Electronic Supplementary Information

A general route to make non-conjugated linear polymers luminescent

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1. Experimental Section

Preparation of PDs: Polyvinyl alcohol (PVA) dots were prepared as follows: PVA was dissolved in DI-water with the concentrations of 0.4-50 mg/mL. Then the solution was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (30 mL) and heated at 160-340 ºC for 0.1-10 h (Microwave-assisted hydrothermal route can accelerate the reactions, so the optimal reaction conditions were different). After the above reaction, the reactors were cooled to room temperature by water or naturally. The product was brown and transparent. The product was subjected to dialysis (Mw=3500) to completely remove un-reacted impurities (4 days, changed DI-water every 8 hours).

For a typical reaction condition: PVA (M_w=13000-23000; 31000-50000; ca. 77000) 10 mL (10 mg/mL), temperature=240 ºC, time=6 h.

PEI (10 mL: 1-20 mg/mL) was treated through the same route to obtain the PDs. For PEG and PEO (10 mL: 1-20 mg/mL), quantitative NaOH (0.02 M) should be added to improve the carbonizing process.

Cellular toxicity test: Mouse osteoblastic cell line (MC3T3-E1) cells (10^4 cells/150 μL) were cultured for 24 h in an incubator (37 ℃, 5% CO_2), and for another 24 h after the culture medium was replaced with 100 μL of Dulbecco's modified Eagle's medium (DMEM) containing the PDs at different doses (0, 10, 20, 50, 100, 200, 400

μg/mL). Then, 20 μL of 5 mg/mL MTT solution was added to every well. The cells were further incubated for 4 h, followed by removing the culture medium with MTT, and then 150 μL of DMSO was added. The resulting mixture was shaken for ca. 5 min at room temperature. The optical density (OD) of the mixture was measured at 490 nm. The cell viability was estimated according to the following equation:

Cell Viability [%] = $(OD_{treated} / OD_{control}) \times 100$ %

(Where $OD_{Control}$ was obtained in the absence of PDs, and $OD_{Treated}$ was obtained in the presence of PDs.)

Cellular imaging: The cells were cultured in DMEM supplemented with 10% fetal bovine serum and 1% penicillin/streptomycin. Suspensions (5 mg/mL) of PDs from the stock solution were prepared with Dulbecco's phosphate buffer saline (DPBS). After sonication for 10 min to ensure complete dispersion, an aliquot (typically 0.1 mL) of the suspension was added to the well with a chamber slide, then incubated at 37 ℃ in a 5% CO_2 incubator for 20 h. Before the fixation of the cells on the slide for inspection with a confocal fluorescence microscope, the excess PDs were removed by washing 3 times with warm DPBS.

Characterization: High-resolution transmission electron microscope (HR-TEM) was recorded on FEI Tecnai F20. Fluorescence spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer. UV-vis absorption spectra were obtained using a Shimadzu 3100 UV-vis spectrophotometer. IR spectra were taken on a Nicolet AVATAR 360 FT-IR spectrophotometer. The confocal microscopy images were collected on Olympus Fluoview FV1000. X-ray Photoelectron Spectroscopy (XPS) was investigated by using ESCALAB 250 spectrometer with a mono X-Ray source Al Kα excitation (1486.6 eV). Binding energy calibration was based on C1s at 284.6 eV. AFM images were recorded in the tapping mode with a Nanoscope IIIa scanning probe microscope from Digital Instruments under ambient conditions. NMR was done on AVANCE III500 (Bruker).

Time-resolved photoluminescence. Nanosecond fluorescence lifetime experiments were performed by the time-correlated single-photon counting (TCSPC) system under

right-angle sample geometry. A 379/405 nm picosecond diode laser (Edinburgh Instruments EPL375, repetition rate 2 MHz) was used to excite the samples. The fluorescence was collected by a photomultiplier tube (Hamamatsu H5783p) connected to a TCSPC board (Becker&Hickel SPC-130). The time constant of the instrument response function (IRF) was about 300 ps.

Femtosecond transient absorption setup. The TA setup consisted of 400 nm pump pulses doubled from 800 nm laser pulses (~100 fs duration, 250 Hz repetition rate) were generated from a mode-locked Ti: sapphire laser/amplifier system (Solstice, Spectra-Physics) and broadband white-light probe pulses were generated from 2-mm-thick water or 5-mm-thick CaF_2 substrate. The relative polarization of the pump and the probe beams were set to the magic angle. The TA data were collected by a fiber-coupled spectrometer connected to a computer. The group velocity dispersion of the transient spectra was compensated by a chirp program. All the measurements were performed at room temperature. Pump-power dependent measurements were carried out. In the acceptable range, no pump intensity-dependent dynamics was observed.

Scheme S1. The possible reaction in the carbonizing process (for PVA only, the different linear polymer may have different carbonizing mechanisms). After (or during) dehydration, the carbonization may further occur. The precise structure contributed to fluorescence may also be the conjugated system, so detailed work should be carried out in the near future. The percentage of carbonization center was also very low. So the most PVA chains were preserved.

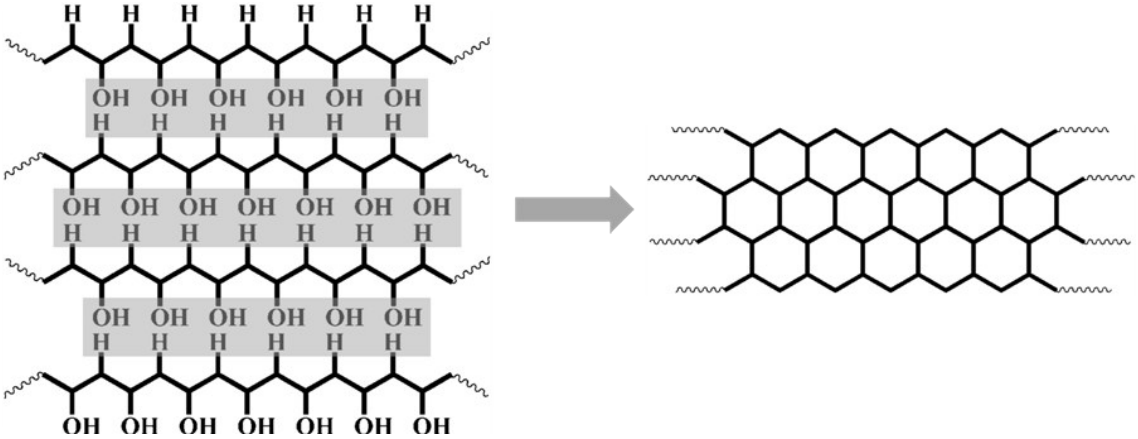


Figure S1 The H-NMR (a) and C-NMR (b) spectra PDs. The sample was dissolved in 9:1 H_2O and D_2O.

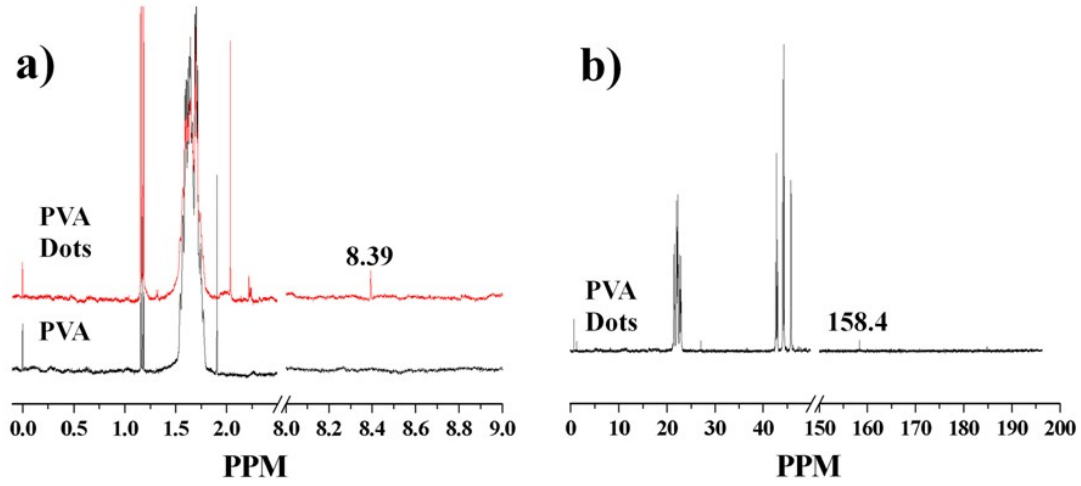


Figure S2. FTIR spectra of the PVA and PVA dots, respectively.

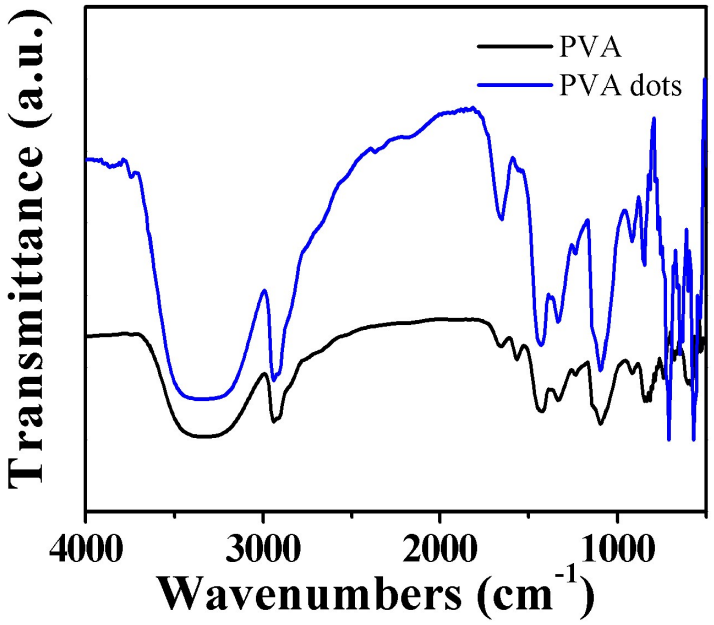


Figure S3. XPS of PVA and PVA dots, respectively.

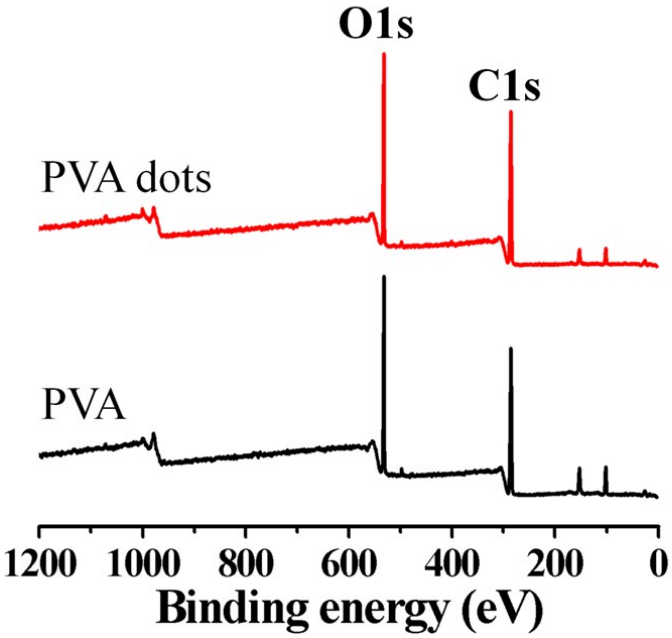


Figure S4. Only one excited state was observed in broadband (350-750 nm) TA testing. All wavelength sections have the same decay tendency.

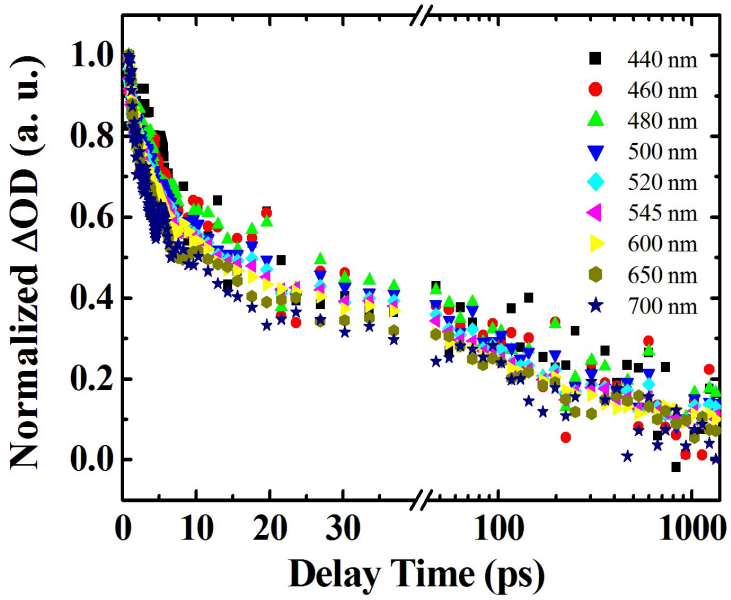
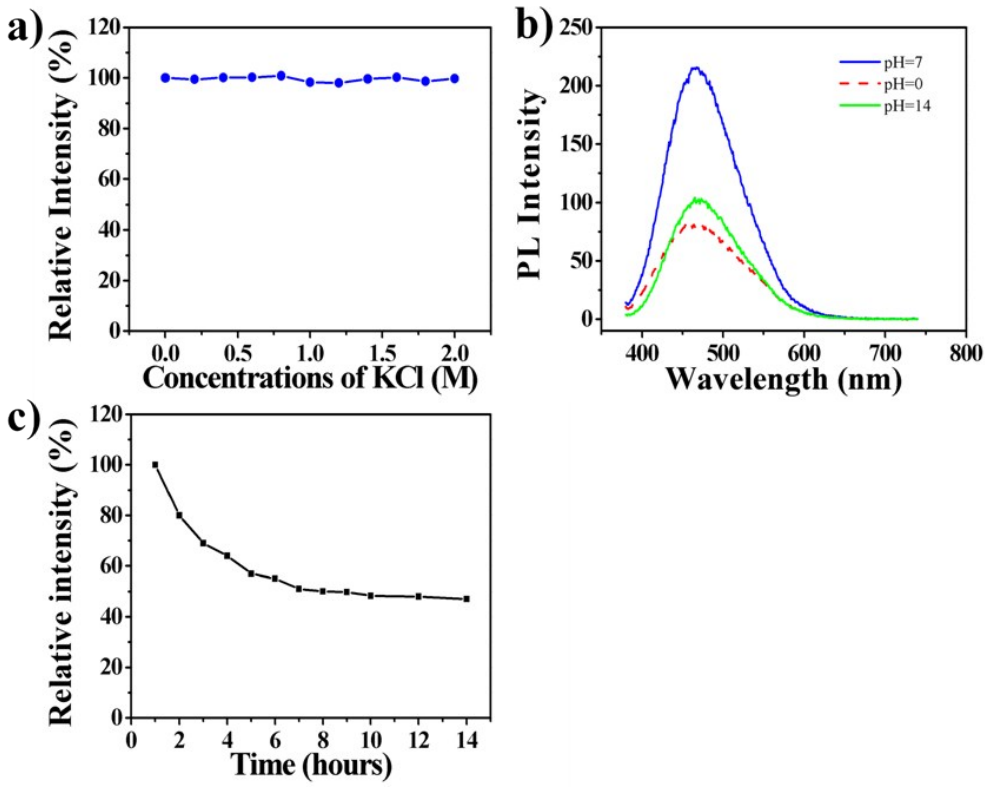


Figure S5. Stability of PDs. a) Effect of ionic strengths on the fluorescence intensity of PDs (ionic strengths were tuned by various concentrations of KCl). b) Effect of pH on the fluorescence intensity of PDs. c) Dependence of fluorescence intensity on excitation time for PDs in DI water.



Quantum yield (QY) measurement.

Aqueous quinine sulfate solution in 0.1 M sulfuric acid (QY = 0.54) was chosen as a standard for quantum yield (QY) determination of the PDs. The QY of PDs (in water) was calculated according to:

$$\phi_x = \phi_{st}(I_x / I_{st})(\eta_x^2 / \eta_{st}^2)(A_{st} / A_x)$$

Where φ was the QY, I is the measured PL intensity, η was the refractive index of the solvent, and A was the optical density. The subscript *"st"* referred to standard and *"x"* referred to the sample. The absorption in the 10 mm fluorescence cuvette was kept below 0.10 at 360 nm.

Table S1. Quantum yield of PDs.

Sample	Integrated emission intensity *(I)*	Abs. at 360 nm *(A)*	Refractive index of solvent *(η)*	Quantum Yields *(φ)*
quinine sulfate	69351.8	0.100	1.33	0.54 (known)
PDs	741.8	0.046	1.33	0.0126

Figure S6. PEI dots were prepared by the hydrothermal method from different PEI (M_w=1800, 10000, 25000).

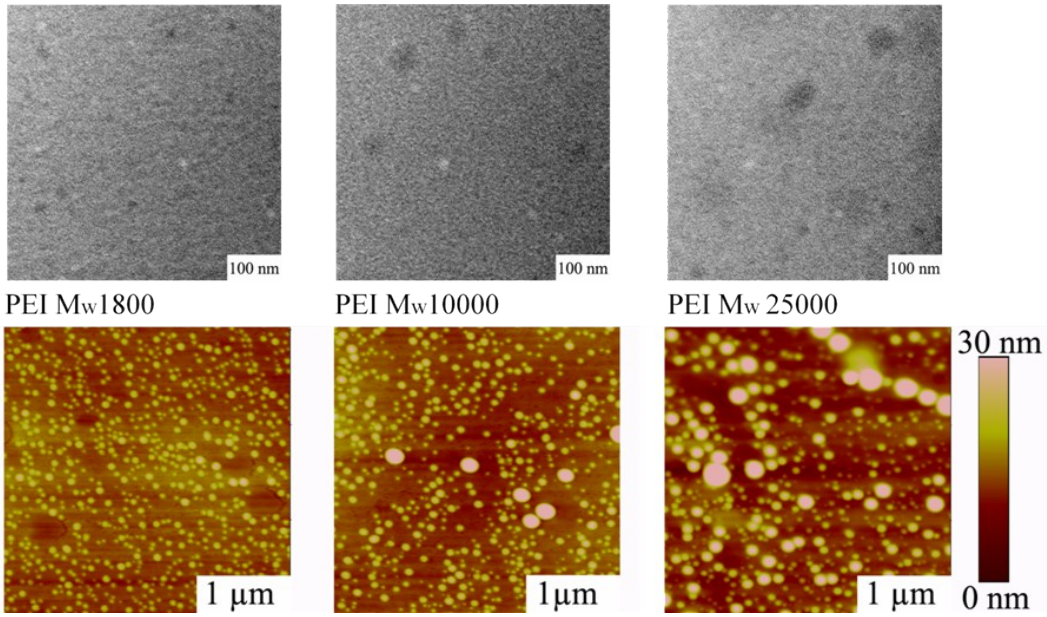


Figure S7. Optical properties of PEI dots (prepared from PEI 1800). The precise structure contributed to fluorescence may also be amine-based groups instead of graphite center and conjugated system.