Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Triple Optically Modulated and Enzymatically Responsive Organic Afterglow Materials for Dynamic Anti-counterfeiting

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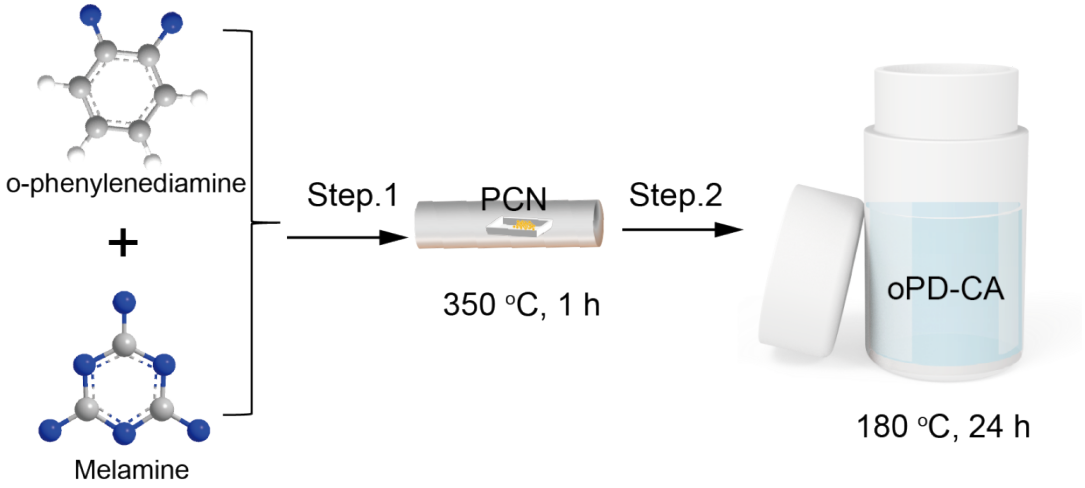

Scheme S1. Illustration of the oPD-CA system. Step.1. preparation of the precursor PCN by thermal polymerization. Step.2. preparation of the phosphorescence material oPD-CA by hydrothermal method.

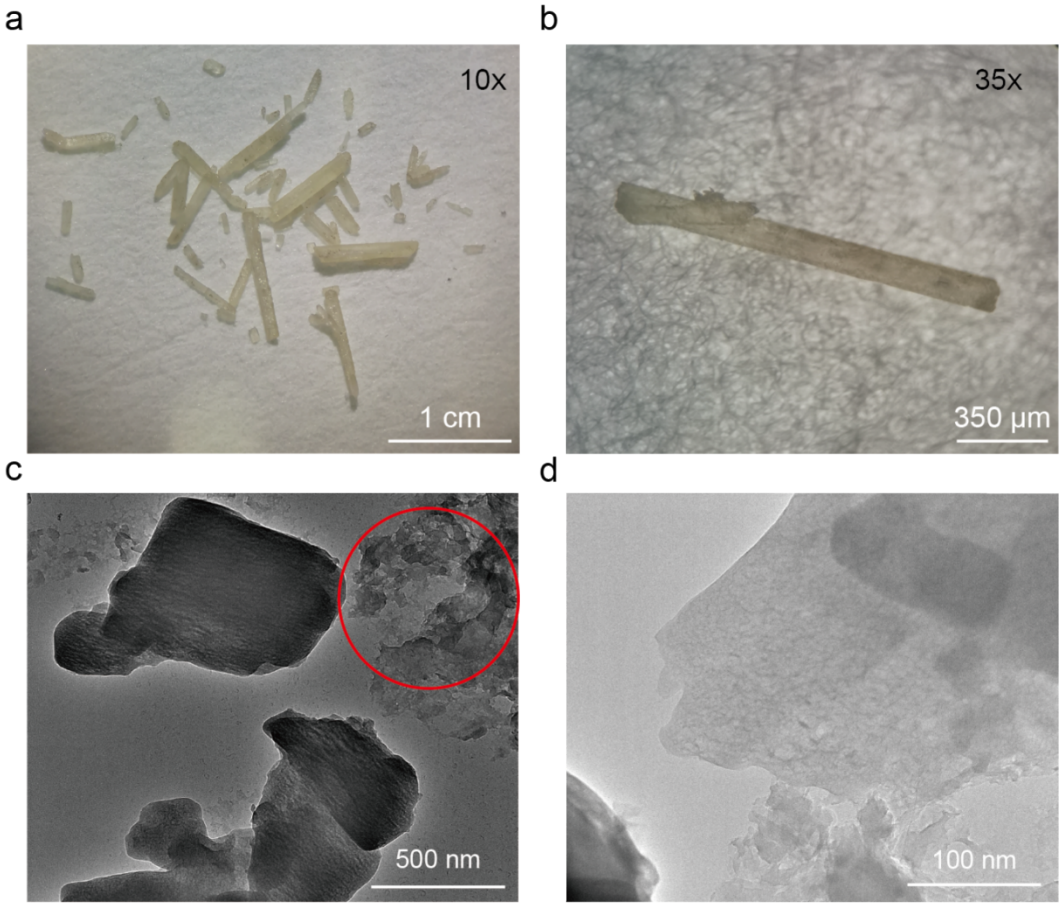

Fig. S1 Photographs of the oPD-CA taken by optical microscope, a) 10× and b) 35×. Typical transmission electron microscopy (TEM) images of oPD-CA after grinding, c) 500 nm and d) 100 nm.

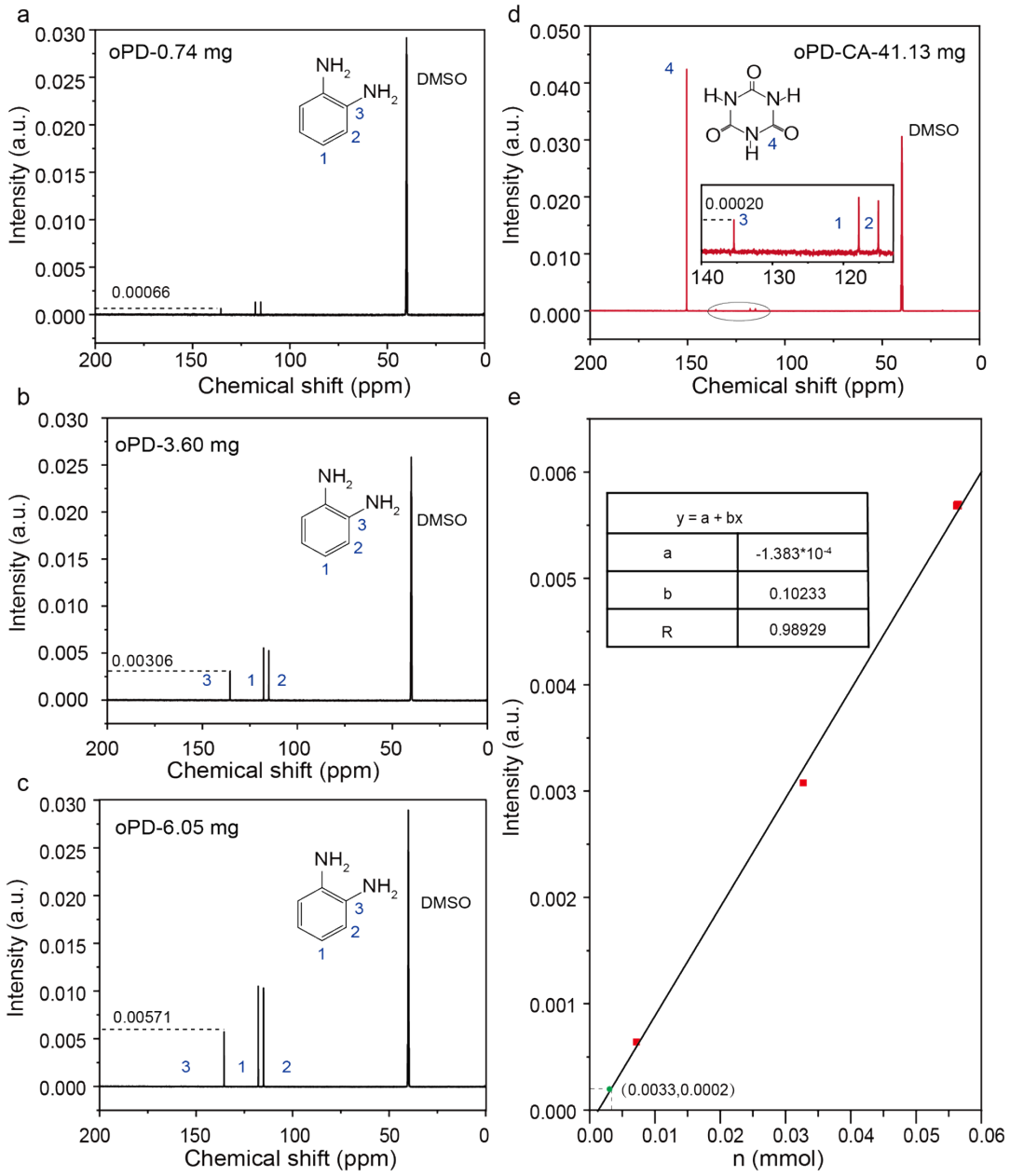

Fig. S2 The calculation of experimental molecular doping by external standard method. a) ^{13}C-NMR spectra of oPD-0.74 mg, b) oPD-3.60 mg, c) oPD-6.05mg, and d) oPD-CA-41.13 mg.

Dissolve 0.74 mg, 0.033 mmol, 3.6 mg, 0.056 mmol, and 6.05 mg o-phenylenediamine (oPD) and 41.13 mg oPD-CA in 0.55 ml Methyl sulfoxide-d^6 (DMSO-d^6), respectively. The result ^{13}C-NMR were shown in the **Fig. S2a-d**. The concentration-intensity relationship curve of oPD was obtained (**Fig. S2e**), through the results in **Fig. S2a-c**. The actual doping amount of oPD in cyanuric acid was calculated by the external standard method. The experimental oPD doping concentration calculated is 0.0033 mmol (from 41.13 mg oPD-CA). The remaining cyanuric acid base is 0.3161 mmol from the above results. Hence,the experimental molecular doping concentration calculated is 96:1 (molar ratio of CA : oPD).

Note S1. The calculation of the relative intensity of hydrogen bond.

$$I_R = \frac{I_{hydrogen\ bond} - I_{C=O}}{I_{C=O}} \times 100\% \quad (1)$$

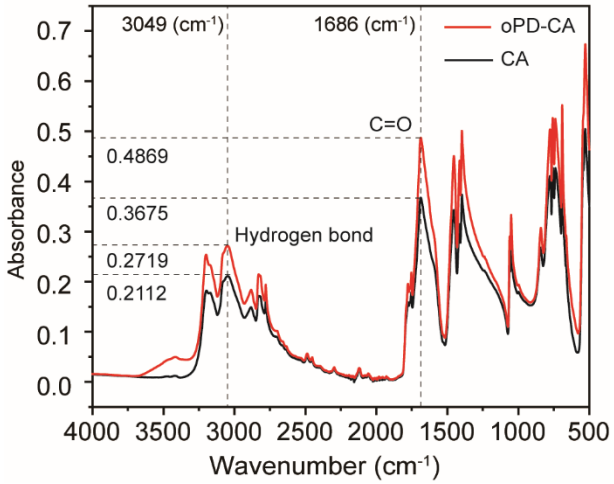

Fig. S3 FTIR absorbance spectra of as-synthesized oPD-CA and pristine CA.

In the **Equation (1)**, I_R represent the relative intensity of hydrogen bond. $I_{hydrogen\ bond}$ and $I_{C=O}$ represent the intensity of hydrogen bond and C=O recorded by Nicolet iS50 FT/IR Spectrophotometer, respectively. For oPD-CA, the absorption of hydrogen bond and C=O at 3049 and 1686 cm^{-1} is 0.2719 and 0.4868, respectively (**Fig. S3**). For CA, the transmittance of hydrogen bond and C=O at 3049 and 1686 cm^{-1} is 0.2112 and 0.3675, respectively (**Fig. S3**). (The test condition of CA is consistent with that of oPD-CA). The results show that $I_{R\text{-}oPA\text{-}CA}$=44.15%＞$I_{R\text{-}CA}$=42.53%.

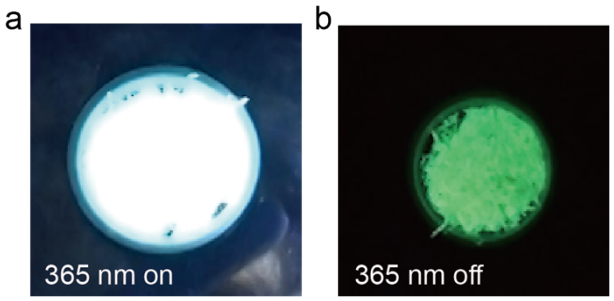

Fig. S4 Optical images of the catechol-CA powder in air under UV lamp (365 nm) on (left column) and off (right column).

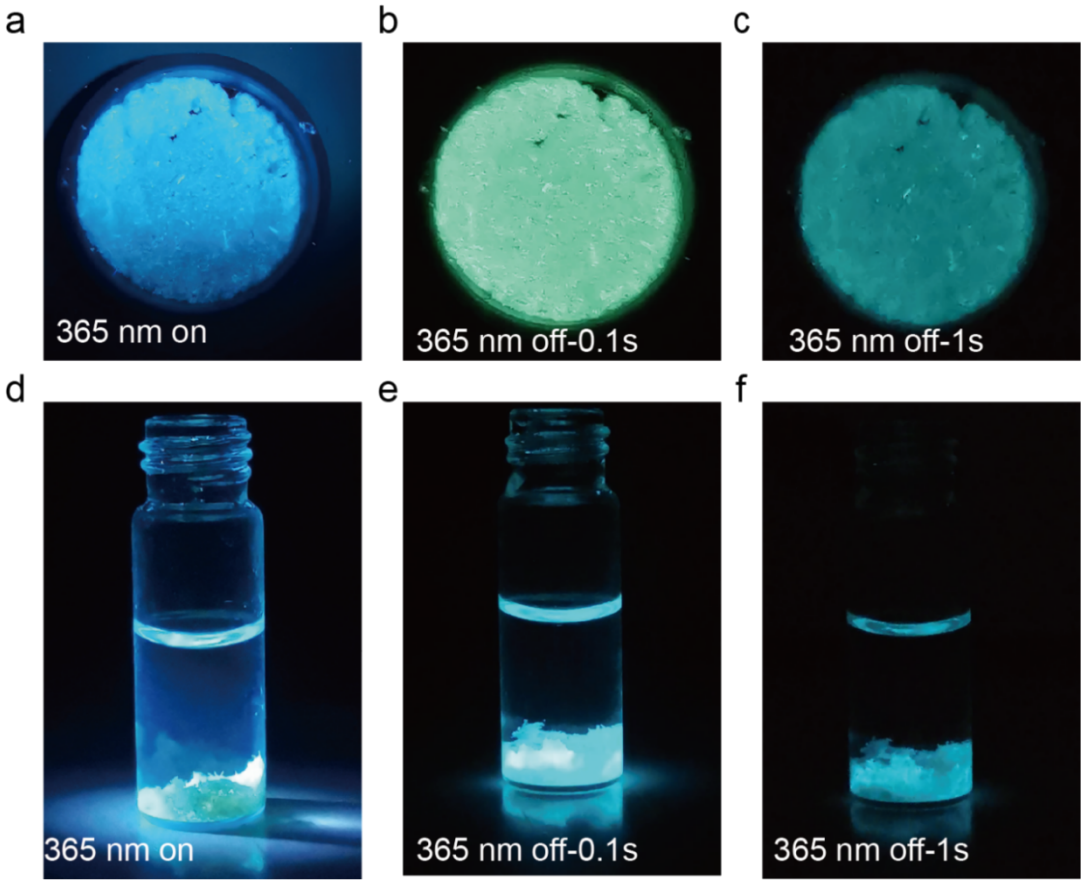

Fig. S5 Optical images of the oPD-CA powder in air (top row) and in water (bottom row) under UV lamp (365 nm) on (left column), off-0.1 s (middle) and off-1s (right column).

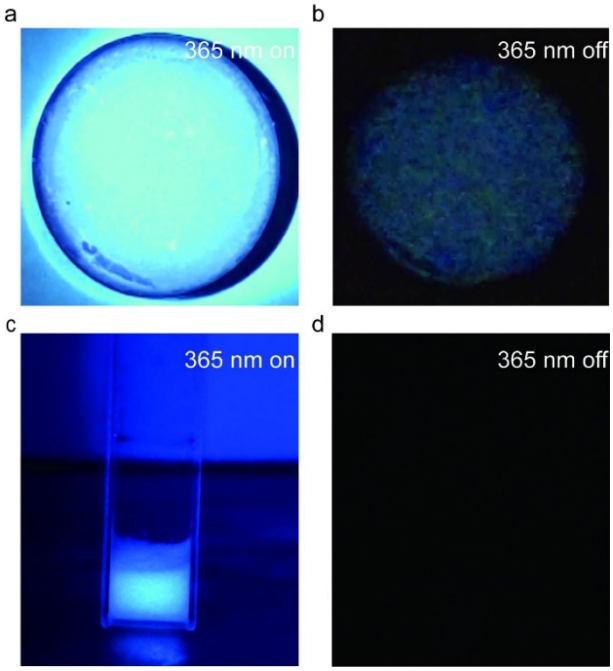

Fig. S6 Optical images of the CA powder in air (top row) and in water (bottom row) under UV lamp (365 nm) on (left column) and off (right column).

Table S1. Photoluminescence efficiency (Φ_{total}), fluorescence quantum yield and phosphorescence quantum yield of oPD-CA.

Componud	Φ_1 (%)	Φ_2 (%)	Φ_3 (%)	Φ_4 (%)	Φ_5 (%)	$\Phi_{avg.}$ (%)
Φ_{total}	24.6	24.6	24.8	24.7	24.7	24.7
FQY	10.5	10.5	10.6	10.5	10.5	10.5
PQY	14.1	14.1	14.2	14.2	14.2	14.2

Table S2. Phosphorescence lifetimes (τ) of oPD-CA, depend on excitation temperature (Ex=365 nm, Em=419 nm), corresponding to **Fig 3c**.

Em(nm)	T(K)	A_1	τ_1 (ms)	A_2	τ_2 (ms)	A_3	τ_3 (ms)	r^2
419	110	877.6	0.7	74.4	5.3	6.5	39.3	1.12
419	230	279.7	3.4	25.3	27.9	15.6	132.6	1.17
419	273	218.2	2.9	62.7	39.4	27.2	149.0	1.11

Table S3. Phosphorescence lifetimes (τ) of oPD-CA, depend on excitation temperature (Ex=365 nm, Em=450 nm, Em=503 nm and Em=533 nm), corresponding to **Fig 3d-f**.

Em(nm)	T(K)	A_1	τ_1 (ms)	A_2	τ_2 (ms)	A_3	τ_3 (ms)	r^2
450	110	622.2	148.5	314.6	1216.1	323.1	1216.0	0.98
450	230	750.6	150.0	381.3	1052.3	398.4	1052.4	0.99
450	273	839.2	133.4	352.1	992.4	407.7	992.6	0.98

503	110	1209.7	127.4	535.9	1088.3	55.7	2770.7	0.99
503	230	1061.7	135.9	299.9	1114.4	366.2	1114.2	0.99
503	273	1102.8	130.9	254.7	1037.4	384.1	1037.4	0.99
533	110	1623.8	122.4	417.5	122.4	301.5	997.3	0.99
533	230	1036.8	115.1	534.8	115.1	291.9	984.2	0.99
533	273	1195.6	105.8	492.6	105.7	283.6	894.1	0.99

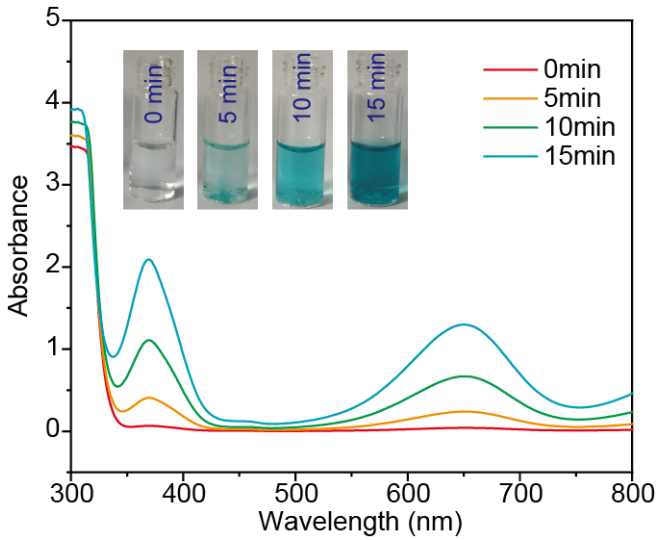

Fig. S7 UV-Vis absorption spectrum and images at different time (as inset) of the oPD-CA in the TMB-H_2O_2 solution.

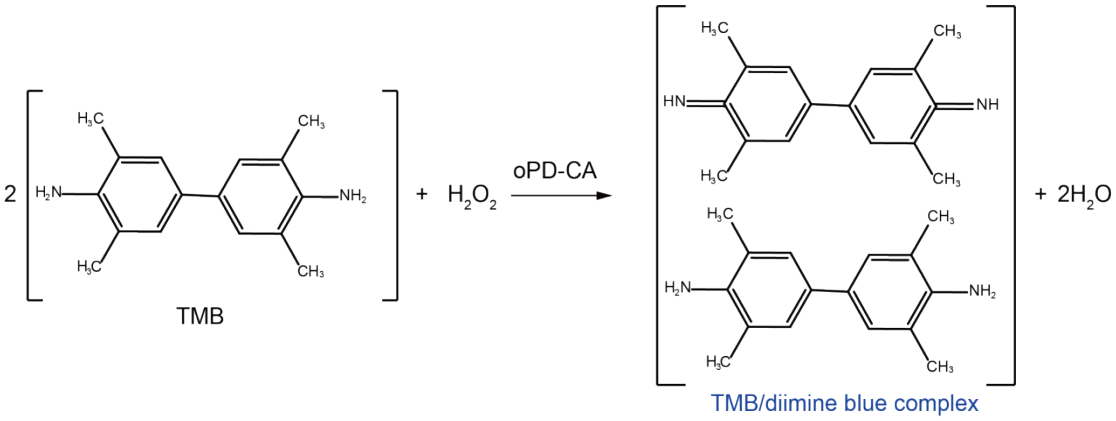

Fig. S8 The peroxidase-like activity of oPD-CA was revealed by catalysis of colorimetric reaction in the presence of TMB substrate (colorless) and H_2O_2 to produce a TMB diimine (blue) product and water.