Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

A Triplet State Energy Transfer Material Design Concept Enables Enhanced Visualization Applications

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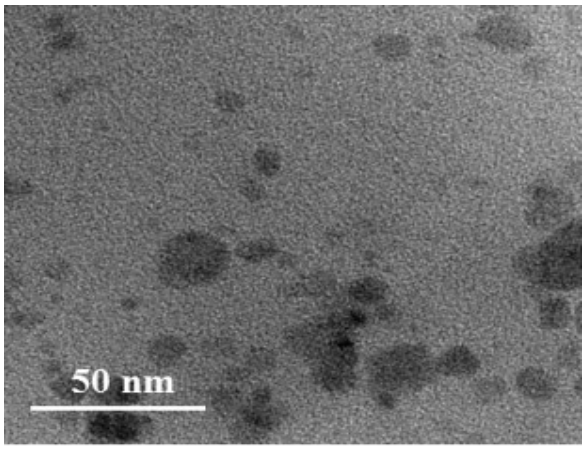

Fig. S1 TEM image of CD powder.

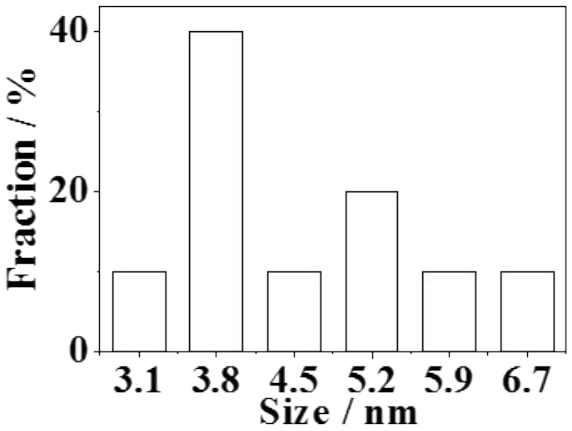

Fig. S2 Particle size distribution of CD powder.

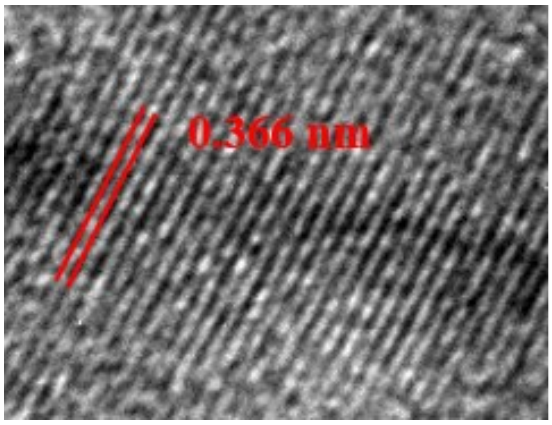

Fig. S3 HRTEM of CD.

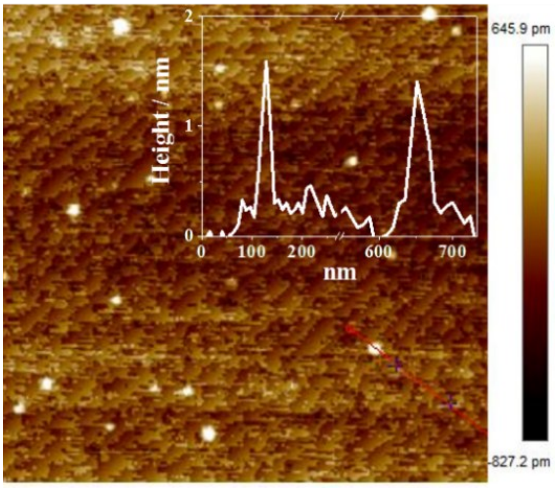

Fig. S4 AFM image of CD.

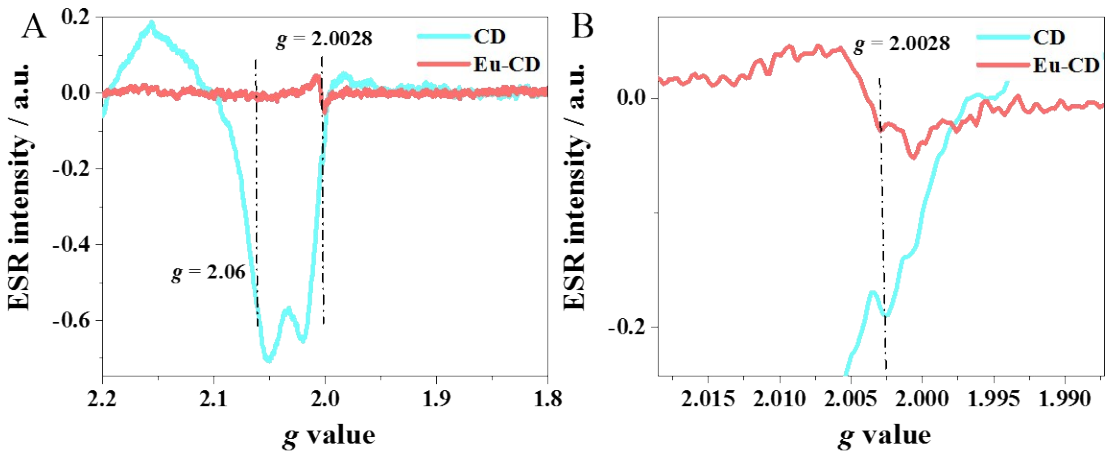

Fig. S5 (A) ESR spectrum of CD and Eu-CD powder. (B) The partial amplification of (A).

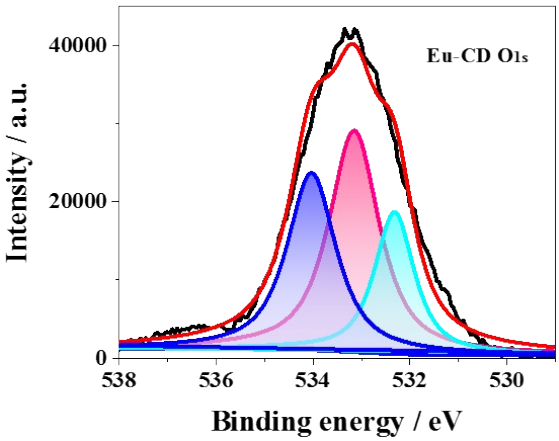

Fig. S6 XPS spectrum of Eu-CD.

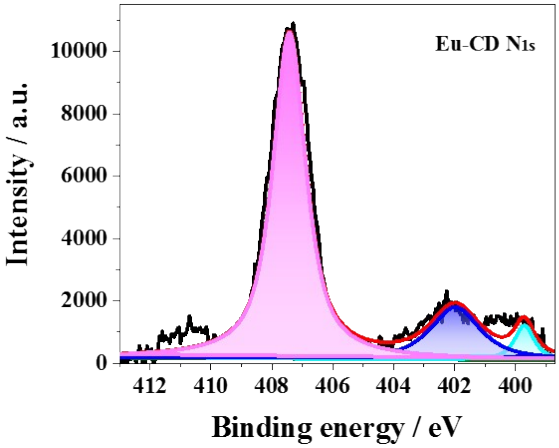

Fig. S7 XPS spectrum of Eu-CD.

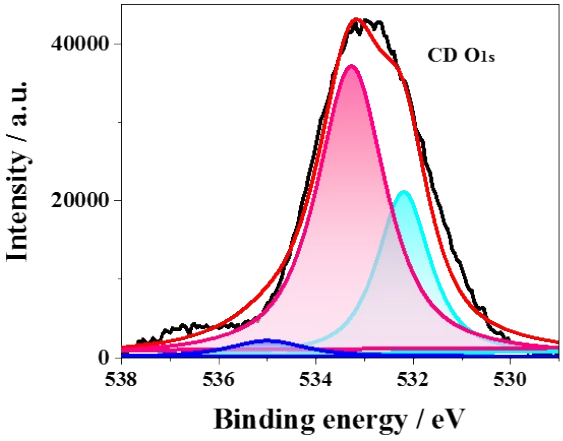

Fig. S8 XPS spectrum of CD powder.

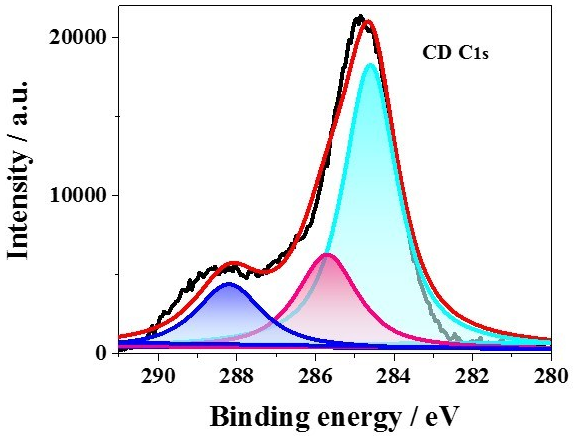

Fig. S9 XPS spectrum of CD powder.

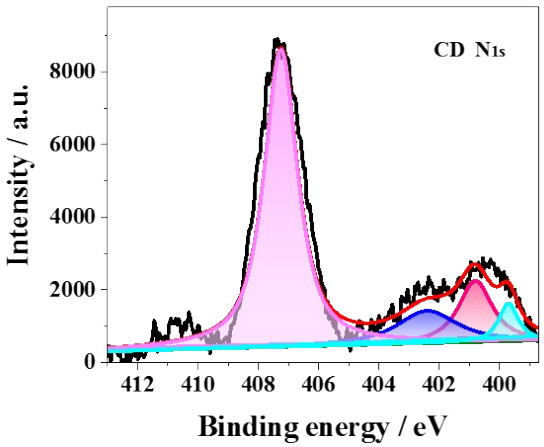

Fig. S10 XPS spectrum of CD powder.

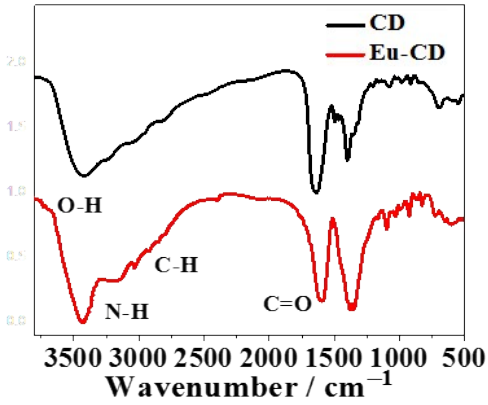

Fig. S11 FT-IR spectra of CD and Eu-CD powder.

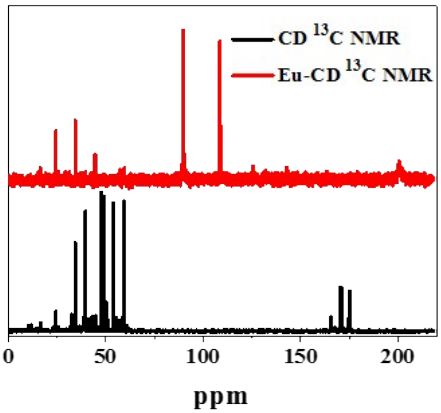

Fig. S12 ^{13}C NMR spectra of CD and Eu-CD powder.

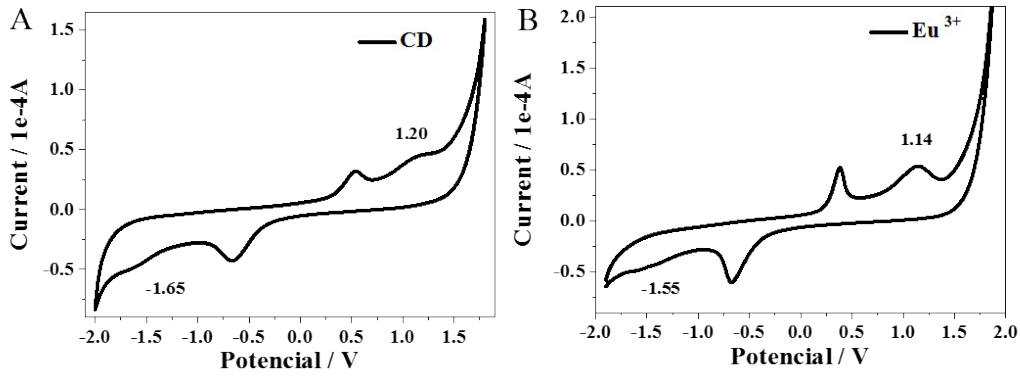

Fig. S13 (A) The cyclic voltammogram curves of CD. (B) The cyclic voltammogram curves of Eu^{3+}.

Experimental detail: First, the working electrodes were polished with polishing powder, and the surface oxides were removed by full grinding. Then the working electrodes were ultrasonic cleaned with ethanol and pure water, respectively. After that, 10 μL CD or $Eu(NO_3)_3$ solution was dripped onto the polished working electrode surface, dried with nitrogen, and quickly put into PB solution to test the cyclic voltammetry curve. The onset of oxidation (E_{ox}) and reduction (E_{red}) potential were obtained.

The HOMO and LUMO energy levels of CD were calculated according to the following equations:

$$E_{(HOMO)} = -e\,(E_{ox} + 4.4)\ (eV)$$
$$E_{(LUMO)} = -e\,(E_{red} + 4.4)\ (eV)$$

Where E_{ox} and E_{red} are the onset of oxidation and reduction potential, respectively. E_{ox} and E_{red} were determined to be 1.20 V and –1.65 V for CD.

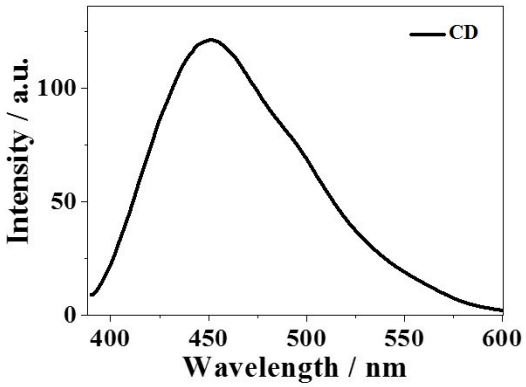

Fig. S14 Fluorescence emission spectra of CD powder.

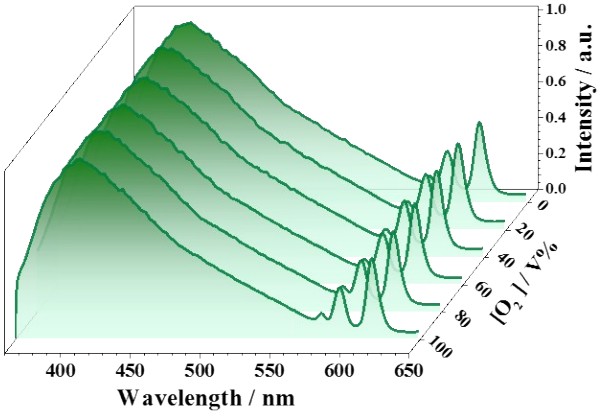

Fig. S15 Emission spectra of Eu-CD/PVA film under different oxygen concentrations.

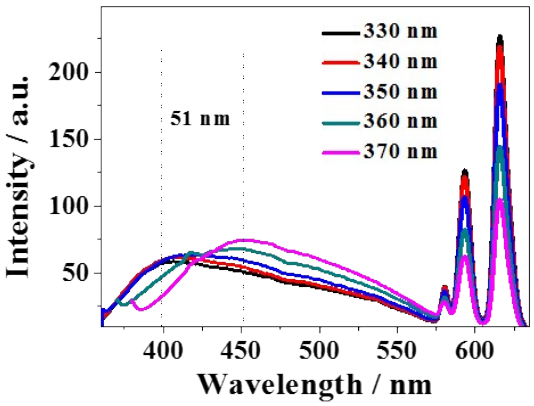

Fig. S16 Fluorescence spectra of Eu-CD powder with different excitation wavelength.

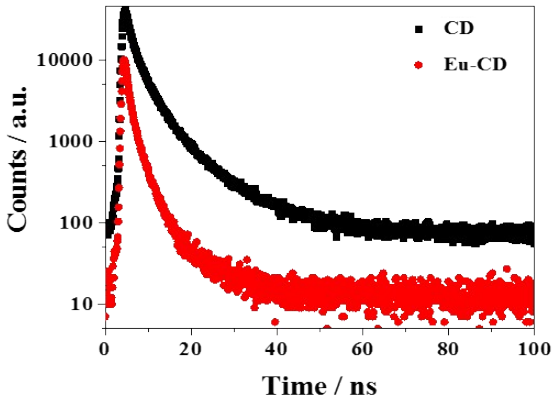

Fig. S17 Time-resolved fluorescence decays (λ_{em} = 450 nm).

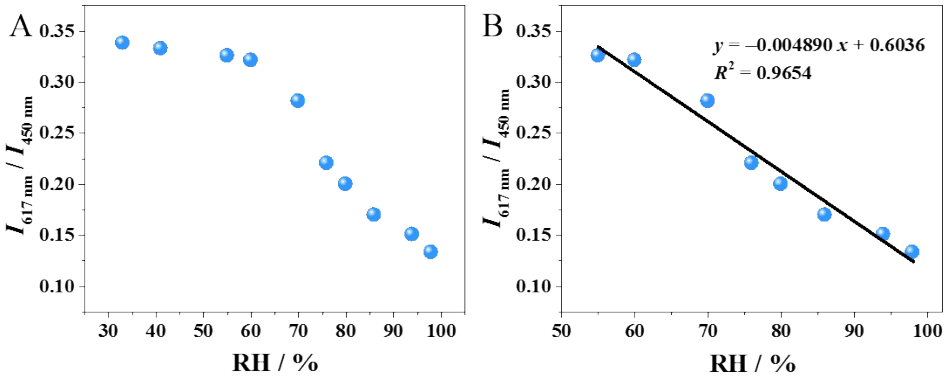

Fig. S18 (A) Emission intensity ratio of Eu-CD ($I_{617\ nm}/I_{450\ nm}$) vary with RH (33%–98%). (B) Plots of $I_{617\ nm}/I_{450\ nm}$ as a function of RH (55%–98%).

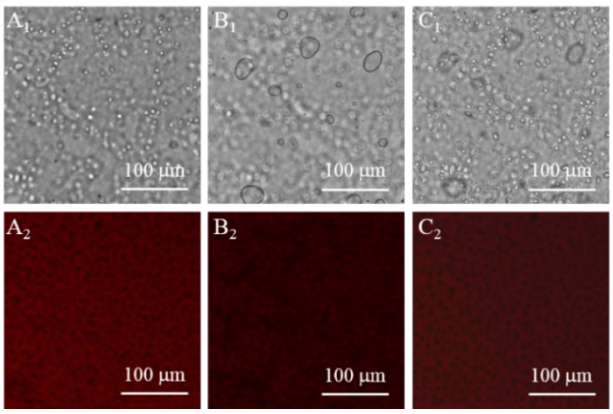

Fig. S19 Bright field (A_1, B_1 and C_1) and dark field (A_2, B_2 and C_2) of real-time 2D fluorescence image of Eu-CD/PVA film. Original film (A_1 and A_2), wet film (B_1 and B_2) and recycled film (C_1 and C_2).

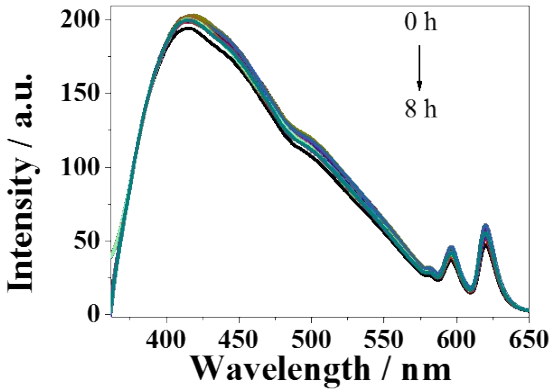

Fig. S20 Fluorescence emission spectra of Eu-CD/PVA film at 98% humidity. Spectra were recorded from 0 to 8 h at 0.5 h intervals.

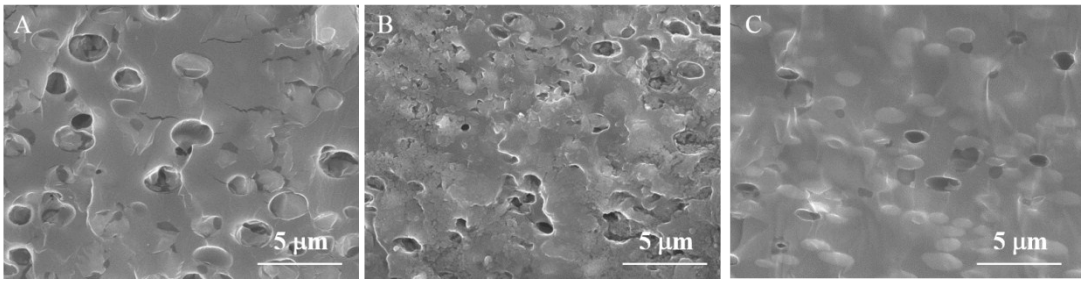

Fig. S21 The magnified cross section SEM images of Eu-CD/PVA film. (A) original film; (B) wet film; (C) recycled film.

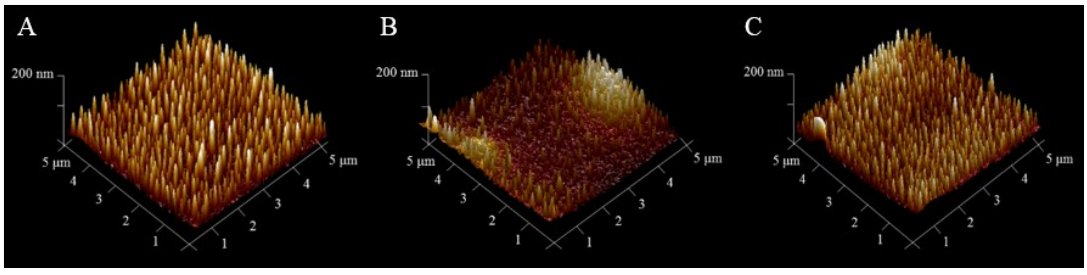

Fig. S22 AFM images of Eu-CD/PVA film. (A) original film; (B) wet film; (C) recycled film.

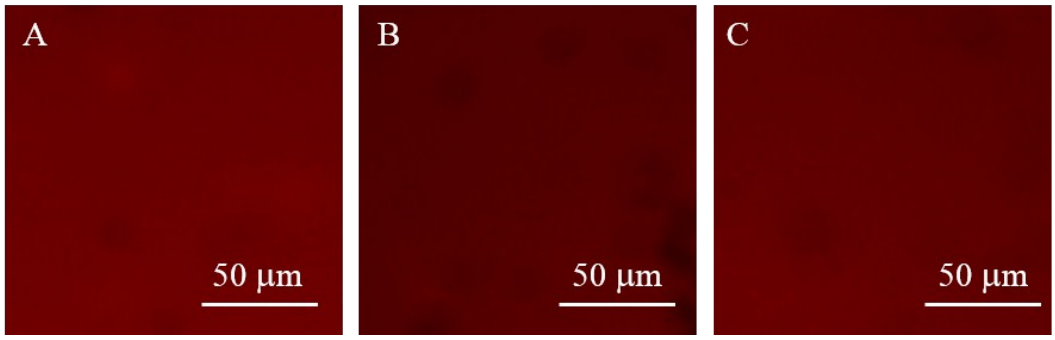

Fig. S23 Fluorescence microscopy images of Eu-CD/PVA film during the drying-wetting treatment. (A) Original film; (B) Wet film; (C) Recycled film.

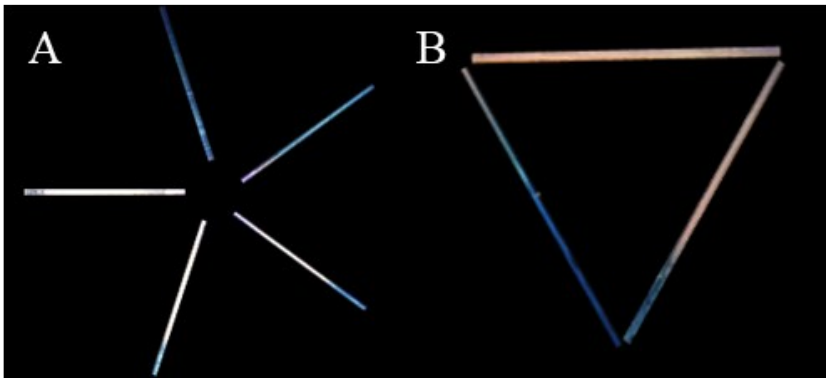

Fig. S24 The color change of the glass tube after it encounters water vapor.

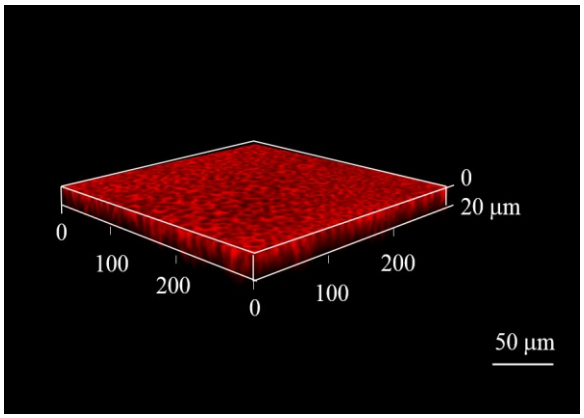

Fig. S25 3D-representation of fluorescence confocal microscopy images of Eu-CD/PVA film (300 ×300 μm^2).

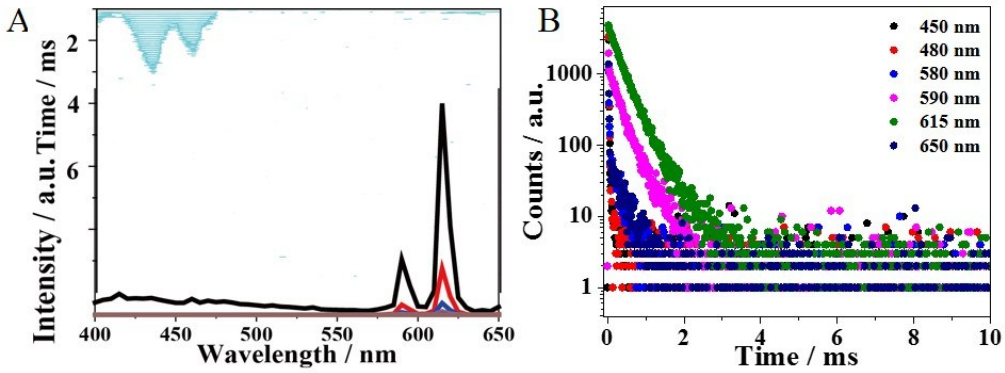

Fig. S26 (A) Time-resolved emission spectra of Eu^{3+}/PVA film were recorded from 0 to 10 ms after excitation at 200 μs intervals at RH of 33%. The upper inset shows a transient luminescence decay image of Eu^{3+}/PVA film recorded at 300 K. (B) Time-resolved decay curves of Eu^{3+}/PVA film with different emission wavelengths at RH of 33%. Luminescence decay curves were recorded as a function of the emission wavelength in the range 400–650 nm (wavelength increment of 5 nm).

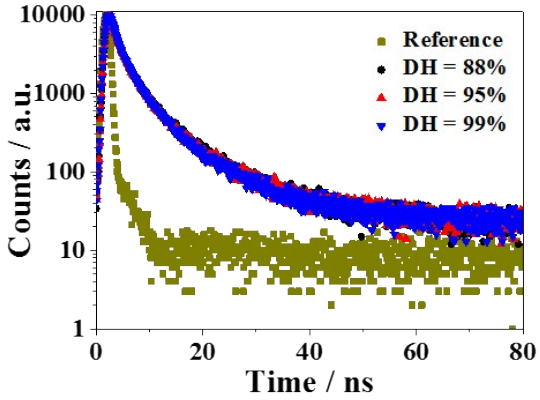

Fig. S27 Time-resolved fluorescence decays of Eu-CD/PVA film with different degrees of hydrolysis (DH).

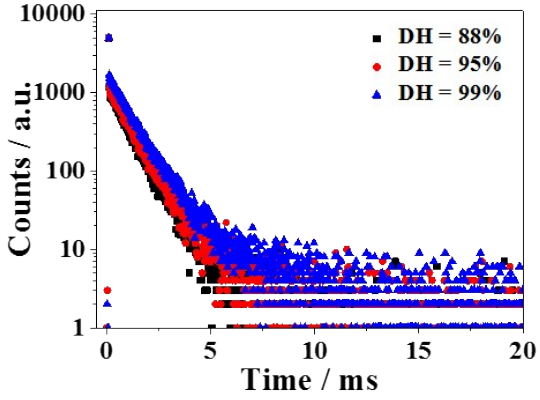

Fig. S28 Time-resolved phosphorescence decays of Eu-CD/PVA film with different DH.

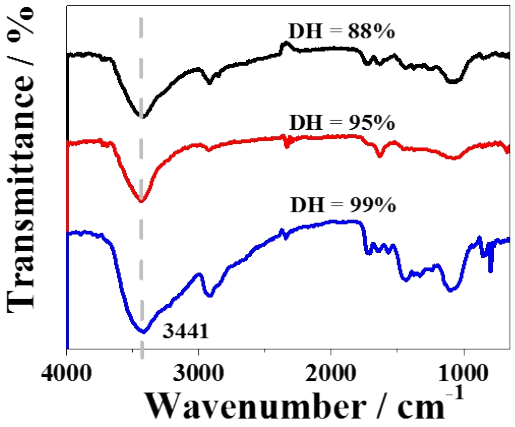

Fig. S29 FT-IR curves of pure PVA powder.

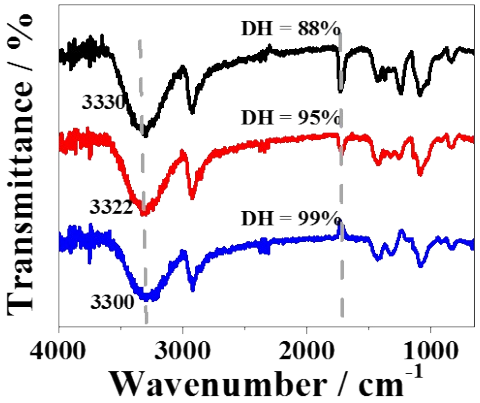

Fig. S30 FT-IR curves of pure PVA film.

Table S1 The parameters of phosphorescent lifetime for CD at different states (pure CD and Eu-CD).

Samples	τ_{ave} [ns]	η_{ET} [%]	τ_{Eu} [μs]
CD (Eu^{3+} : CD = 0 : 1)	9.74×10^8	-	-
Eu-CD (Eu^{3+} : CD = 0.1 : 1)	4.51	100	584
Eu-CD (Eu^{3+} : CD = 1 : 1)	3.11	100	790
Eu-CD (Eu^{3+} : CD = 2 : 1)	3.13	100	530
Eu^{3+} (Eu^{3+} : CD = 1 : 0)	-	-	167

Where τ_{ave} is the lifetime of the pure CD donor and that of Eu-CD with the different ratio of Eu^{3+} acceptor at 525 nm, respectively.

Table S2 The parameters of lifetime for CD at different states (pure CD and Eu-CD).

Samples	τ_{ave} [ns]	$\eta_{total\ ET}$ [%]	k_{total} [s^{-1}]	k_{ET} [s^{-1}]
CD (Eu^{3+} : CD = 0 : 1)	6.83	-	1.46×10^8	-
Eu-CD (Eu^{3+} : CD = 0.1 : 1)	2.98	56.4	3.35×10^8	1.89×10^8
Eu-CD (Eu^{3+} : CD = 1 : 1)	2.20	67.8	4.54×10^8	3.08×10^8
Eu-CD (Eu^{3+} : CD = 2 : 1)	3.54	48.2	2.82×10^8	1.36×10^8
Eu^{3+} (Eu^{3+} : CD = 1 : 0)	-	-	-	-

Where τ_{ave} represents the lifetime at 450 nm, and the total ET efficiency ($\eta_{total\ ET}$) was calculated according to equation (1).
The total decay rate (k_{total}) was calculated using the following equation (2):

$$k_{total} = \left(k_r + k_{nr}\right) = \frac{1}{\tau_{Eu}} \quad (2)$$

Table S3 Quantum yield (QY) of CD, Eu-CD and $Eu(NO_3)_3$ powder.

Samples	Emission range [nm]	QY [%]	Total QY [%]	Temperature [K]
CD	400–650	0.84	0.84	77
Eu-CD	400–650	-	-	77
CD	400–550	1.62	2.38	298
Eu-CD	400–550	1.17	7.08	298
Eu-CD	550–650	7.45	12.5	298
$Eu(NO_3)_3$	550–650	3.55	3.96	298

Table S4 The parameters of lifetime (λ_{em} = 450 nm) for Eu-CD (Eu^{3+} : CD = 1 : 1) powder at different temperatures.

Temperature [K] / Samples	97	157	217	277	297
τ_{CD} [ns]	4.68	4.83	4.59	4.47	4.09
$\tau_{Eu\text{-}CD}$ [ns]	1.64	1.74	1.42	1.27	1.15
η_{ET} [%]	64.9	63.9	69.0	71.6	71.8
k_{ET} [s^{-1}]	3.96×10^8	3.68×10^8	4.86×10^8	5.64×10^8	6.25×10^8

Table S5 The parameters of lifetime of Eu-CD/PVA film (λ_{em} = 617 nm) with different relative humidity (RH).

Samples	τ_1 [μs]	A_1 [%]	τ_2 [μs]	A_2 [%]	τ_3 [μs]	A_3 [%]	τ_{ave} [μs]
Eu-CD/PVA film (RH = 33%)	744.4	11.60	1.088	78.96	3.516	9.440	1695
Eu-CD/PVA film (RH = 55%)	5627	9.430	990.5	79.40	2937	11.17	1562
Eu-CD/PVA film (RH = 76%)	4592	17.37	766.8	64.81	1802	17.85	1172
Eu-CD/PVA film (RH = 86%)	5112	49.36	955.5	47.58	2941	3.060	1039
Eu-CD/PVA film (RH = 98%)	8820	14.91	475.4	85.81	-	-	474.0

Table S6 The parameters of fluorescence lifetime of Eu-CD/PVA film (λ_{em} = 450 nm) with different degrees of hydrolysis (DH).

Samples	τ_1 [ns]	A_1 [%]	τ_2 [ns]	A_2 [%]	τ_3 [ns]	A_3 [%]	τ_{ave} [ns]	χ^2
Eu-CD/PVA film (DH = 88%)	0.838	30.5	3.28	48.4	10.4	21.1	4.04	1.06
Eu-CD/PVA film (DH = 95%)	0.764	26.9	2.76	47.3	8.85	25.8	3.79	1.08
Eu-CD/PVA film (DH = 99%)	0.831	30.7	2.95	45.2	8.65	24.1	3.67	1.04

Table S7 The parameters of phosphorescence lifetime of Eu-CD/PVA film (λ_{em} = 617 nm) with different DH.

Samples	τ_1 [μs]	A_1 [%]	τ_2 [μs]	A_2 [%]	τ_{ave} [μs]	χ^2
Eu-CD/PVA film (DH = 88%)	786	87.1	1758	12.9	1028	1.07
Eu-CD/PVA film (DH = 95%)	873	83.2	1704	16.8	1085	1.31
Eu-CD/PVA film (DH = 99%)	876	80.5	1805	19.5	1345	1.37

Table S8 Fluorescence QY of Eu-CD/PVA film with different DH.

Samples	QY [%]
Eu-CD/PVA film (DH = 88%)	9.18
Eu-CD/PVA film (DH = 95%)	9.49
Eu-CD/PVA film (DH = 99%)	10.2