Supplementary Information

Universal Gd^{3+}-based Hydrogel Matrix Hydrogel Matrix for Room-Temperature Phosphorescence Inducing

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Section S1. Experimental Section

S1.1 Materials

The detailed information on the materials was given in Table S1.

Table S1. The information on the materials used in this work.

Name	CAS No.	Specification	Supplier
adenosine 5'-monophosphatedisodium salt (AMP)	4578-31-8	99%	Aladdin, Shanghai, China
Gadolinium chloride hexahydrate ($GdCl_3 \cdot 6H_2O$)	13450-84-5	99.9%	Aladdin, Shanghai, China
N-2-hydroxyethyl piperazine-N'-2-taurine (HEPES)	7365-45-9	99%	Aladdin, Shanghai, China
Thioflavin T (ThT)	2390-54-7	-	Aladdin, Shanghai, China
Thiazol Orange (TO)	107091-89-4	~90%	Aladdin, Shanghai, China
Rhodol	3086-44-0	> 98%	Aladdin, Shanghai, China
Pt(II) meso-tetra (4-carboxyphenyl) porphine (PtTCPP)	94288-45-6	> 98%	frontier scientific, America
1-pyrenecarboxylic acid (PCA)	19694-02-1	> 97%	Aladdin, Shanghai, China
1,8-Naphthalimide (NpA)	81-83-4	> 98%	Aladdin, Shanghai, China
[1,1'-Biphenyl]-3,3',4,4'-tetracarboxylic acid (BPDA)	22803-05-0	> 98%	Aladdin, Shanghai, China
Lanthanum chloride hexahydrate ($LaCl_3 \cdot 6H_2O$)	17272-45-6	99.99%	Aladdin, Shanghai, China

Cerium chloride hexahydrate ($CeCl_3 \cdot 7H_2O$)	16651-27-7	99.99%	Aladdin, Shanghai, China
Praseodymium chloride hexahydrate ($PrCl_3 \cdot 7H_2O$)	10025-90-8	99%	Aladdin, Shanghai, China
Neodymium chloride hexahydrate ($NdCl_3 \cdot 6H_2O$)	13477-89-9	99.9%	Aladdin, Shanghai, China
Samarium chloride hexahydrate ($SmCl_3 \cdot 6H_2O$)	13465-55-9	99%	Aladdin, Shanghai, China
Europium chloride hexahydrate ($EuCl_3 \cdot 6H_2O$)	13759-92-7	99.9%	Aladdin, Shanghai, China
Terbium chloride hexahydrate ($TbCl_3 \cdot 6H_2O$)	13798-24-8	99.9%	frontier scientific, America
Dysprosium chloride hexahydrate ($DyCl_3 \cdot 6H_2O$)	15059-52-6	99.9%	Aladdin, Shanghai, China
Holmium chloride hexahydrate ($HoCl_3 \cdot 6H_2O$)	14914-84-2	99.9%	Aladdin, Shanghai, China
Erbium nitrate hexahydrate ($Er(NO_3)_3 \cdot 6H_2O$)	13476-05-6	99.99%	Aladdin, Shanghai, China
Thulium chloride hexahydrate ($TmCl_3 \cdot 6H_2O$)	1331-74-4	99.99%	Aladdin, Shanghai, China
Ytterbium chloride hexahydrate ($YbCl_3 \cdot 6H_2O$)	10035-01-5	99.99%	Aladdin, Shanghai, China
Lutecium chloride hexahydrate ($LuCl_3 \cdot 6H_2O$)	15230-79-2	99.9%	Aladdin, Shanghai, China
Yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$)	10025-94-2	99.9%	frontier scientific, America
22AG DNA	-	-	Sangon Biotech, Shanghai, China

S1.2 Apparatus

All the instrumental information used for characterizations was given in Table S2.

Table S2. The instrumental information used in this work.

Characterization items	Type	Manufacturer
UV/Vis absorption spectra	Lambda-365 spectormeter	Perkin Elmer, USA
Fourier Transform infrared spectra	INVENIO®R	Bruker, Germany
PL spectra & time-resolved emission spectrum (TRES)	FluoroMax-4P spectrofluorometer	Horiba Scientific, USA
Phosphorescence lifetime & QY	Fluolog-3 spectrofluorometer with an integration sphere (IS80, Labsphere) Lifetime excitation: Spectra LED	Horiba Jobin Yvon, USA
Scanning electron microscope	JSM-7500F	Japan electron optics laboratory co., ltd, Japan
Transmission electron microscope	Tecnai G2 F20 S-TWIN	FEI, USA
Confocal Laser Microscope	N-SIM/A1R MP+	Nikon, Japan
Dynamic frequency sweep	Kinexus Prime lab+	NETZSCH, Germany
X-ray Photoelectron Spectroscopy	AXIS Ultra DLD	Kratos, England

S1.3 Experimental Information

Preparation of Gd^{3+}-AMP hydrogel. Adenosine 5'-monophosphate sodium salt (AMP, 100 mM, 1 mL) was dissolved in HEPES buffer (100 mM, pH 7.4), then $GdCl_3$ solution (10 mM, 1 mL) was added dropwise. Then the mixture was stirred for 2 h at room temperature.

Preparation of dye gels. Potential phosphorescent molecules (10 mM in DMSO, 20 μL) were mixed with AMP solution (100 mM in HEPES buffer, 1 mL). Then, $GdCl_3$ solution (10 mM, 1 mL) was dropwise added with stirring to obtain dye-doped hydrogels (dye gel).

Preparation of ThT @ G4. ThT (100 μM, 1 mL) was dissolved in Tris buffer (50 mM, pH 7.2), then 22AG DNA (12.5 μM,1 mL) was added with stirring to obtain ThT@G4.

Characterization of hydrogels. Transmission Electron Microscopy (TEM) was performed on a Philips CM10 microscope. A drop of sample dispersion (1 mg/mL) was placed on a 230-mesh holy carbon copper grid. After 30 s, the excess solution was removed by a piece of filter paper. The above prepared hydrogel was lyophilized to obtain solid powders for X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) analysis.

Phosphorescence measurements. Phosphorescence spectra of the dye gels were recorded using a HORIBA FluoroMax-4P spectrofluorometer with a delay time of 0.1 ms. The phosphorescence lifetimes and the time-resolved emission spectra (TRES) of

dye gels were collected on the HORIBA FluoroLog-3 spectrofluorometer with spectra LEDs as the excitation sources. The phosphorescence quantum yields (Φ_P) of dye gels were measured in an integrating sphere (IS80, Labsphere).

Photoluminescence quantum yield. Absolute quantum yield (Φ) of dye gel was measured by the Fluolog-3 spectrofluorometer with an integration sphere (IS80, Labsphere) in this work. The peak areas of fluorescence emission, RTP emission, and integration absorption are integrated by Origin 2016.

In vitro **imaging.** For cell imaging, L929 mouse fibroblast cells and 4T1 breast cancer cells were chosen as the model. PtTCPP (100 μL to 1 mL culture medium) was added to confocal dishes containing 10^5 cells, and co-incubated for different times. The excitation wavelength was 405 nm, and the Cy5 channel was used to collect the phosphorescence emission.

In vivo **imaging.** Healthy female BALB/c mice were chosen in this work. To establish a tumor-bearing model, 10^6 4T1 cells in 100 μL PBS were subcutaneously injected, then waited for 1 week. Through intratumorally injecting 50 μL PtTCPP and PtTCPP gel, the photographs of mice were collected by the IVIS imaging system.

Three-dimensional code establishment. Guest gels were prepared as above. Then, the hydrogels were added to square molds and slightly dried to form the 3D code. For scanning, the code was taken with a smartphone app, namely 3D code.

White light-emitting hydrogel. PtTCPP (20 mM in DMSO, 5 μL) and ThT (20 mM in DMSO, 35 μL) were mixed with AMP solution (100 mM in HEPES buffer, 1 mL). Then, $GdCl_3$ solution (10 mM, 1 mL) was dropwise added with stirring to obtain PtTCPP and ThT co-encapsulated white light hydrogels (PtTCPP & ThT gel). The water contents were calculated through weighing hydrogels before and after drying.

Section S2. Materials Characterization

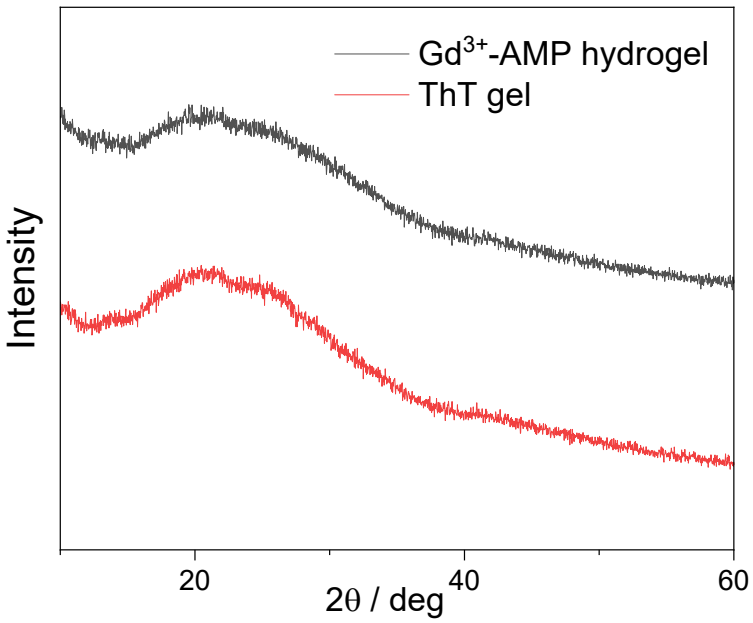

Figure S1. XRD of Gd^{3+}-AMP hydrogel and ThT gel.

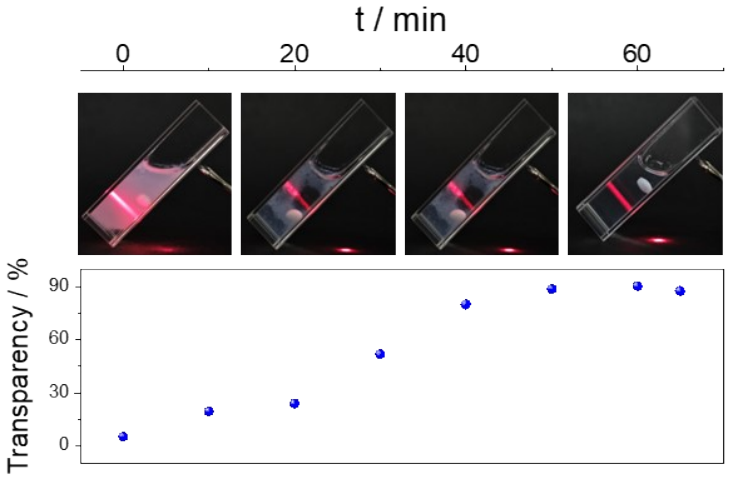

Figure S2. Photographs at predesigned time intervals in Gd^{3+}-AMP hydrogel formation.

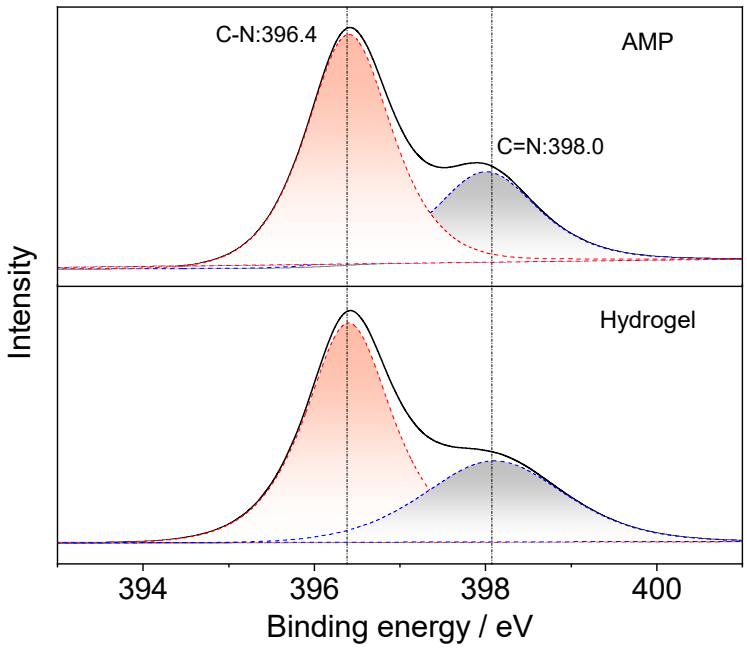

Figure S3. N 1s XPS spectra of AMP and Gd-AMP hydrogel.

Section S3. Spectroscopic characterization of ThT gel

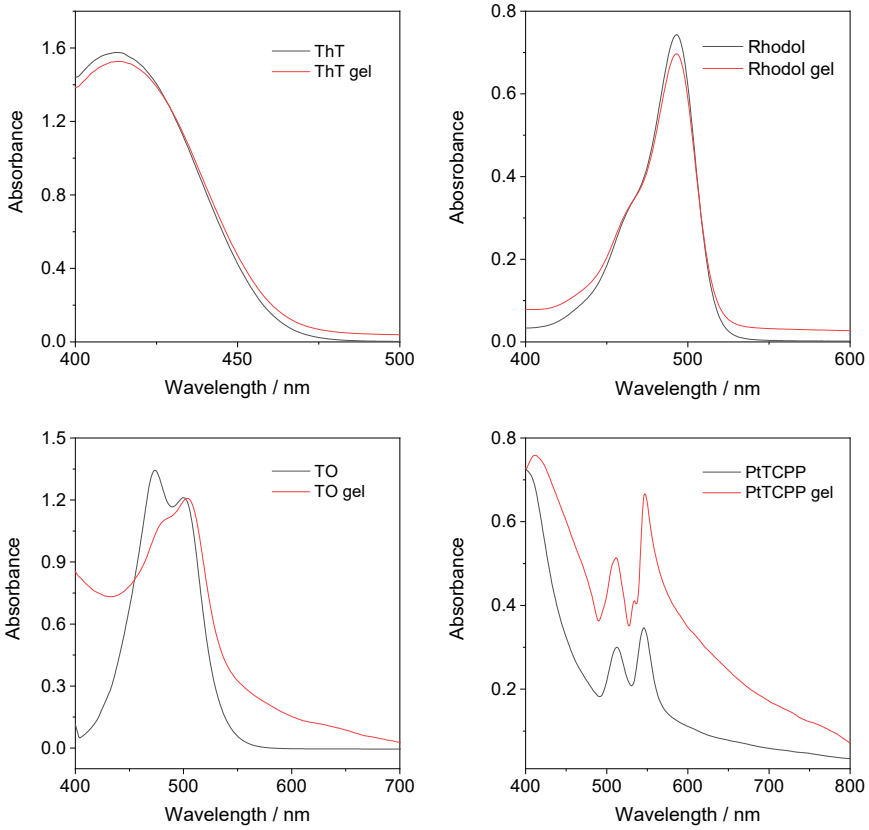

Figure S4. UV/vis absorption spectra of dye@Gd^{3+}-AMP hydrogel (red line, without centrifugation) and corresponding aqueous dye (black line, [dye] = 62.5 mM). Quartz cell with a 1 cm path length was used.

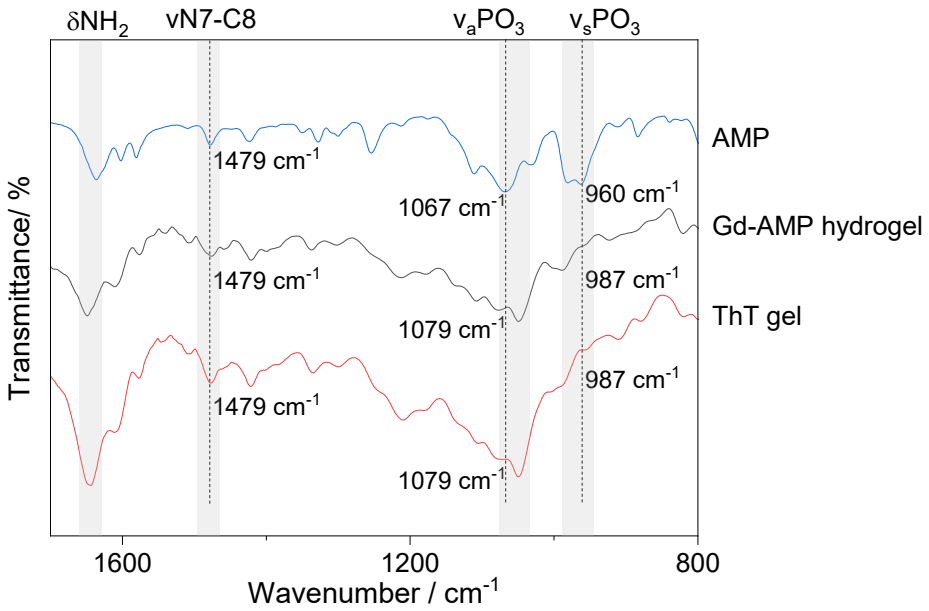

Figure S5. FTIR spectra of AMP, Gd-AMP hydrogel and ThT gel.

Table S3. Changes in wavenumbers of stretching vibrations in Figure S5.

	wavenumber (cm^{-1})		
	ν(N7-C8)	$\nu_a(PO_3)$	$\nu_s(PO_3)$
5'-AMP disodium salt	1479	1067	960
Gd-AMP hydrogel	1479	1079	987
ThT gel	1479	1079	987

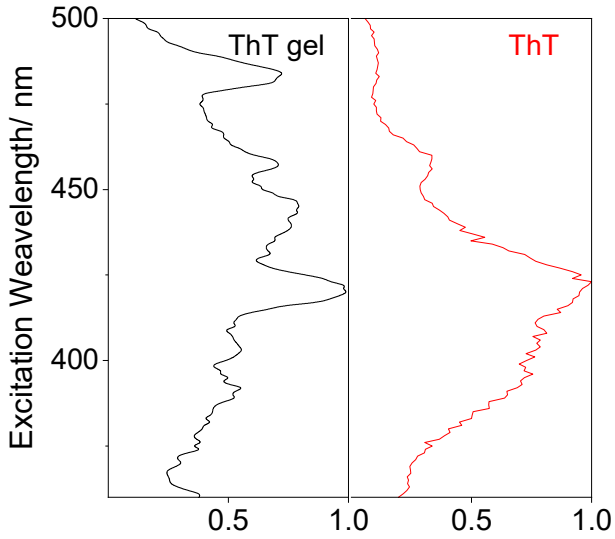

Figure S6. Phosphorescence excitation of free ThT and ThT gel (λem = 570 nm).

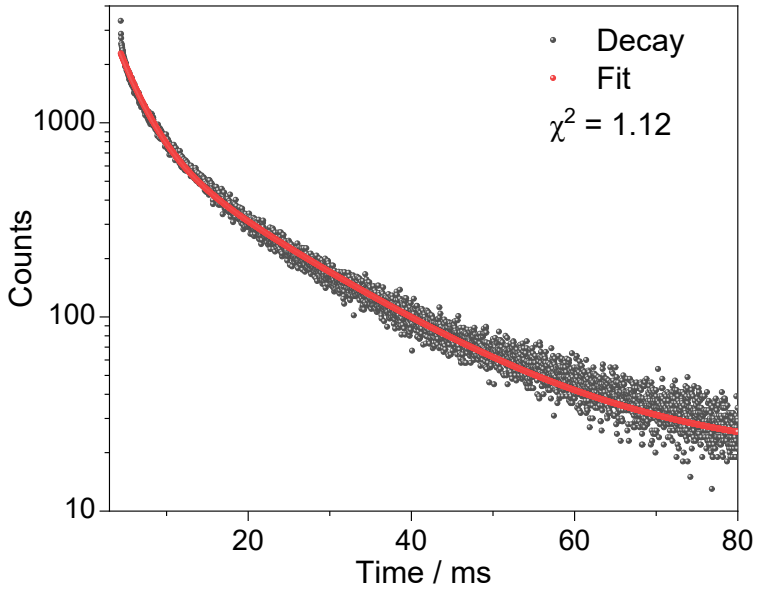

Figure S7. Phosphorescence lifetimes of ThT gel (λ_{em} = 570 nm).

Section S4. Universal hydrogel matrix for inducing aqueous RTP

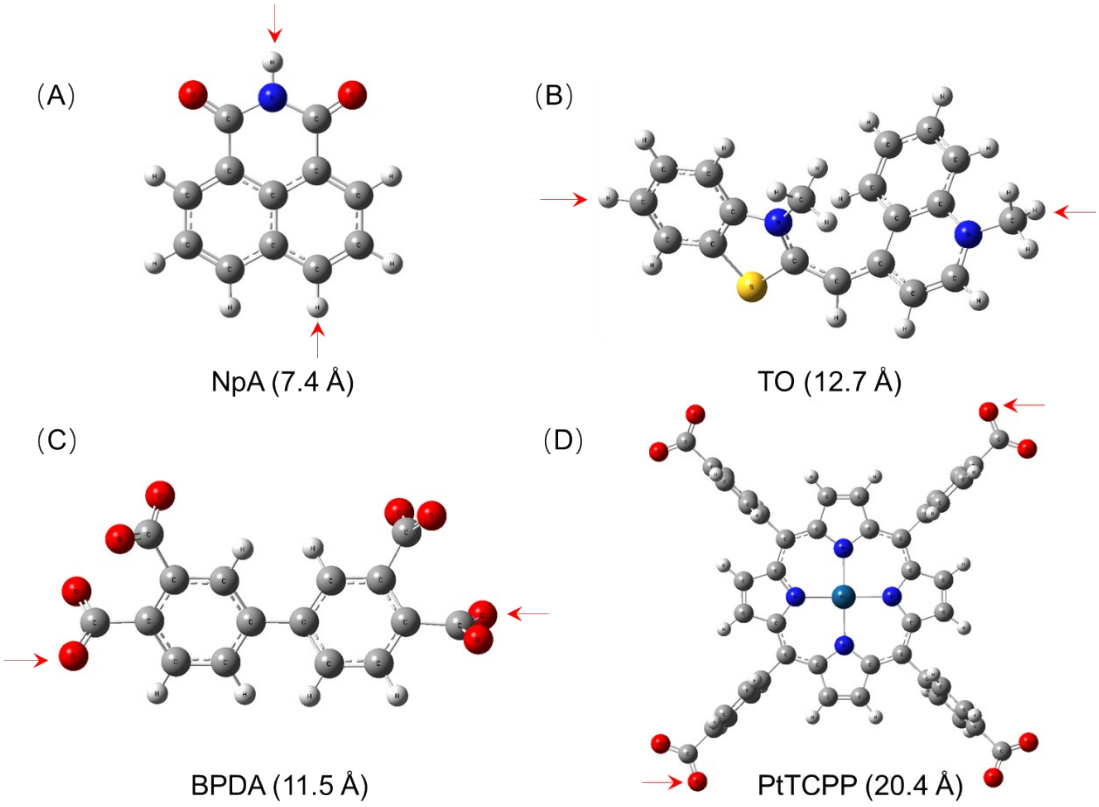

Figure S8. The optimized molecular structures of NpA, TO, BPDA and PtTCPP.

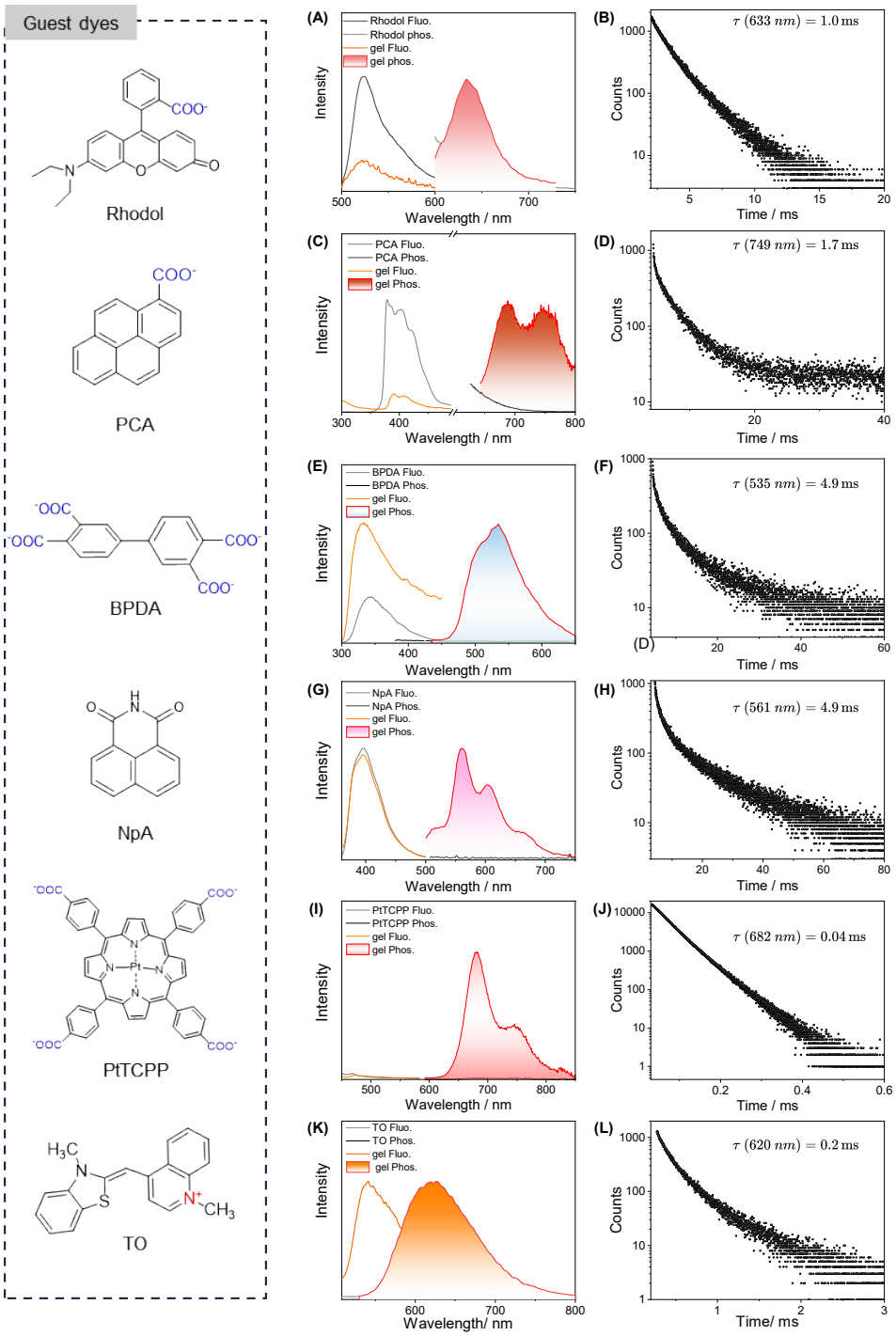

Figure S9. The steady-state and delayed emission spectra of (A) Rhodol and Rhodol gel; (C) PCA and PCA gel; (E) BPDA and BPDA gel; (G) NpA and NpA gel; (I) PtTCPP and PtTCPP gel; (K) TO and TO gel; the phosphorescence lifetimes of (B) Rhodol and Rhodol gel (λ_{em} = 633 nm); (D) PCA and PCA gel (λ_{em} = 749 nm); (F) BPDA and BPDA gel (λ_{em} = 535 nm); (H) NpA and NpA gel (λ_{em} = 561 nm); (J) PtTCPP and PtTCPP gel (λ_{em} = 682 nm); (L) TO and TO gel (λ_{em} = 620 nm).

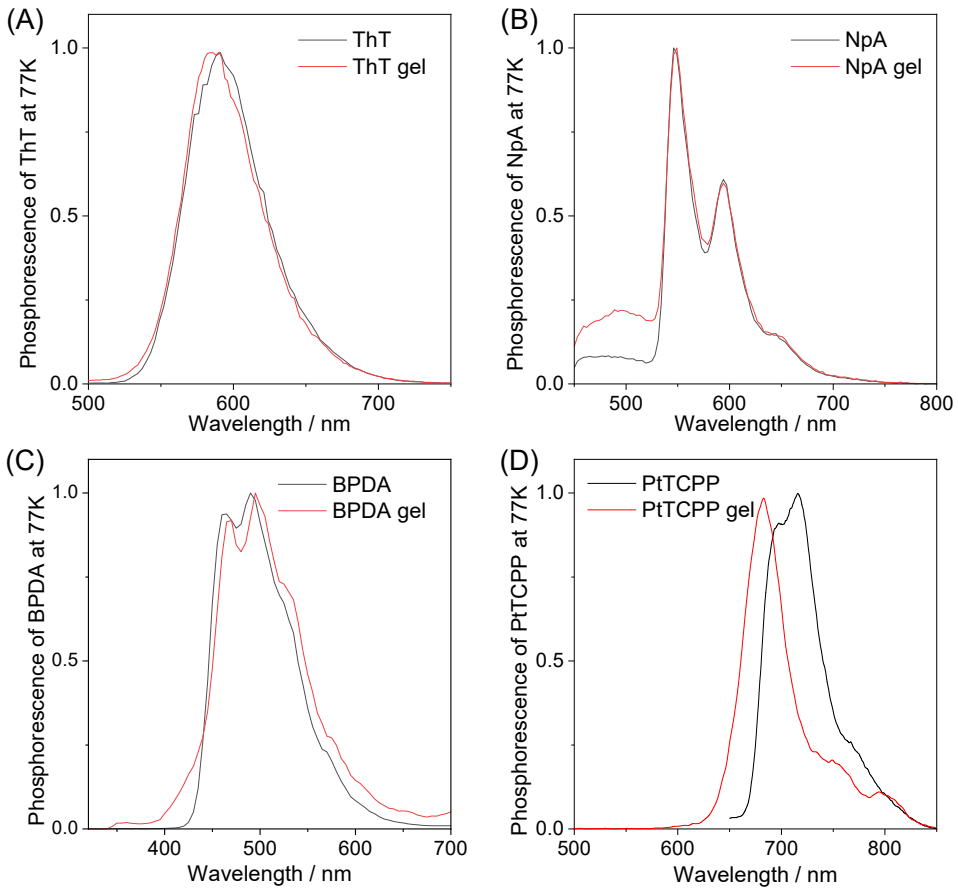

Figure S10. Phosphorescence spectra of (A) ThT and ThT gel, (B) NpA and NpA gel, (C) BPDA and BPDA gel, (D) PtTCPP and PtTCPP gel under 77K.

Section S5. PtTCPP gel for bioimaging.

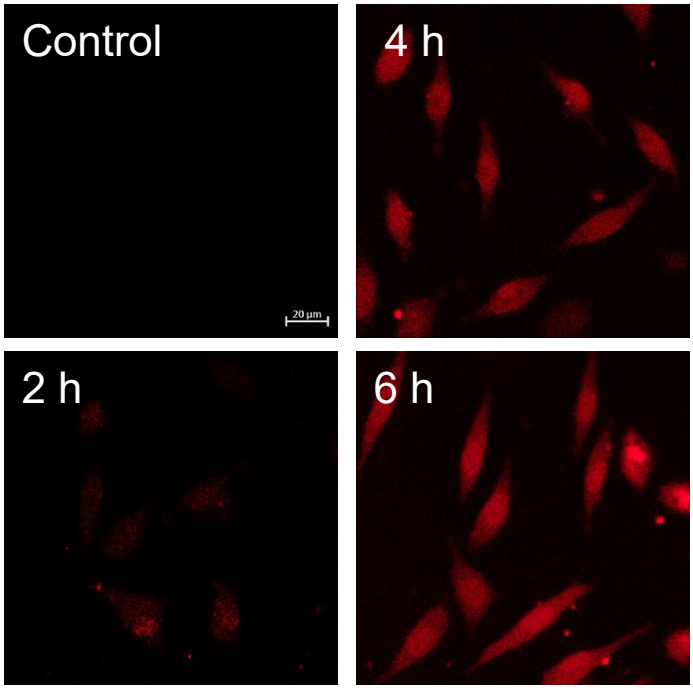

Figure S11. Phosphorescence confocal imaging of L929 cells with different incubation times.

Section S6. Guest gel for information coding.

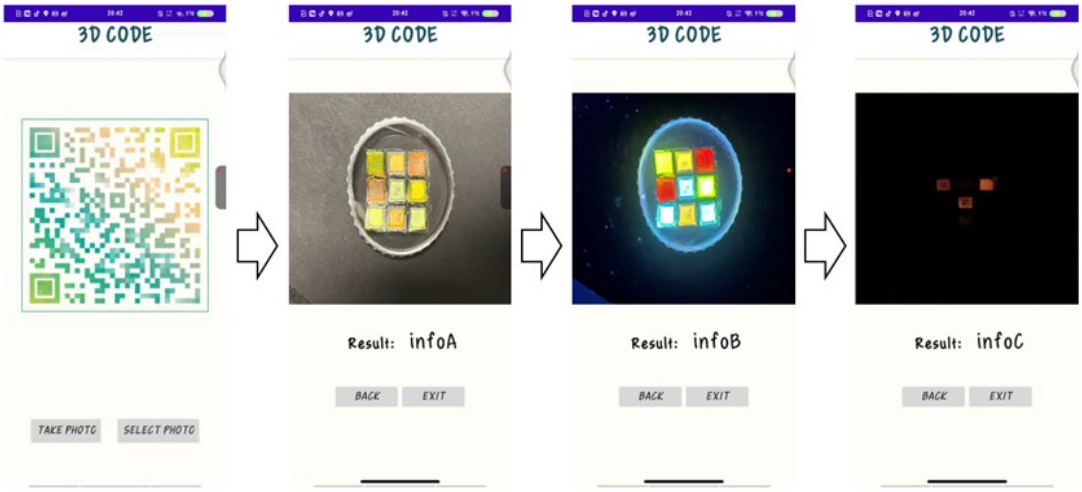

Figure S12. The process of using smart phone app to read out information.

Section S7. Construction of white light-emitting hydrogel.

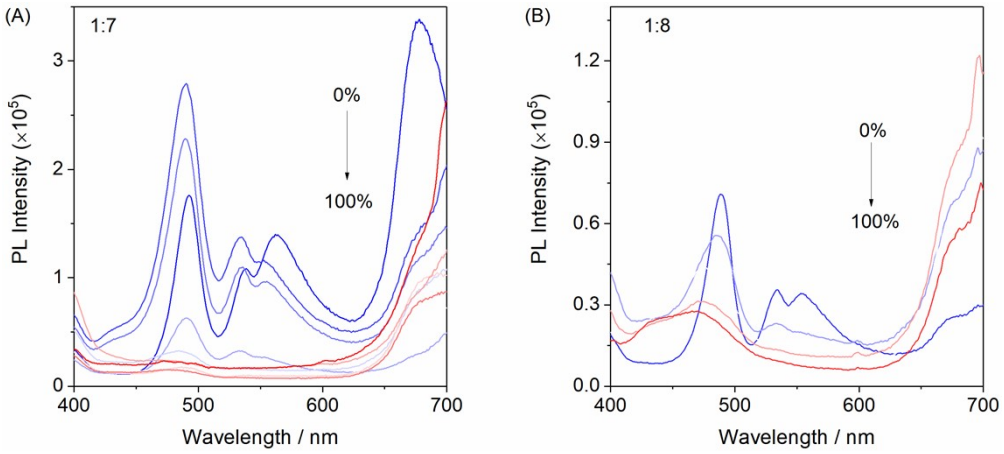

Figure S13. PL spectra of ThT and PtTCPP co-encapsulated hydrogels with different water contents: (A) ThT : PtTCPP = 1:7; (B) ThT : PtTCPP = 1:8.