Supporting Information

AIE cation functionalized layered zirconium phosphate nanoplatelets: ion-exchange intercalation and cell imaging†

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Experimental procedure

Materials.

Zirconium oxychloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, 98%, Tianjin Fuchen Chemical Co., Ltd.), phosphoric acid (H_3PO_4, 85% v/v, Beijing Beihua Chemical Co., Ltd.), triethylamine (Tianjin Guangfu Fine Chemical Co., Ltd.), butylamine (BA, Tianjin Fuchen Chemical Co., Ltd.). All other reagents in this work were used without further purification.

Synthesis of nano-sized α-ZrP.

A sample of 10.0 g $ZrOCl_2 \cdot 8H_2O$ was added into 100 mL 4.5 M H_3PO_4, and allowed to reflux at 100 ^oC for 24 h. The reaction mixture was filtered and washed with water and then with ethanol. The white α-ZrP product was dried at 60 ^oC.

Intercalation experiment.

Butylamine (0.2 mL) was added into 20 mL of aqueous solution containing α-ZrP (0.5 g), and then the resulting suspension was sonicated at room temperature for 20 min. The intercalation compound was centrifuged, washed with distilled water and air-dried, marked as ZrPBA.

In a typical intercalation experiment for ZrP3, ZrPBA (50 mg) was suspended in water (17 mL) under sonicated. Then the suspension solution was added to 33 mL of water containing TPEN (28.8 mg), with the molar ratio of TPEN to ZrP in this intercalation mixture of 0.3: 1. After the solution was stirred at 40 ^{o}C for 24 h, centrifuged and washed with abundant water, and freeze-dried to obtain ZrP3. Other loading levels were obtained with the same process just by varying the molar ratio of TPEN to α-ZrP, as shown in Table S1.

Cell viability (MTT assay)

The in vitro cytotoxicity of the α-ZrP and ZrP3 were investigated by MTT assays. In brief, HepG2 cells were plated in 200 μL media per well in a 96 well plate, with 8 wells left empty for blank controls. This was incubated in Dulbecco's modified Eagle's medium (DMEM) (3 mL) containing 10% fetal bovine serum (FBS) at 37 °C under a humidified atmosphere containing 5% CO_2, the cell culture medium changed once every other day to allow the cells to attach to the wells. ZrP3 powder (300 mg) was sterilized under ultraviolet irradiation for about 0.5 h, and then DMEM medium with 10% FBS culture medium was added. After incubated at 37 °C for 24 h, the powder was flitted. Then the extract solution was diluted to a specific concentration of 0.3, 0.6, 1.3, 2.5, 5, 10 and 20 mg/mL, respectively and immediately added into the cells with incubation for 24 h at 37 °C. The culture medium and 20 μL MTT solution (5 mg/mL) were added to each well. After cultured for 4 h, the culture medium was removed and 150 μL of

DMSO was added to each well, and then the plate was placed on a shaking table for about 10 min, and the absorbance of the suspension was measured at 492 nm.

Confocal laser scanning microscopy (CLSM).

HeLa cells were cultured in DMEM supplemented with 10% FBS at 37 °C and 5% CO_2. To check cellular uptake, HeLa cells (20–50% confluent) seeded on coverslips in a 12-well plate were incubated with ZrP3 (20 mg mL^{-1}) in culture medium at 37 °C and 5% CO_2. At 3 h post-incubation, the medium was removed and the cells were washed five times with PBS (pH = 7.4) and fixed with 2% formaldehyde in PBS for 10 min at room temperature.

Characterizations.

Powder X-ray diffraction (XRD) patterns were recorded on Rigaku D/MAX 2500/PC X-ray diffractometer with CuKα radiation and the scanning speed was 2^{o} min^{-1}. Transmission-electron-microscopy (TEM) images were recorded with a Tecnai F20 electron microscope. Infrared (IR) measurements of the samples dispersed in KBr pellets were performed on a Perkin-Elmer spectrum 430 FT-IR spectrometer. Scanning-electron-microscopy (SEM) images were recorded with a Tecnai F20 electron microscope. The UV/Vis excitation and emission spectra were obtained on a Shimadzu RF-5301PC spectrofluorometer. Laser scanning confocal microscope images were recorded on FluoView FV1000, Olympus. CHN elemental analyses were performed on a varioMICRO elemental analyzer.

Table S1. Textural parameters of the TPEN-containing ZrP materials.

Name	TPEN: ZrP intercalation molar ratio	Weight percentage of TPEN containing ZrP (%)	Interlayer distance (Å)
ZrP1	0.05:1	5.4	17.1
ZrP2	0.15:1	17.0	17.8
ZrP3	0.3:1	24.0	19.6

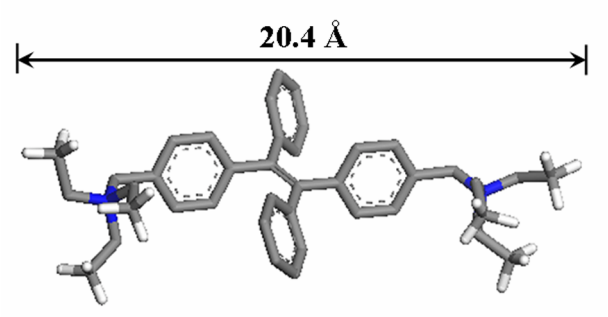

Figure S1. Molecular modeling of TPEN using Materials Studio program for molecular minimization. The end-to-end distance of TPEN is estimated to be 20.4 Å.

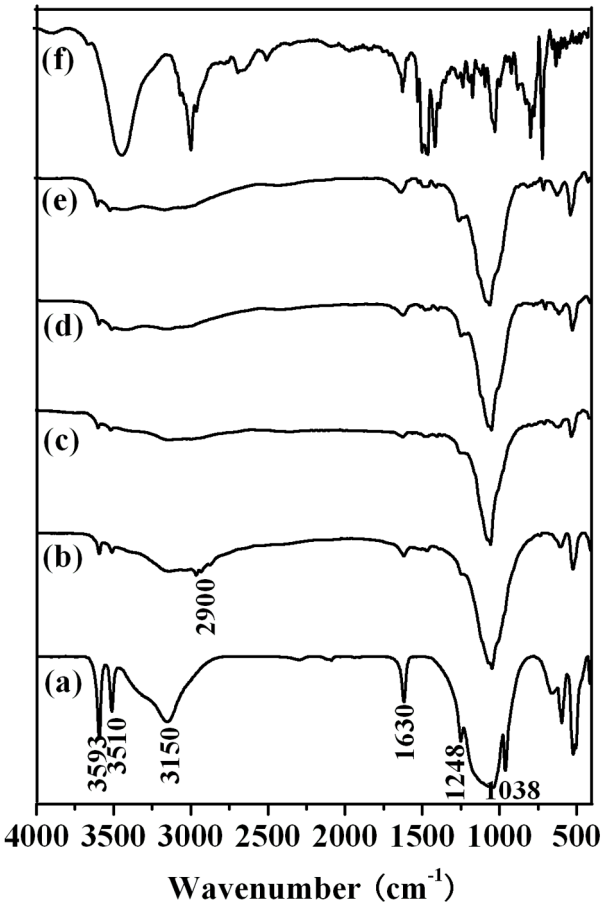

Figure S2. FT-IR spectra of (a) α-ZrP; (b) ZrPBA; (c) ZrP1; (d) ZrP2; (e) ZrP3; (f) TPEN.

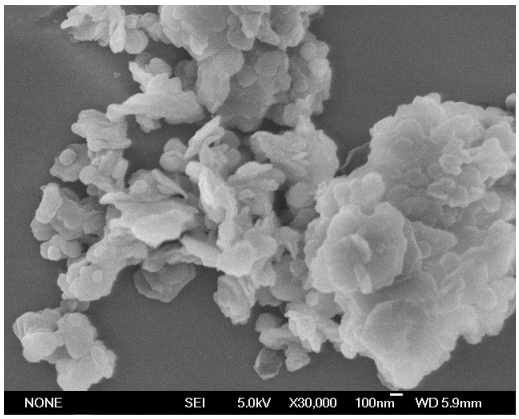

Figure S3. SEM of ZrP3.

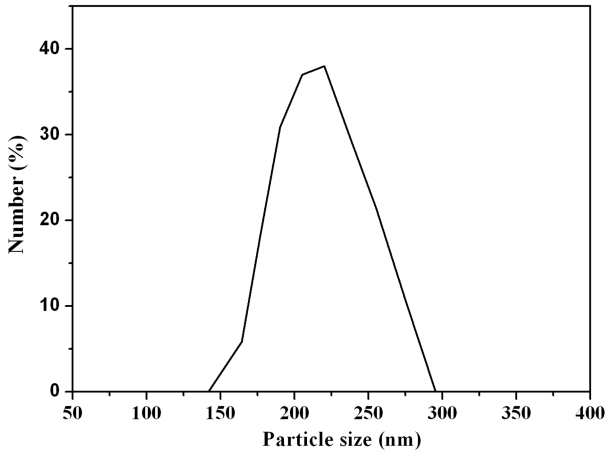

Figure S4. The hydrodynamic diameter of ZrP3 dispersed in water measured with the DLS method.

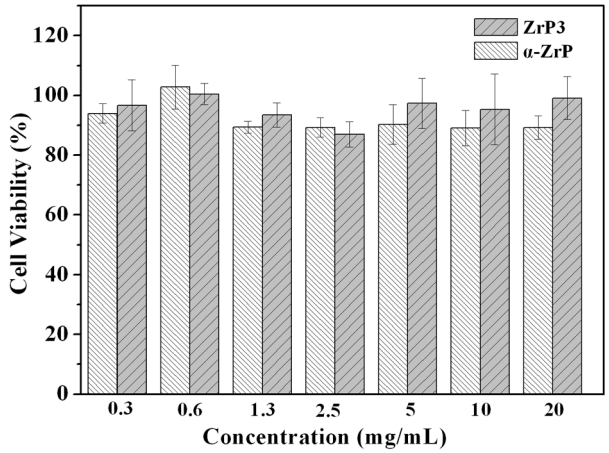

Figure S5. Cell viabilities of HepG2 cells incubated with the extract solutions of α-ZrP and ZrP3 at different concentrations.