9 ¹	poor	n. a.
16	Toluene	92.14	27.9 ¹	poor	n. a.
17	Chloroform	119.38	26.7 ¹	good	Strong blue (D, D') ^c
18	Tetrahydrofuran	72.11	26.40 ²	good	n. a.
19	Vinyl acetate	86.09	23.8 ³	poor	n. a.
20	Isopropyl alcohol	60.10	23.3 ¹	poor	n. a.
21	Acetone	58.08	23.0 ¹	good	n. a.
22	Methanol	32.04	22.1 ¹	poor	n. a.
23	Ethanol	46.07	22.0 ¹	poor	n. a.
24	<i>n</i> -Hexane	86.18	18.43 ¹	poor	n. a.

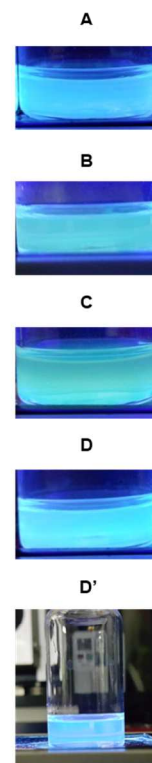


Table S1. Twenty-four organic solvents in various solvent categories with different surface tensions and molecular weights were tested toward the liquid-phase exfoliation of BP flake.

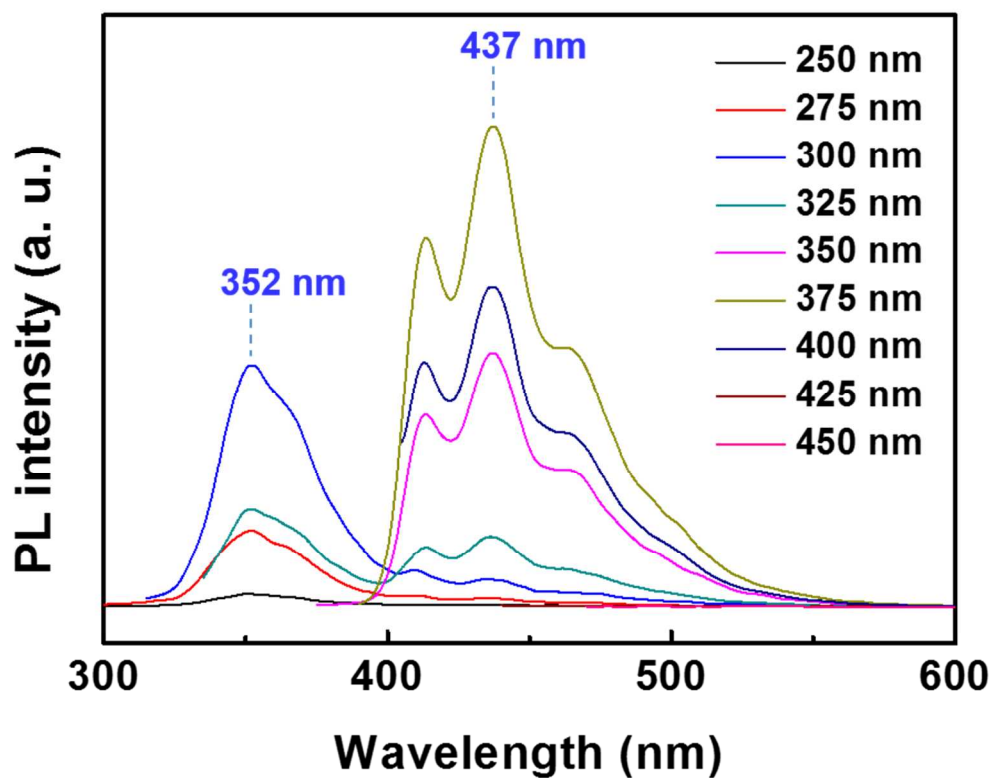


Figure S1. The highest PL emission intensity was observed for the BPQD dispersion in chloroform at 437 nm, and the position of the maximum emission peak did not show any noticeable shift regardless of the excitation wavelength.

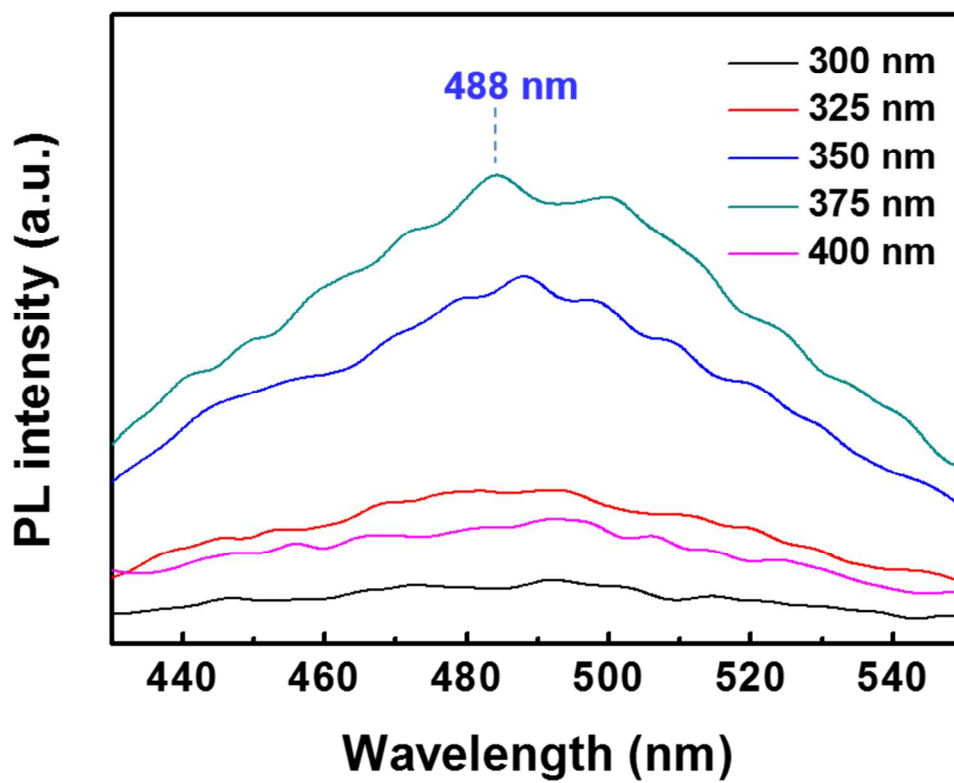


Figure S2. Excitation-independent PL emission was observed when DMAc was used as the organic solvent during the liquid-phase exfoliation of BP.

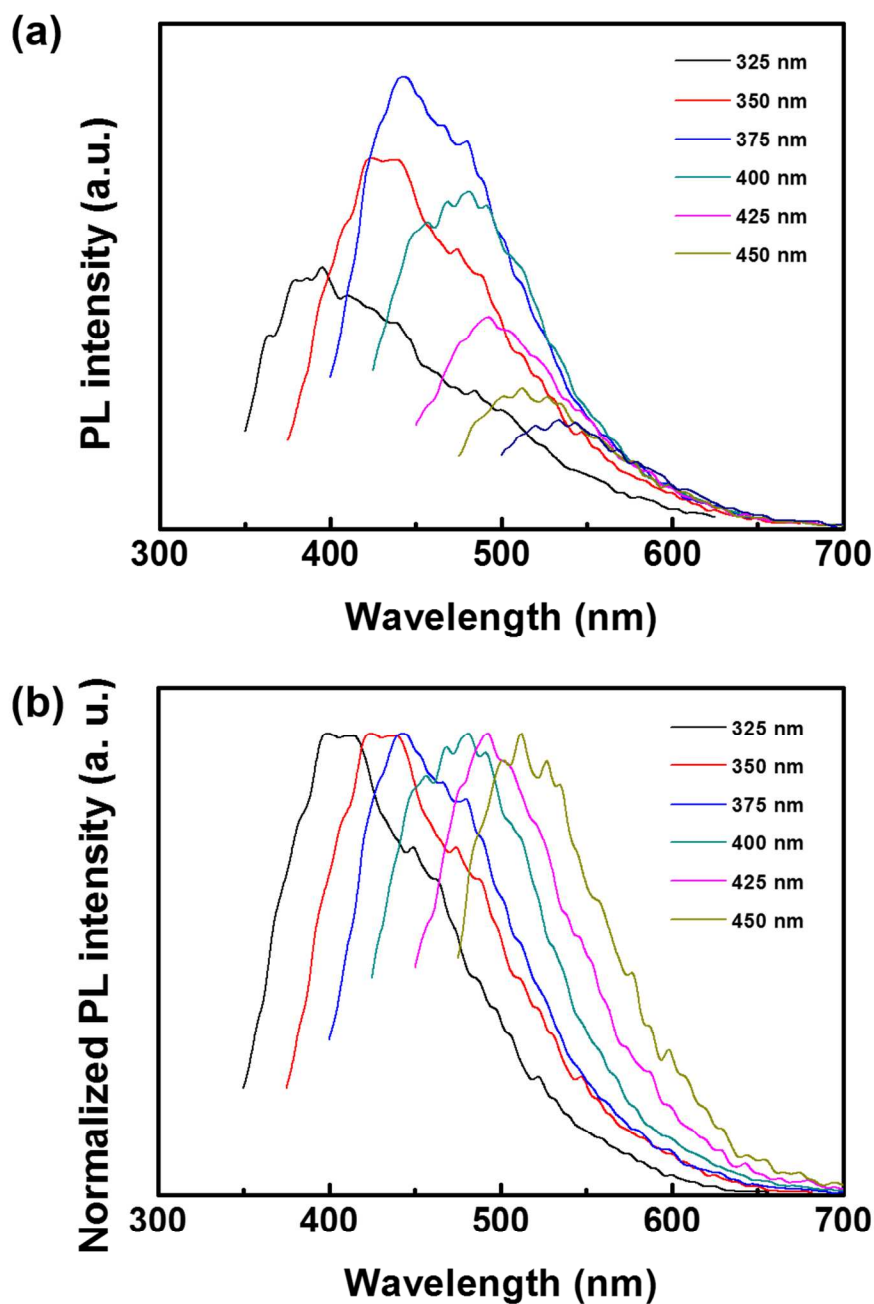


Figure S3. (a) Excitation-dependent PL emission intensity was observed when pyridine was observed similarly to the PL emission behavior of certain CQDs or CDs showing tunable fluorescence emissions through the surface defect-derived origins. (b) Normalized PL intensity of Figure S3(a).

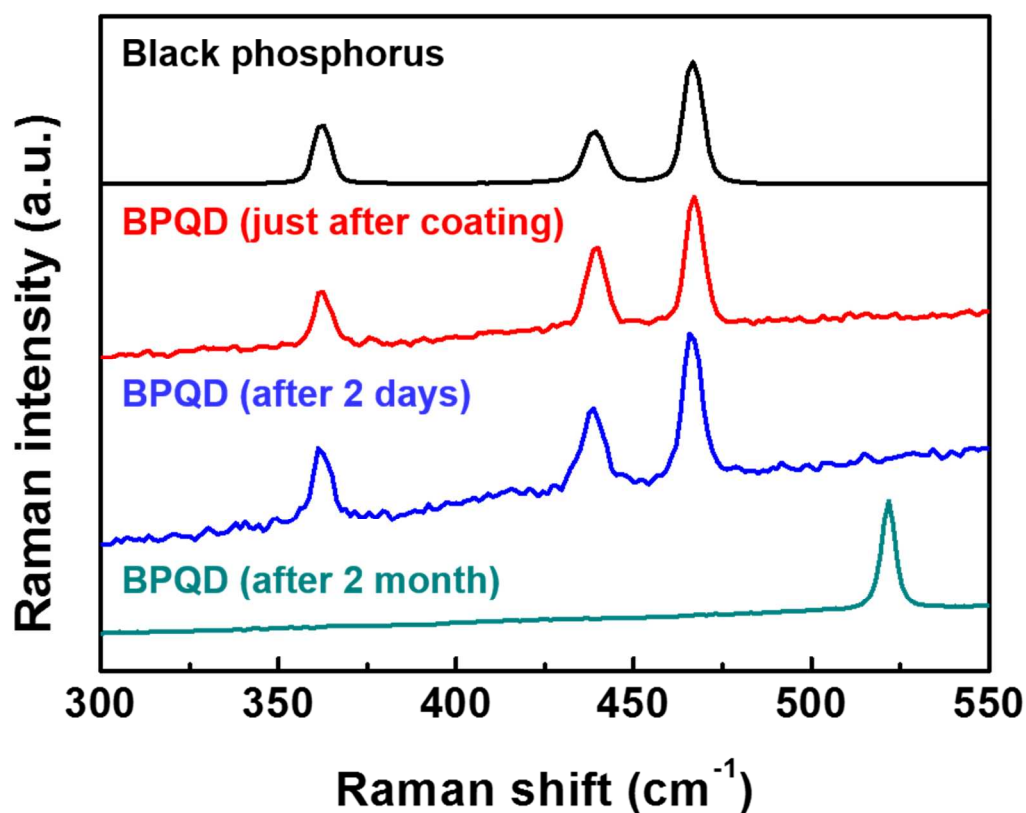


Figure S4. Raman spectroscopy characterization of four different samples: (a) Pristine BP flake (black line); Raman spectra acquired (b) Just after coating (red line); (c) After 2 days (blue line); and (d) After 2 month (green line) on the few-layered BPQDs prepared by the liquid-phase exfoliation of BP crystal in chloroform.

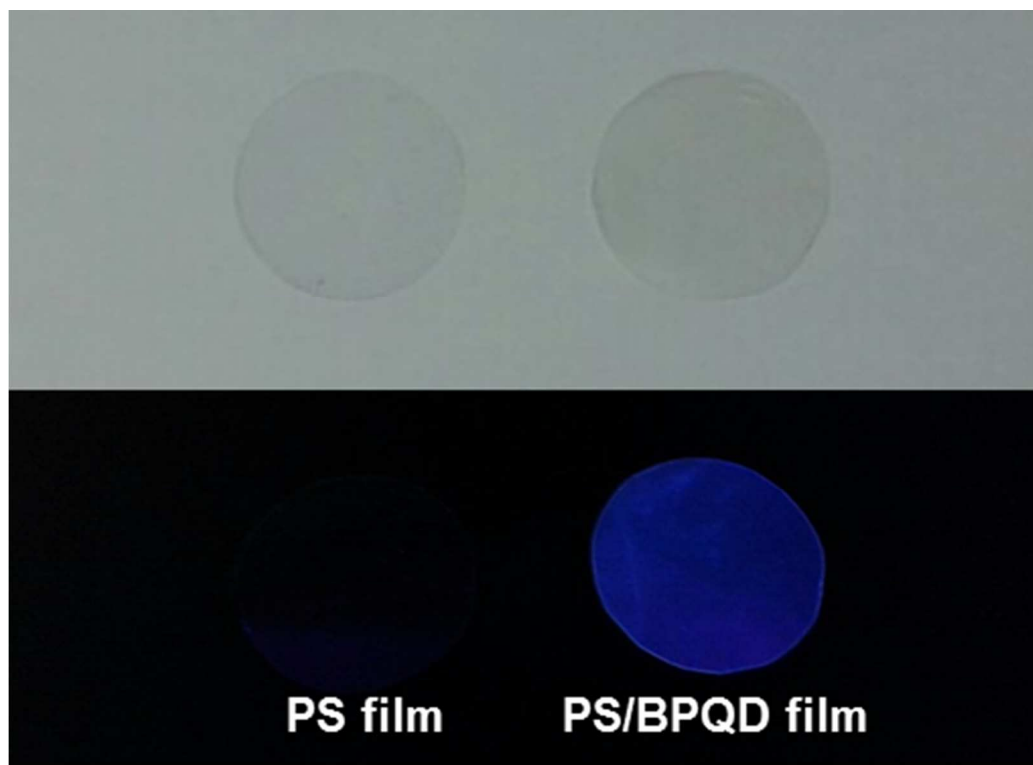


Figure S5. Digital photo images of PS and PS/BPQD composite film (2 wt.-% BPQDs) in the daylight (upper image) and under dark with UV irradiation (lower image).

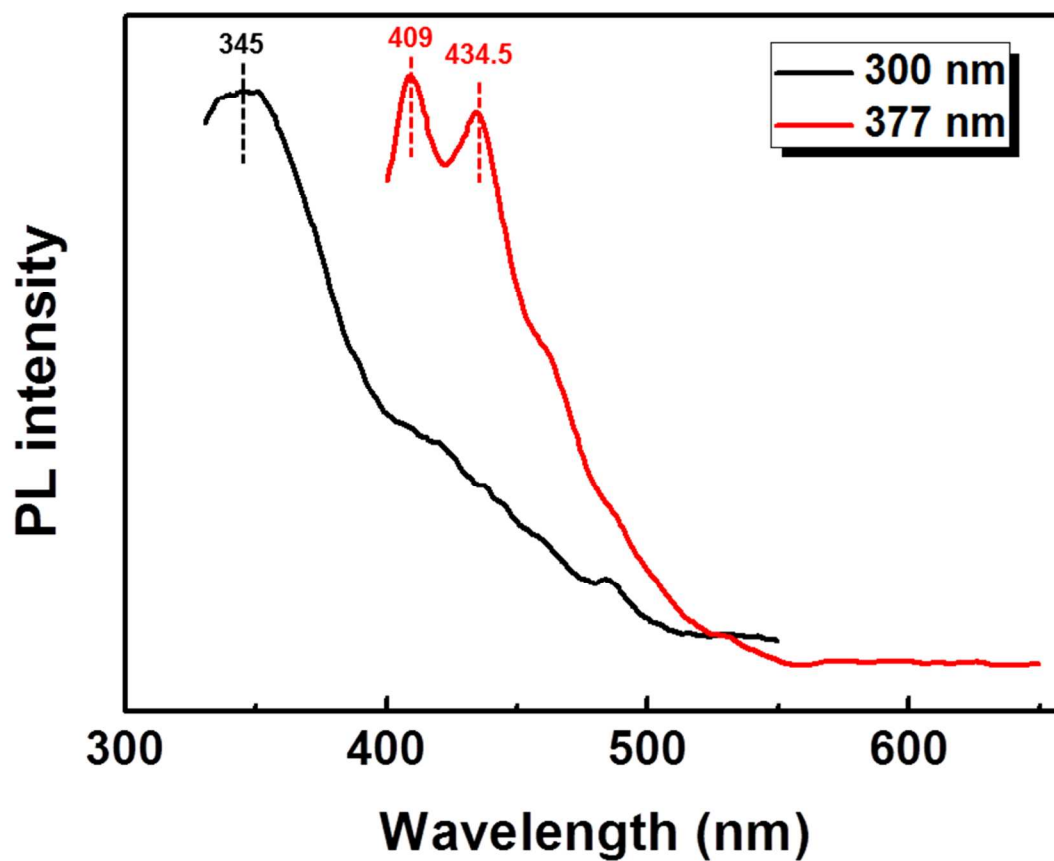


Figure S6. Fluorescence spectra of PS/BPQD composite film (2 wt.-% BPQDs) with the excitation wavelength of 300 and 377 nm.

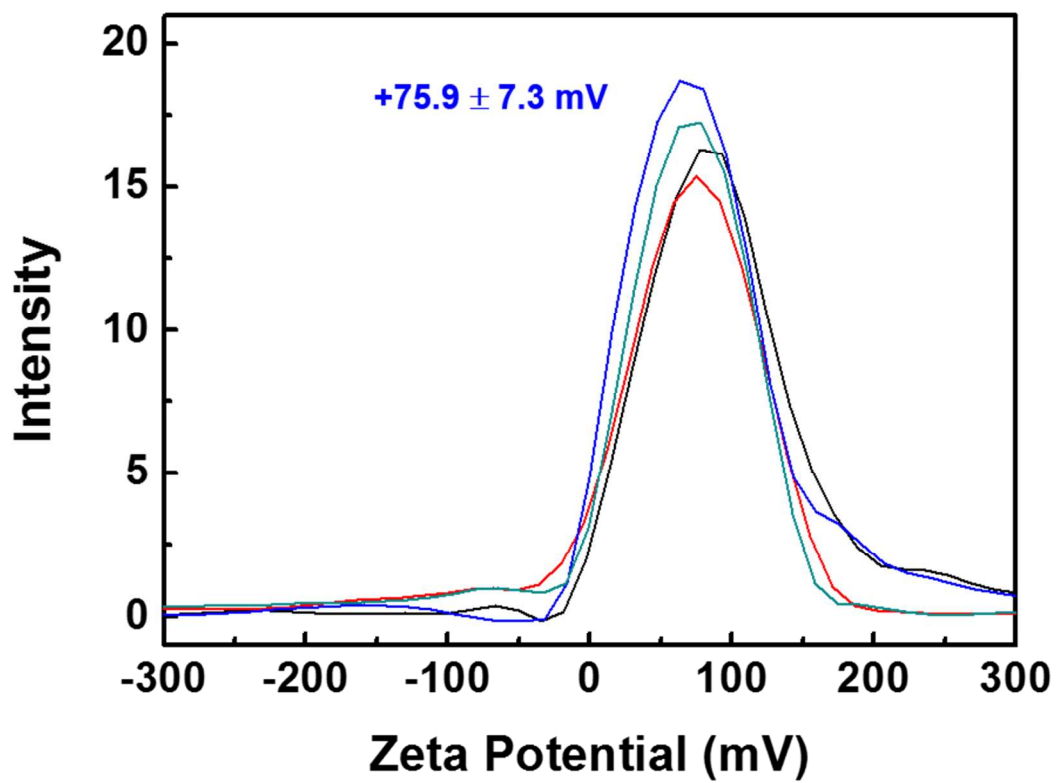


Figure S7. Positive zeta-potential was repeatedly observed for the chloroform dispersion of the BPQDs.

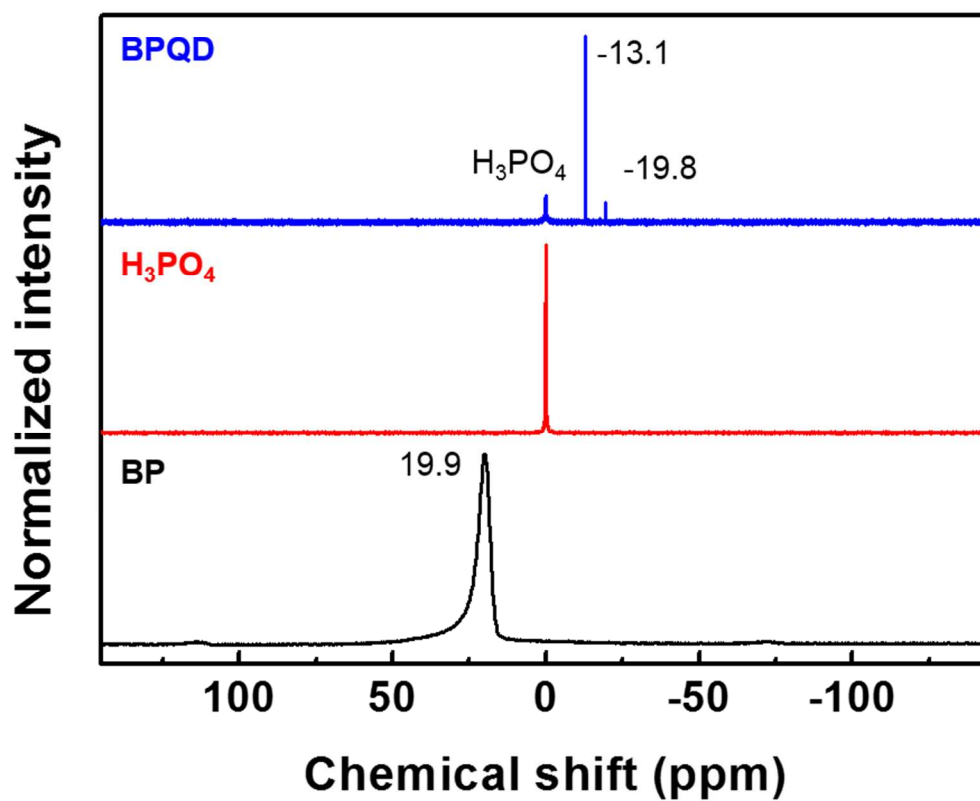


Figure S8. ^{31}P -NMR spectroscopy was recorded for both the BPQD dispersion (blue line) and pristine BP (black line) measured in CDCl_3 with 85% phosphoric acid as the reference.

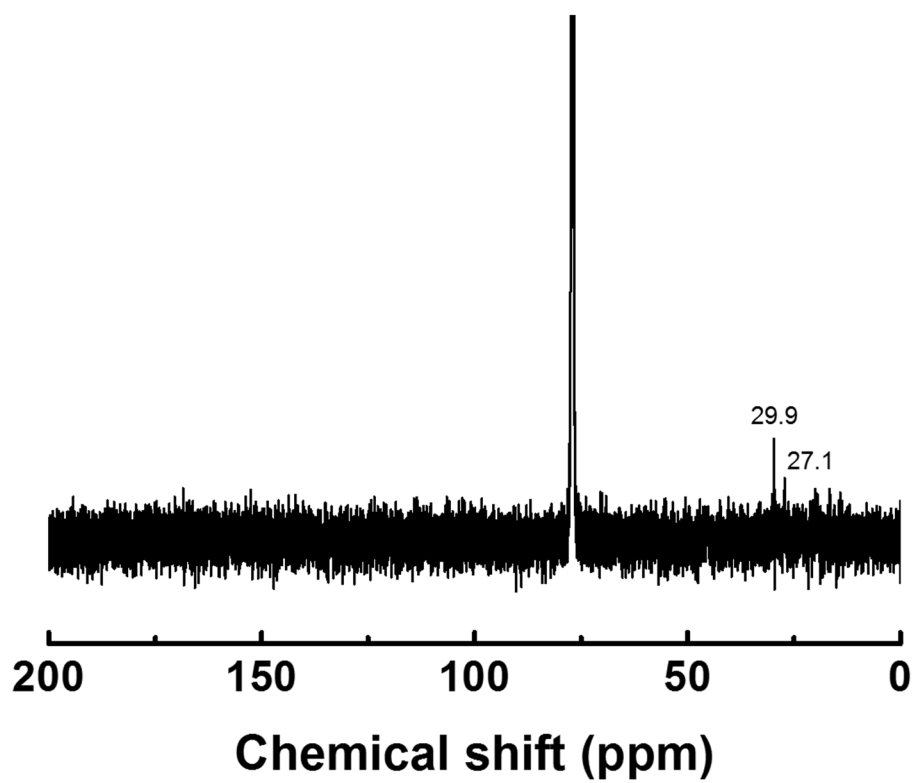


Figure S9. ^{13}C -NMR spectrum of BPQD clearly shows carbon peaks at 29.9 and 27.1 ppm.

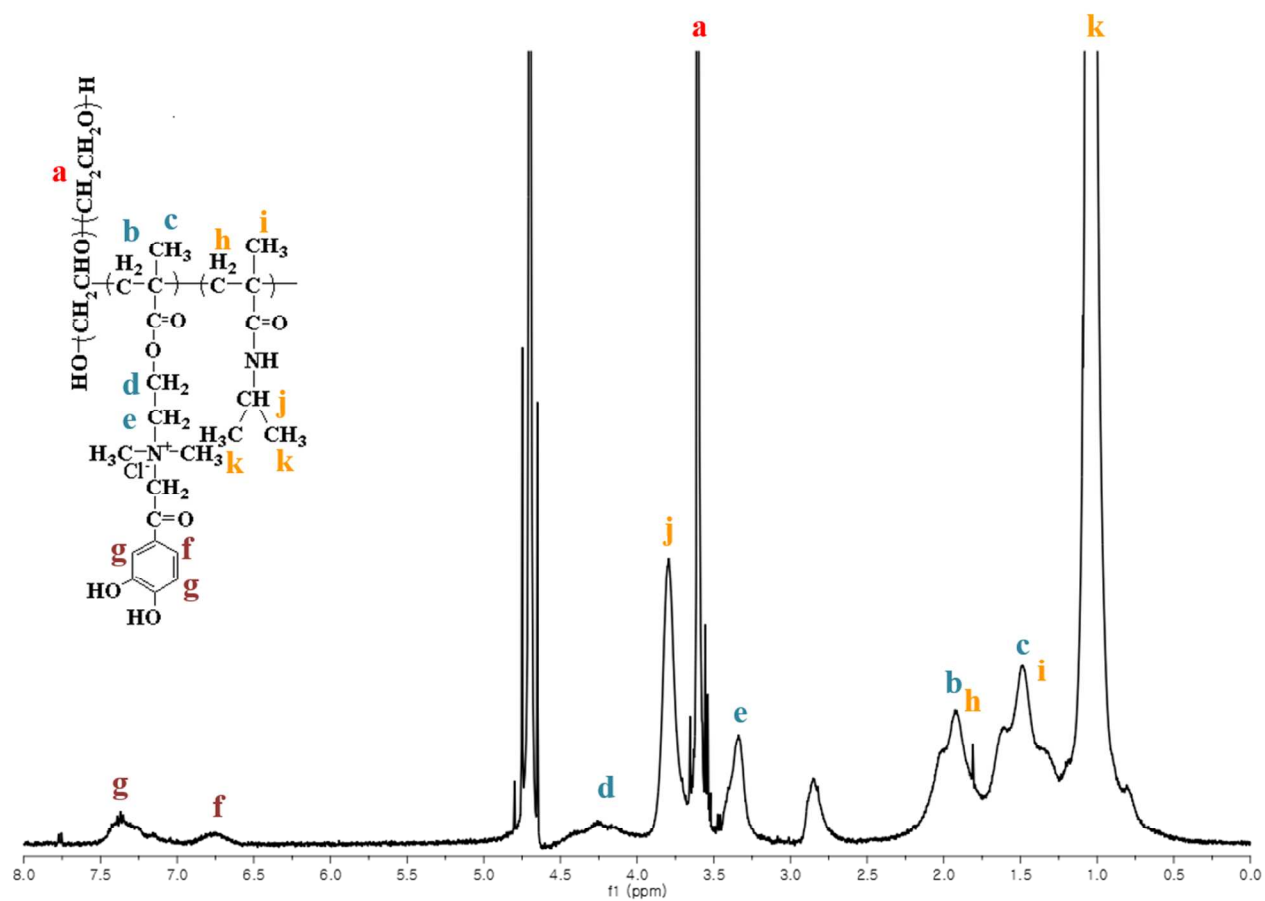


Figure S10. ^1H -NMR spectrum of the prepared CA-PEG.

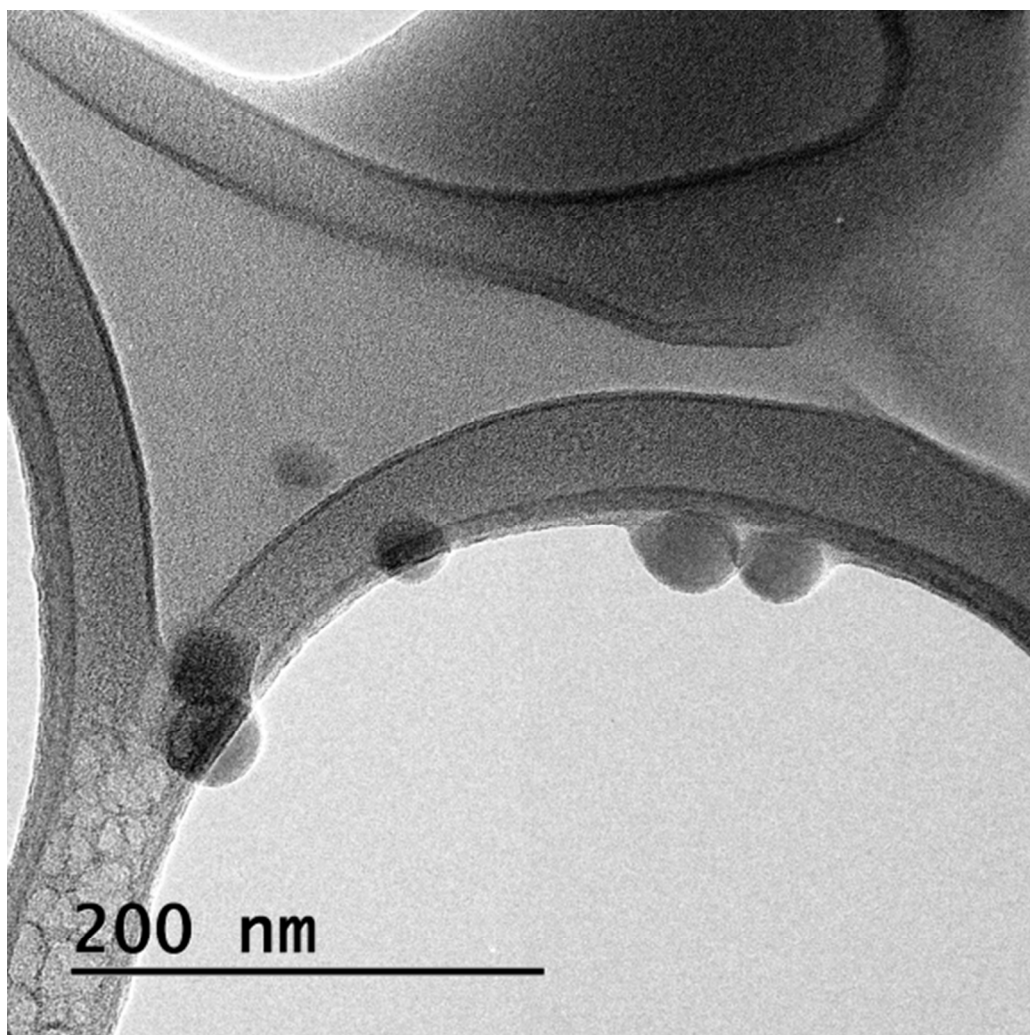


Figure 11. TEM image of PEG-BPQDs on carbon coated Cu grid.

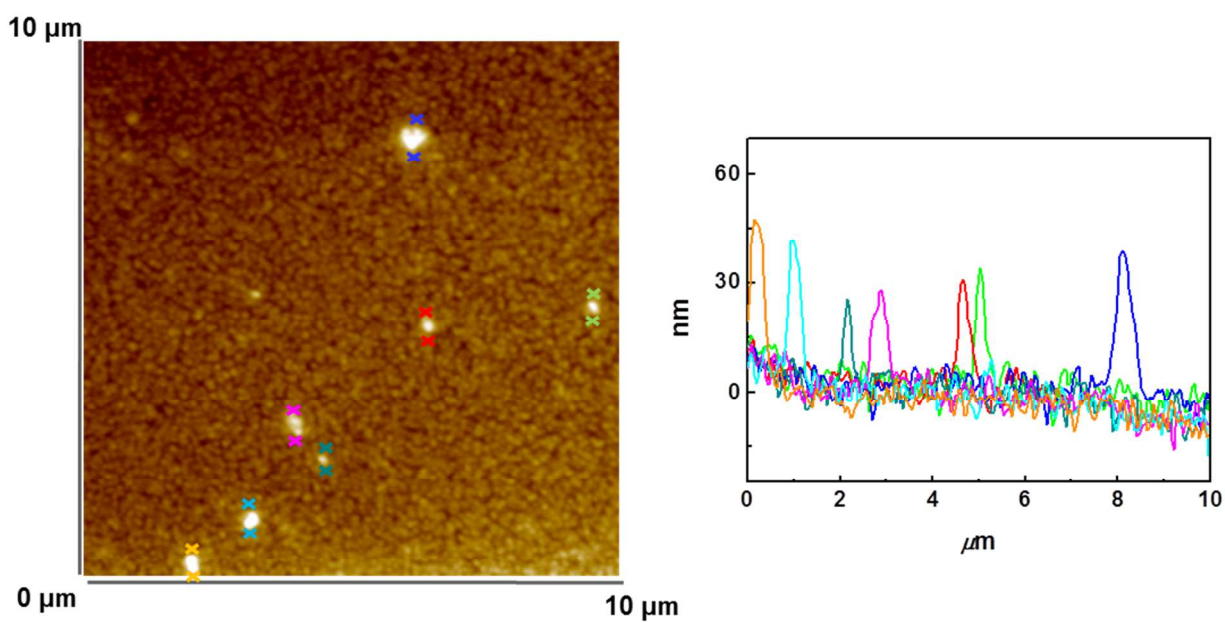


Figure 12. AFM images of BPQDs on Si wafer (the right is the height profiles of selected lines in the AFM image).

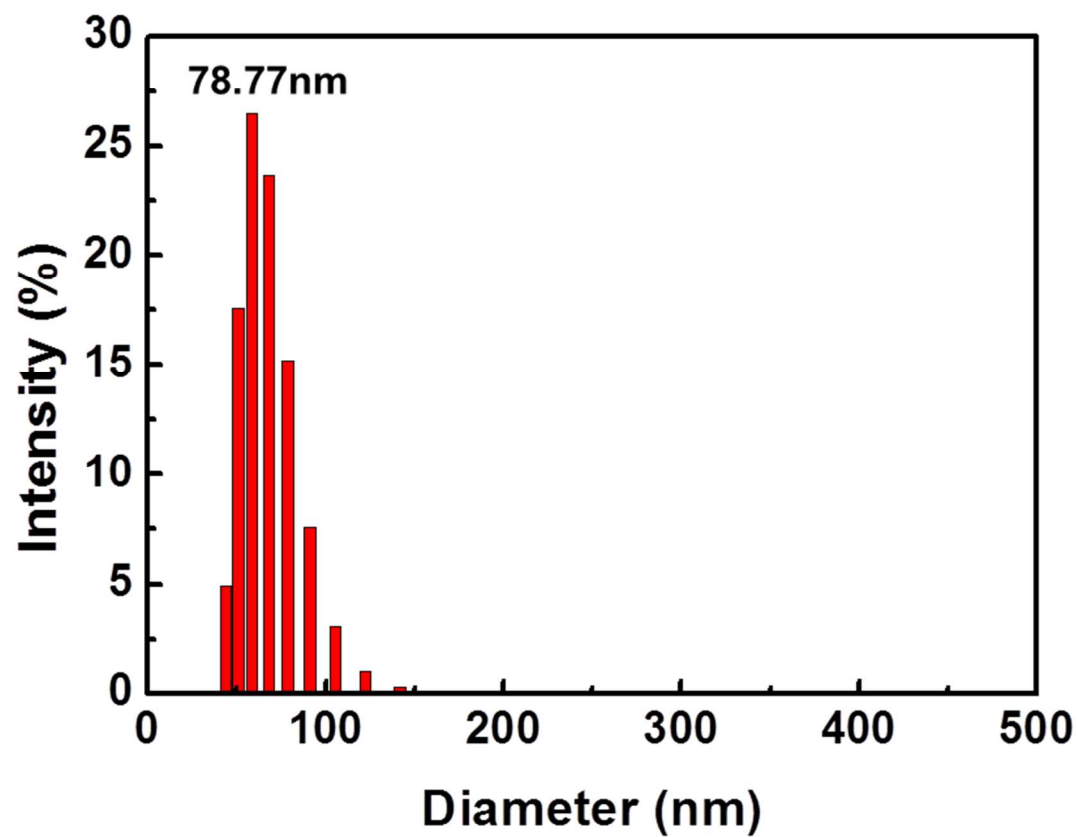


Figure 13. Size distribution profile of PEG-BPQDs (0.5 mg/mL in water) measured by DLS

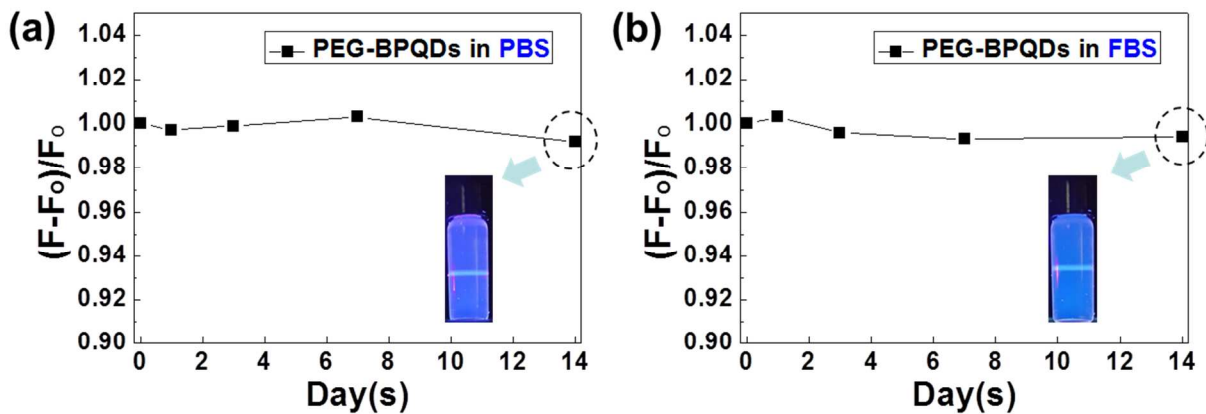


Figure 14. Relative fluorescence intensity of PEG-BPQDs (1 mg/mL) in 2% aqueous buffer solutions, (a) PBS and (b) FBS (the insets are photo images of PEG-BPQDs in the buffer solution after 14 days of storage under ambient condition).