Electronic Supplementary Information (ESI)

Bio-inspired mineral fluorescent hydrogels cross-linked by amorphous rare earth carbonates

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Experimental

Synthesis of RE-PAA hydrogels

All reagents were purchased commercially (Aladdin or Macklin) and used without further purification. Into a vigorously stirred 0.5 M aqueous solution of PAA (Mw ~ 250,000 g/mol) and 0.1 M $M^{3+}N_3$ (M = Eu^{3+}, Tb^{3+}, Yb^{3+}, Er^{3+}, Y^{3+}; N = Cl^- or NO_3^-), a 0.1 M Na_2CO_3 solution was added dropwise at room temperature. A sticky precipitate gradually formed around the stirring bar accompanied with a turbid solution containing non-gelling fractions. The pH of the mixture solution increased from ~ 1 to ~ 3. After 1 h, the turbid solution was discarded and the hydrogel was washed with deionized water several times until the supernatant solution was clear. All the hydrogels were then air-dried overnight at 50 °C.

Synthesis of ACC-PAA hydrogel

Into a vigorously stirred 0.1 M PAA (Mw ~ 250,000 g/mol) and 0.1 M $CaCl_2$, a 0.1 M Na_2CO_3 solution was added dropwise at room temperature. Complete hydrogel formation (Ca-PAA) was obtained within 1 h with the pH increasing from ~ 2 to ~ 7. The resultant hydrogel was purified and dried as described above.

Reaction with La^{3+} and Ce^{3+}

Into a vigorously stirred 0.5 M PAA (Mw ~ 250,000 g/mol) and 0.1 M $M^{3+}Cl_3$ (M = La^{3+}, Ce^{3+}), a 0.1 M Na_2CO_3 solution was added dropwise at room temperature, resulting in non-swellable and non-plastic agglomerates.

Characterizations.

Thermo gravimetric analysis (TGA) of dried hydrogels was performed on a Mettler Toledo TGA/1100SF by heating from 50 to 800 °C with a heating rate of 10 K/min under oxygen flow. Energy dispersive X-ray spectra (EDX) were acquired on a Hitachi S-4800. ATR-FTIR was carried out on a Thermo Scientific Nicolet 6700 (equipped with a diamond ATR crystal). The rheological behavior of hydrogels was investigated by a TA DHR-3 using 20-mm parallel-plate geometry at 25

ºC in the oscillation mode without pre-drying. Fluorescence spectra were measured with an Edinburgh FS5 at room temperature. X-ray diffraction (XRD) data were recorded on Bruker D8 diffractometer (Germany) with Ni-filtered Cu Kα radiation (40 kV, 40 mA).

Figures

X-ray diffraction (XRD)

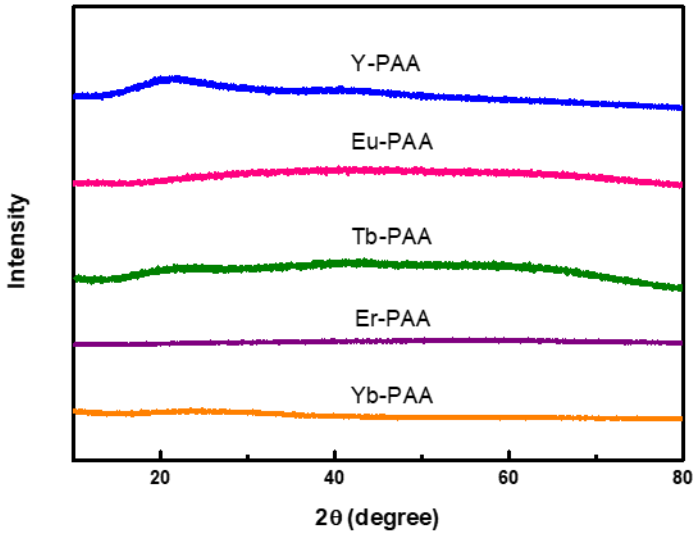

Fig. S1 X-ray diffraction patterns of all synthesized RE-PAA hydrogels in the dry state.

Energy Dispersive X-Ray Spectroscopy (EDX)

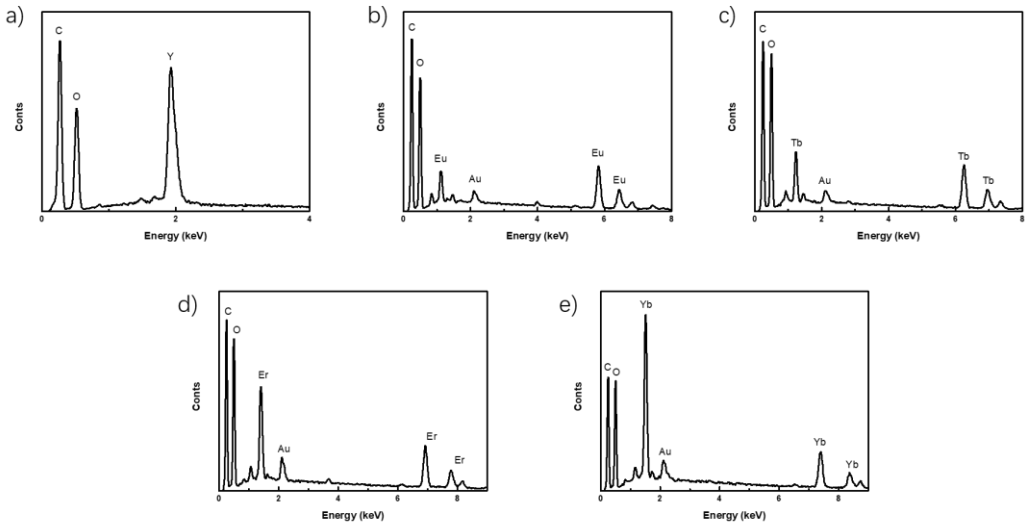

Fig. S2 EDX spectra of all synthesized RE-PAA hydrogels in the dry state: a) Y-PAA, b) Eu-PAA, c) Tb-PAA, d) Er-PAA, e) Yb-PAA. Note that presence of Au results from gold-covering of the sample.

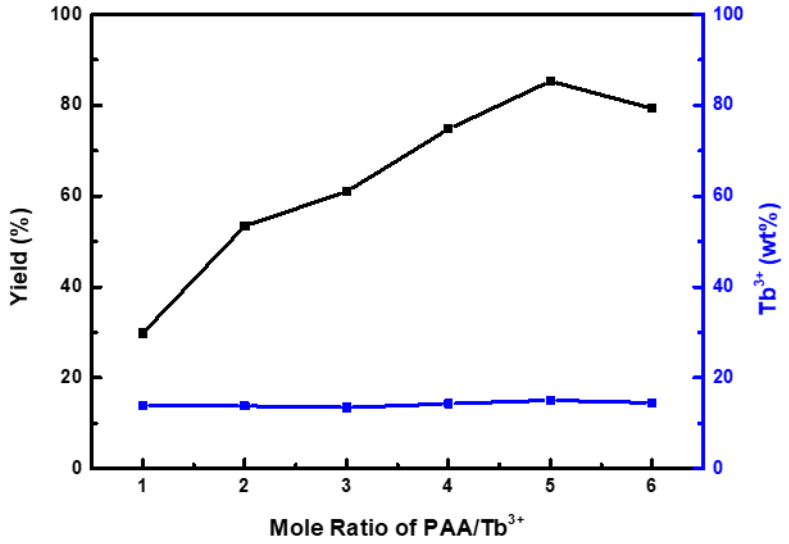

Fig. S3 Hydrogel yields and respective metal contents at different mole radios of PAA/RE. Here we used Tb-PAA hydrogel as the optimization model. The yields were calculated as follows:

$$\text{Yield}(\%) = \frac{m(\text{RE} - \text{PAA})_{\text{dry}}}{m(\text{RE}^{3+}) + m(\text{PAA}) + m(\text{CO}_3^{2-})} \times 100\%$$