D-A-D structured triphenylamine fluorophore with bright dual-state emission for reversible mechanofluorochromism and trace water detection

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Materials and instruments

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a JNM-ECZ400s (Japan) spectrometer, using $CDCCl_3$ as solvent. The UV-vis absorption spectra were recorded using a TU-1901 (Shimadzu, Kyoto, Japan)spectrometer with a 1 cm quartz cell. Fluorescence measurements were performed on a Hitachi FL-7000 spectrofluorimeter (Hitachi High Technologies Corporation, Tokyo, Japan). Infrared spectra were taken on a Nicolet NEXUS 380 (Thermo Fisher Scientific, Waltham, America)spectrometer (4000-400 cm^{-1}, KBr pellets). The absolute fluorescence quantum yield determined by integrating sphere on HORIBA FluoroMax-4 spectrofluorometer. The mass spectra were obtained by LC-MS (Thermofisher, America). Fluorescence quantum yields (Φ) and lifetimes in the solid state were obtained using a HORIBA FluoroMax-4 spectrofluorometer (Paris, French) in the oxygen environment through the absolute method using an integrating sphere. Powder X-ray diffraction (XRD) experiments were carried out on a Bruker SMART APEX-II Single-crystal diffractometer (Japan).

Optical Measurements

UV-vis absorption spectra were recorded in a 1 cm quartz cuvette and fluorescence spectra were recorded in a 1 cm four-side transparent quartz cuvette. All spectroscopic studies were carried out at an ambient temperature and concentrations of the solutions are 1.0×10^{-5} M.

Detecting water in organic solvents

All organic solvents are of analytical reagent grade and were used as received or were dried to eliminate any water residue before being used in the experiments[S1]. 30 μL of the solution of **2TPACHO** (1×10^{-3} M) was added to 3 mL of anhydrous THF as the initial solution. Different volumes of water were separately added into THF solutions of **2TPACHO** to a concentration of 1.0×10^{-5} M. The resultant mixture was

monitored using a fluorescence spectrophotometer. The same procedure was also used to detect water in Diox, Ace, DMF, and DMSO.

Mechanofluorochromism

The ground powders were obtained by grinding the as-prepared powder with a pestle in the mortar. The fumed samples were prepared by fuming the grinding powder with EtOH for 15 min. Fluorescent spectra of the pristine, ground, and recovered samples were recorded on a fluorescence spectrophotometer.

Quantum yield measurements

The quantum yield of fluorescence of **2TPACHO** was measured in diluted solutions using the following equation:

$$\Phi_x=\Phi_s\cdot(F_x/F_s)\cdot(A_s/A_x)\cdot(\eta_x/\eta_s)^2$$

The reference system used was quinine sulfate (Φ = 0.55 in 0.5 M H_2SO_4). Φ represents the quantum yield, F stands for the integrated area under the corrected emission spectrum, A is the absorbance at the excitation wavelength, η is the refractive index of the solution, and the subscripts x and s refer to the unknown and the standard, respectively.

Theoretical Calculations

All quantum chemical calculations were performed using the Gaussian 09 package. HOMO and LUMO distributions were calculated by the B3LYP/6-31G(d) level of theory in a THF solvent.

Crystallographic studies

Single crystal data were collected using a Bruker SMART APEX II (Germany). The crystal structures were solved through the ShelXT and OLEX2 packages. Single crystal data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2131950.

The limit of detection (LoD)

The detection limit is estimated based on the formula LoD = 3σ/k, where σ is the standard deviation of the blank sample and k is the slope of the calibration curve in the region of low water content. The standard deviation (σ) was obtained by fluorescence responses (8~12 times of consecutive scanning on the fluorescence spectrophotometer). The calibration curves for the determination of water in different solvents were obtained as follow:

Dioxane, $F = -3422.06 [H_2O] + 3332.16$
$R^2 = 0.9979$, $[H_2O] = 0\text{-}0.45$ % (1)

THF, $F = -4219.53 [H_2O] + 2474.43$
$R^2 = 0.9893$, $[H_2O] = 0\text{-}0.40$ % (2)

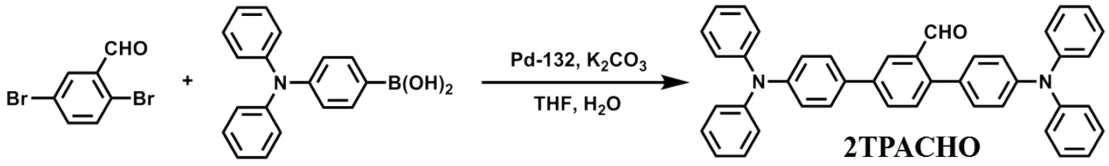
Acetone, $F = -490.14 [H_2O] + 316.17$
$R^2 = 0.9671$, $[H_2O] = 0\text{-}0.30$ % (3)

DMF, $F = -207.64 [H_2O] + 268.51$
$R^2 = 0.9849$, $[H_2O] = 0.35\text{-}0.65$ % (4)

DMSO, $F = -48.92 [H_2O] + 99.71$
$R^2 = 0.9977$, $[H_2O] = 0.25\text{-}0.65$ % (5)

The detection limit values for 2TPACHO are summarized in **Table S5**.

Synthetic experimental



Scheme S1 The synthetic route of 2**TPACHO**.

4-(Diphenylamino)phenylboronic acid (5.78 g 20.00 mmol 20 mmol) and 2,5-dibromobenzaldehyde (1.32g 5.00 mmol 5 mmol) were coupled in a mixture of toluene (10 mL), ethanol (8 mL), aqueous K_2CO_3 (10 mL, 2 M) and Pd-132 (0.5

mol%) at 90 °C, by stirring under nitrogen for 12 h. After cooling, the reaction mixture was poured into water and then extracted with CH_2Cl_2 (3 × 40 mL). The organic portion was dried with anhydrous Na_2SO_4 and evaporated to dryness. The solid residues were purified by column chromatography using dichloromethane/petroleum ether (1:1, v/v) as an eluent to afford the pure coupled products **2TPACHO** as a yellow-green solid (82.2%). IR (KBr pellet, cm^{-1}): 3062, 3031, 2847, 2746, 1682, 1589, 1521, 1467, 1383, 1328, 1280, 1174, 1123, 1078, 1026, 999, 899, 851, 817, 755 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, δ): 10.11 (s, 1H), 8.20 (d, *J*=1.9, 1H), 7.82 (dd, d, *J*=8.1, 2.1, 1H), 7.50~7.55 (m, 3H), 7.25~7.31 (m, 10H), 7.13~7.17 (m, 12H), 7.04~7.08 (m, 4H). ^1H NMR (100 MHz, $CDCl_3$, δ): 192.88, 184.15, 147.89, 147.63, 147.48, 144.08, 139.81, 134.00, 133.24, 131.56, 131.27, 131.05, 130.77, 129.54, 129.45, 127.80, 125.48, 125.01, 124.74, 123.70, 123.59, 123.29, 122.65. HR-MS (APCI-MS): m/z = 593.2589. calcd. for $[C_{43}H_{33}N_2O]^+$ = 593.2593.

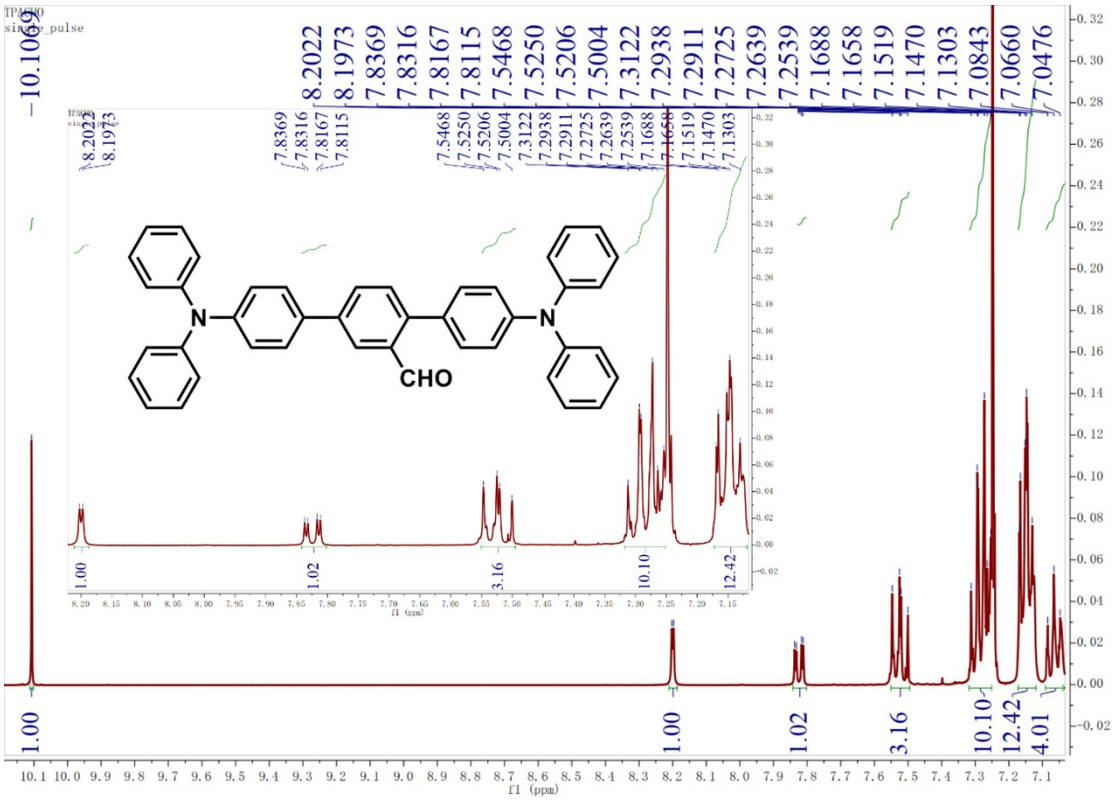


Fig. S1 ^1H NMR spectra of **2TPACHO**

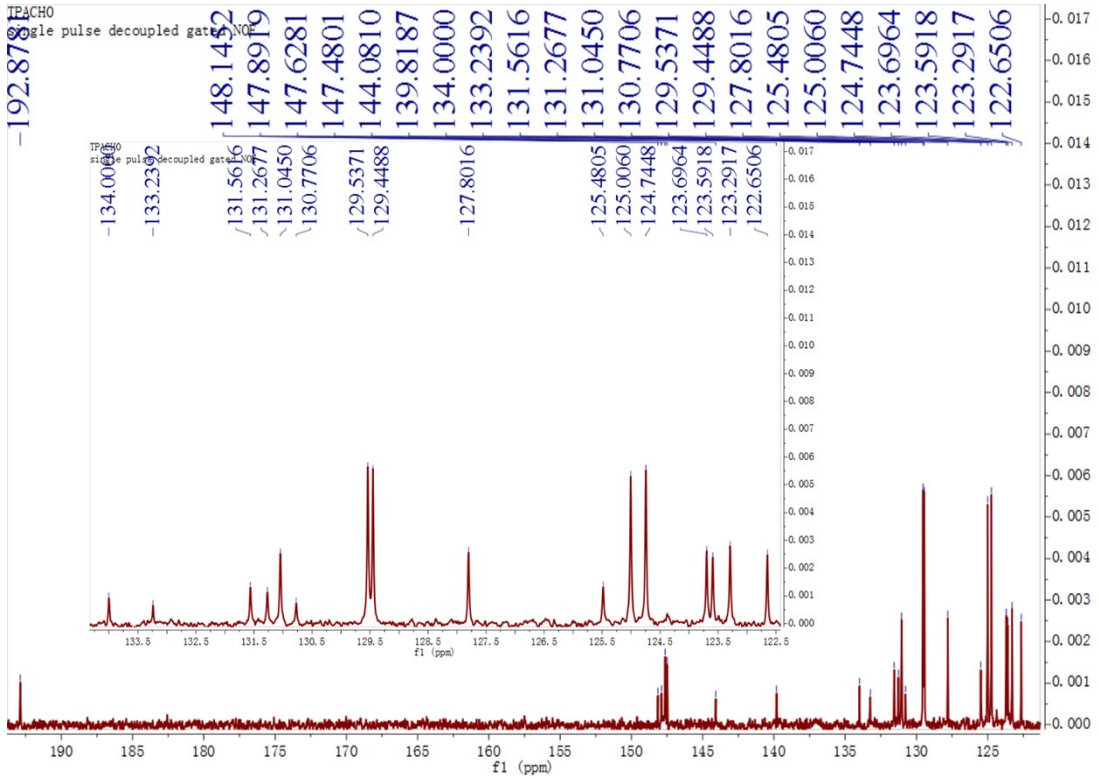


Fig. S2 ^{13}C NMR spectra of **2TPACHO.**

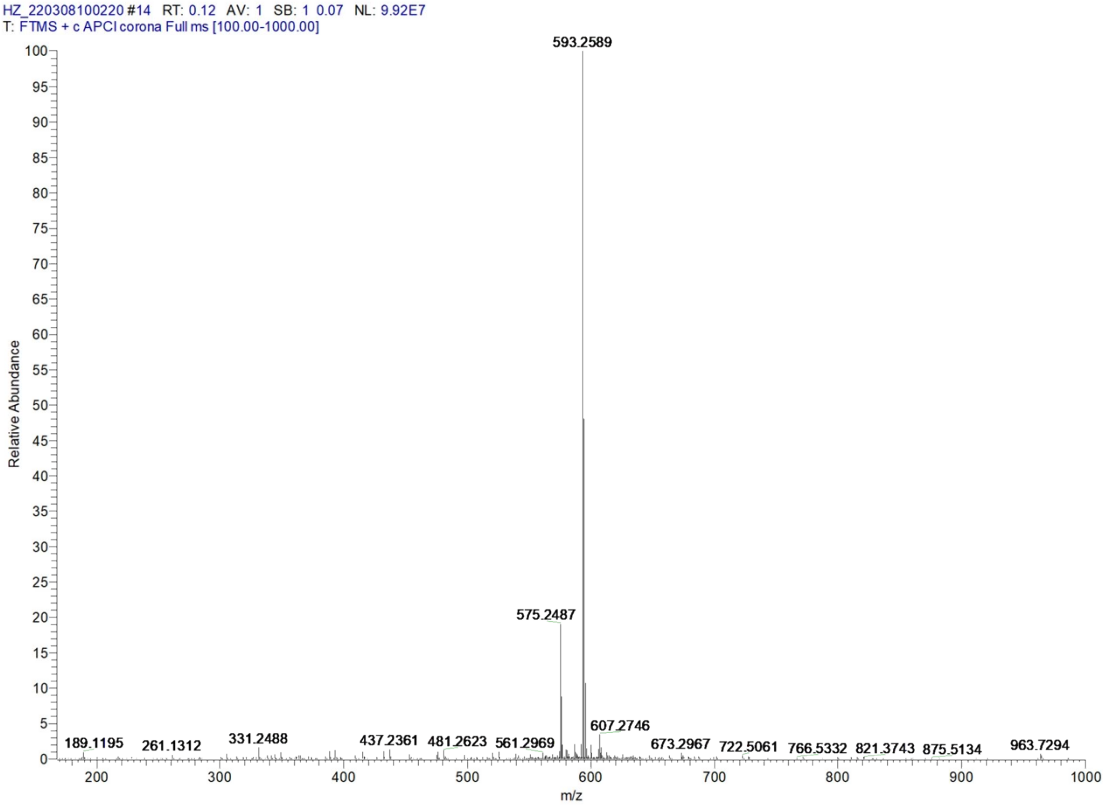


Fig. S3 Mass spectrum of **2TPACHO**

Table S1 The photophysical data of **2TPACHO** in different solvents

Solvents	λ[a] max	λ[b] max	ε (×10⁴)[c]	Δν [d]	**Φ**[e]
Tol	346	456	3.71	6971.91	0.65
Diox	340	470	3.91	8135.16	0.61
EA	341	481	3.52	8535.49	0.43
THF	344	473	3.64	8270.11	0.43
DCM	345	524	3.54	9901.53	0.17
EtOH	342	410	1.70	4849.52	0.11
Ace	341	516	2.91	9945.66	0.07
DMF	345	537	3.56	10363.53	0.09
DMSO	345	546	3.39	10670.48	0.04

[a] The maximum absorption wavelength. [b] The maximum emission wavelength. [c] solvent dielectric constant. [d] Stokes shifts (cm^{-1}). [e] fluorescence quantum yields.

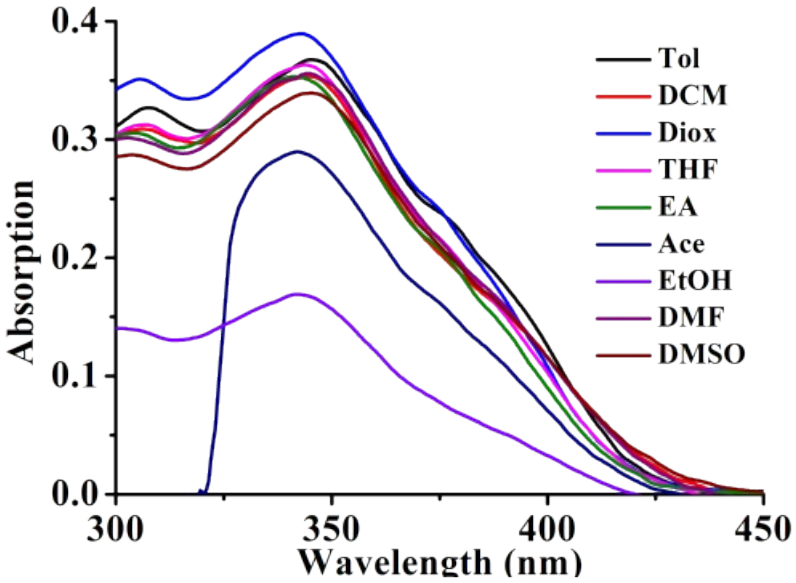


Fig. S4 UV-vis spectra of **2TPACHO** in different solvents.

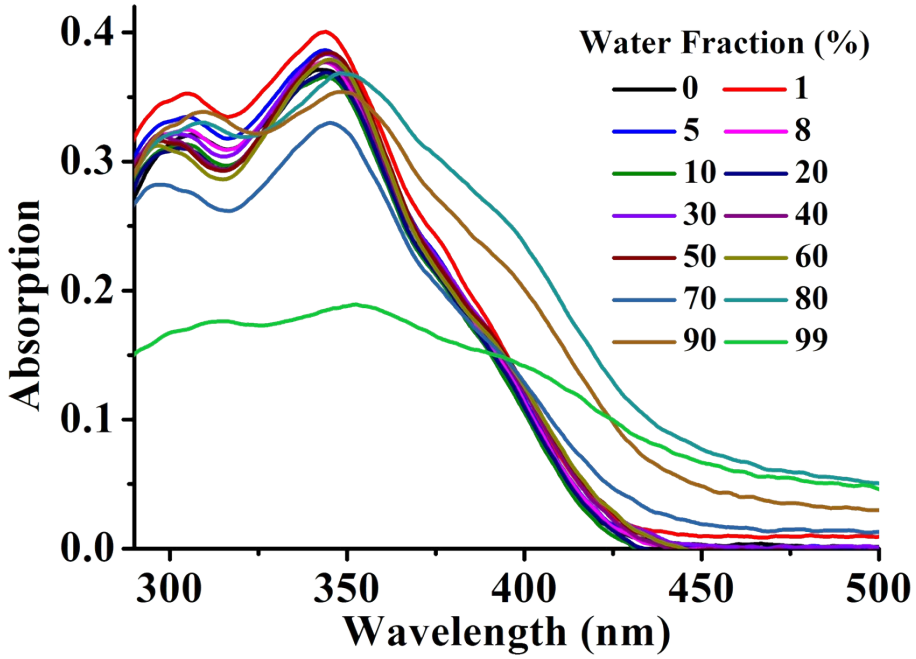


Fig. S5 Absorption spectra of **2TPACHO** in THF/H_2O mixtures with different water contents.

Table S2 Crystal data and structure refinement parament for **2TPACHO**

Compound	**TPACHO**	Calculated density	1.115 (g/cm^{-3})
Formula	$C_{43}H_{32}N_2O$	Absorption coefficient	0.069 mm^{-1}
Z	2	Data/restraints/ parameters	7009/0/415
Temperature	296.15	Goodness-of-fit on F^2	1.060
Crystal system	triclinic	Largest diff.peak and hole	0.30 and -0.39 e.A^{-3}
Space group	*P-1*	Theta range for data collection	1.984 to 54.992 deg.
a (Å)	8.086(7)		-10 ≤ h ≤ 10
b (Å)	10.272(8)	Limiting indices	-12 ≤ k ≤ 12
c (Å)	20.557(17)		-26 ≤ l ≤ 24
β (°)	87.126(11)	F(000)	624.0
α (°)	88.165(12)	Reflection collected / unique	13821/7009[Rint =0.0227, Rsigma = 0.0372]
γ (°)	89.736(12)	Final R indices [I>2σ(I)]	R_1 = 0.0623, wR_2 = 0.1912
Volume(Å^3)	1704(2)	R indices (all)	R1 = 0.0938, wR_2 = 0.2208

Table S3 Bond lengths for **2TPACHO**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C25	1.206(4)	C19	C20	1.383(4)
N1	C6	1.428(3)	C19	C24	1.412(3)
N1	C12	1.425(3)	C20	C21	1.372(4)
N1	C13	1.413(3)	C21	C22	1.387(3)
N2	C31	1.424(3)	C22	C23	1.395(4)
N2	C32	1.428(3)	C22	C26	1.483(3)
N2	C43	1.419(3)	C23	C24	1.390(4)
C1	C2	1.387(4)	C24	C25	1.497(4)
C1	C6	1.388(3)	C26	C27	1.390(3)
C2	C3	1.358(4)	C26	C28	1.399(4)
C3	C4	1.377(5)	C27	C30	1.374(3)
C4	C5	1.389(4)	C28	C29	1.382(3)
C5	C6	1.387(4)	C29	C31	1.384(3)
C7	C8	1.376(4)	C30	C31	1.396(3)
C7	C12	1.395(3)	C32	C33	1.384(3)
C8	C9	1.374(4)	C32	C37	1.385(4)
C9	C10	1.376(4)	C33	C34	1.392(4)
C10	C11	1.380(3)	C34	C35	1.367(5)
C11	C12	1.383(3)	C35	C36	1.376(5)
C13	C14	1.386(3)	C36	C37	1.380(4)
C13	C15	1.397(3)	C38	C39	1.380(4)
C14	C17	1.376(4)	C38	C43	1.392(3)
C15	C16	1.375(3)	C39	C40	1.369(5)
C16	C18	1.392(3)	C40	C41	1.376(4)
C17	C18	1.399(4)	C41	C42	1.380(3)
C18	C19	1.492(3)	C42	C43	1.392(3)

Table S4 Bond angles for **2TPACHO**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	N1	C6	118.04(18)	C20	C21	C22	122.1(2)
C13	N1	C6	121.96(18)	C21	C22	C23	116.4(2)
C13	N1	C12	119.97(18)	C21	C22	C26	121.0(2)
C31	N2	C32	118.00(19)	C23	C22	C26	122.4(2)
C43	N2	C31	118.84(18)	C24	C23	C22	122.0(2)
C43	N2	C32	122.66(18)	C19	C24	C25	122.0(2)
C2	C1	C6	120.6(3)	C23	C24	C19	120.3(2)
C3	C2	C1	120.9(3)	C23	C24	C25	117.4(2)
C2	C3	C4	119.1(3)	O1	C25	C24	124.2(3)
C3	C4	C5	121.1(3)	C27	C26	C22	121.7(2)
C6	C5	C4	119.9(3)	C27	C26	C28	117.3(2)
C1	C6	N1	119.6(2)	C28	C26	C22	121.0(2)
C5	C6	N1	122.0(2)	C30	C27	C26	121.5(2)
C5	C6	C1	118.4(2)	C29	C28	C26	121.6(2)
C8	C7	C12	120.3(2)	C28	C29	C31	120.3(2)
C9	C8	C7	120.7(2)	C27	C30	C31	120.7(2)
C8	C9	C10	119.3(2)	C29	C31	N2	120.2(2)
C9	C10	C11	120.8(2)	C29	C31	C30	118.5(2)
C10	C11	C12	120.3(2)	C30	C31	N2	121.3(2)
C7	C12	N1	120.0(2)	C33	C32	N2	121.5(2)
C11	C12	N1	121.3(2)	C33	C32	C37	118.5(2)
C11	C12	C7	118.7(2)	C37	C32	N2	120.0(2)
C14	C13	N1	121.7(2)	C32	C33	C34	120.0(3)
C14	C13	C15	117.8(2)	C35	C34	C33	121.0(3)
C15	C13	N1	120.5(2)	C34	C35	C36	119.0(3)
C17	C14	C13	121.2(2)	C35	C36	C37	120.6(3)
C16	C15	C13	120.7(2)	C36	C37	C32	120.8(3)
C15	C16	C18	122.1(2)	C39	C38	C43	120.1(3)
C14	C17	C18	121.6(2)	C40	C39	C38	121.1(3)
C16	C18	C17	116.6(2)	C39	C40	C41	119.3(3)
C16	C18	C19	121.2(2)	C40	C41	C42	120.5(3)
C17	C18	C19	122.1(2)	C41	C42	C43	120.5(2)
C20	C19	C18	119.5(2)	C38	C43	N2	122.6(2)
C20	C19	C24	116.8(2)	C42	C43	N2	119.0(2)
C24	C19	C18	123.7(2)	C42	C43	C38	118.4(2)
C21	C20	C19	122.1(2)				

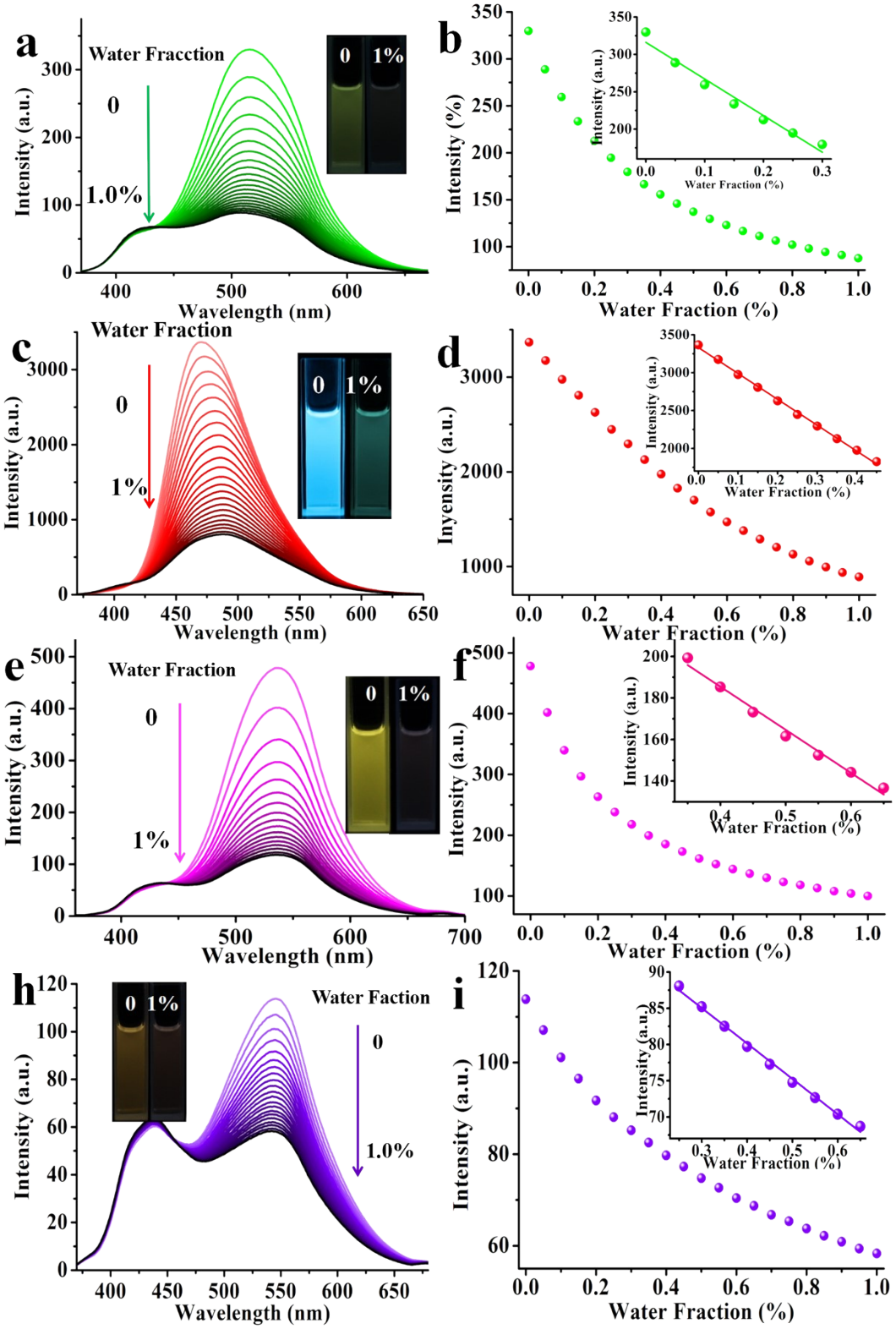
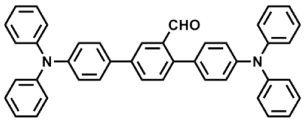
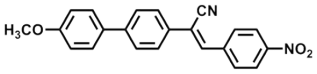
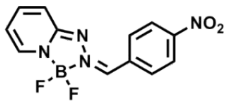
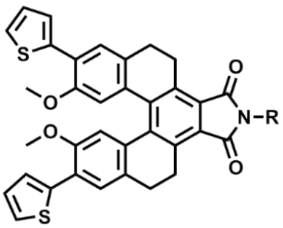
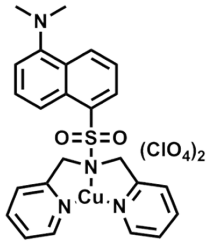


Fig. S6 The emission spectra of **2TPACHO** in (a) Ace, (c) Diox, (e) DMF, (h) DMSO with increasing amounts of water from 0 to 1 % (v/v); Inset: the photos of **2TPACHO** at fw = 0, and 1 % under 365 nm UV illumination. Plot of the maximum peak emission intensities of **2TPACHO** versus varied concentrations of H_2O (0-1%, v/v) in (b) Ace, (d) Diox, (f) DMF, (i) DMSO solution; Inset: the corresponding fitting curve.

Table S5 Comparative accounts of water detection by this work and other reports.

Materials	Solvent	Linear range[%]	LOD[%, v/v]	R^2	Ref
	THF	0-0.40	0.0074	0.9893	This work
	Dioxane	0-0.45	0.0065	0.9979	
	Acetone	0-0.30	0.0026	0.9671	
	DMF	0.35-0.65	0.0284	0.9849	
	DMSO	0.25-0.65	0.0282	0.9977	
	THF	0-0.5	0.0209	-	S2
	Dioxane	0-2	0.21	-	
	THF		0.028	0.9949	S3
	Acetone	0-3.8	0.021	0.9948	
	DMF		0.045	0.9953	
	Dioxane	0.15-20	0.050	0.9941	S4
	THF	0.11-10	0.036	0.9968	
	DMF	0.091-10	0.030	0.9918	
	Acetone	0.20-5	0.065	0.9951	
	Acetone	0-0.5	0.052	0.9996	S5
	THF	0-0.6	0.0030	0.9943	
CDs (CPD)	Dioxane	0-1	0.0460	0.908	S6
	ACN	0-1	0.178	0.986	
	DMSO	0-10	1.25	0.997	
	DMF	0-5	1.10	0.999	
Tb^{3+}@p-CDs/MOF	DMF	0-30	0.33	0.98	S7

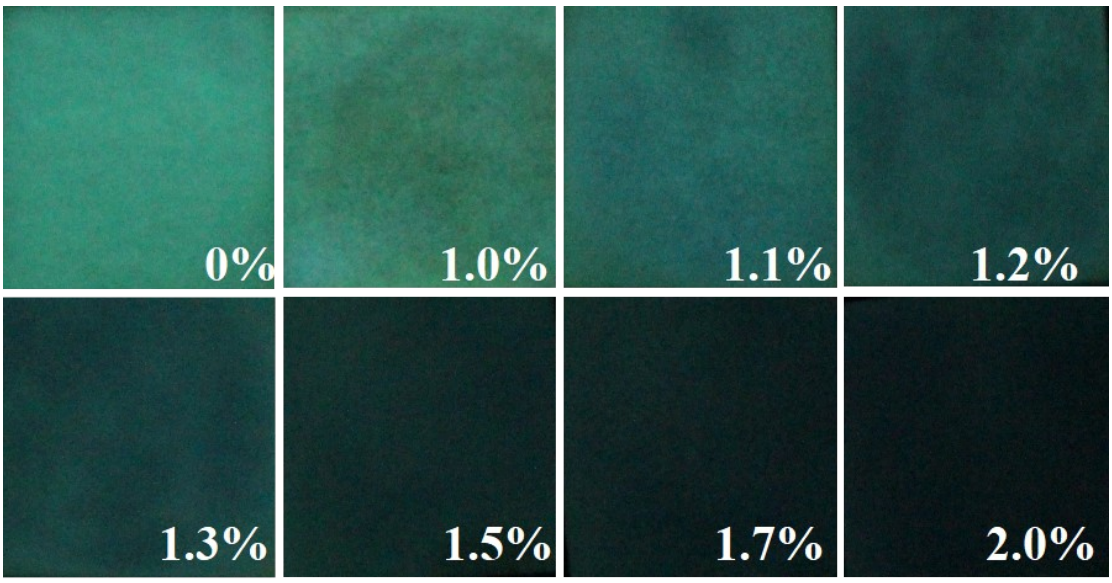


Fig. S7 The fluorescence color changes of **2TPACHO**-coated Whatman paper strips in the presence of THF solutions containing different water contents (0, 1.0, 1.1, 1.2, 1.3, 1.5, 1.7, 2.0 %, v/v) under 365 nm lamp.

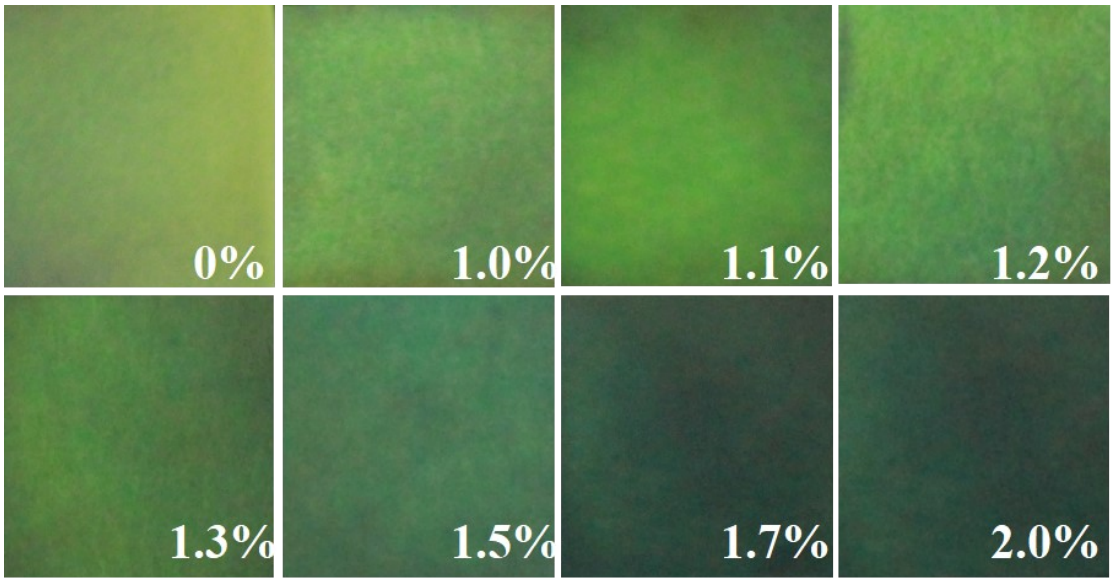


Fig. S8 The fluorescence color changes of **2TPACHO**-coated Whatman paper strips in the presence of acetone solutions containing different water contents (0, 1.0, 1.1, 1.2, 1.3, 1.5, 1.7, 2.0 %, v/v) under 365 nm lamp.

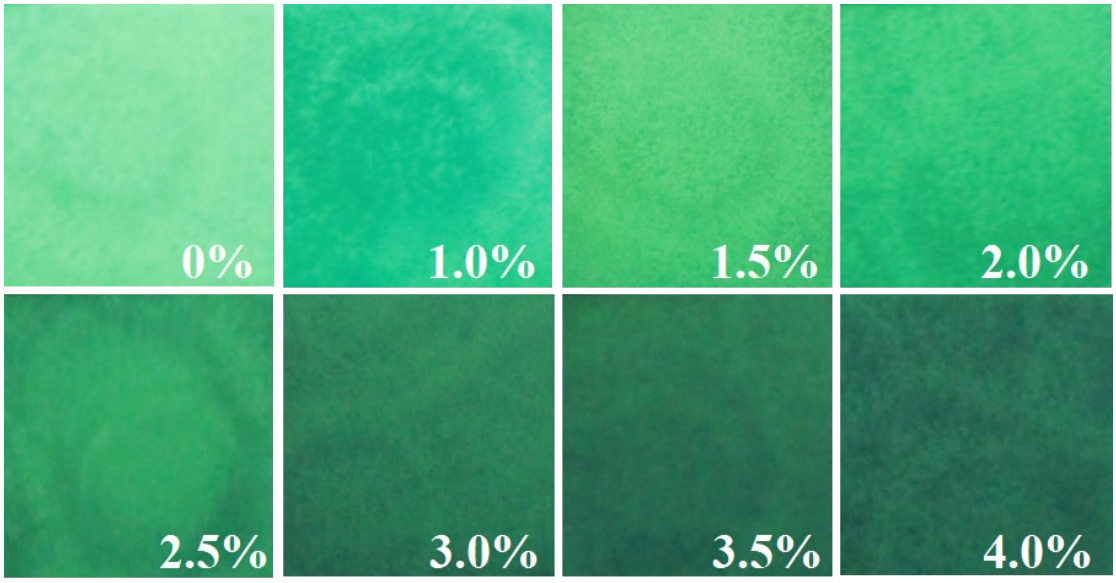


Fig. S9 The fluorescence color changes of **2TPACHO**-coated Whatman paper strips in the presence of dioxane solutions containing different water contents (0, 1.0, 1.1, 1.2, 1.3, 1.5, 1.7, 2.0 %, v/v) under 365 nm lamp.

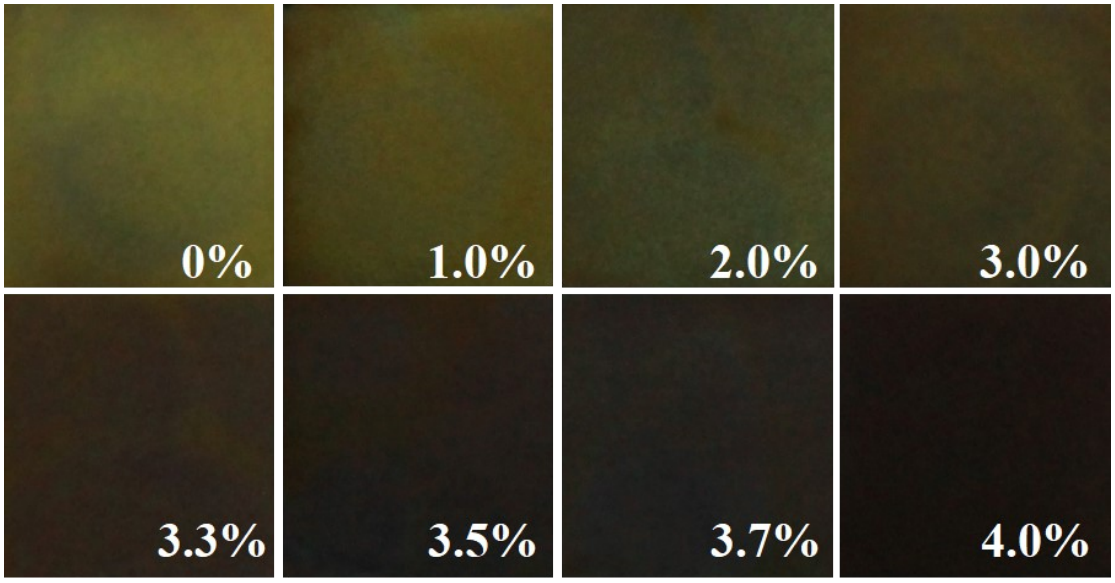


Fig. S10 The fluorescence color changes of **2TPACHO**-coated Whatman paper strips in the presence of DMF solutions containing different water contents (0, 1.0, 1.1, 1.2, 1.3, 1.5, 1.7, 2.0 %, v/v) under 365 nm lamp.

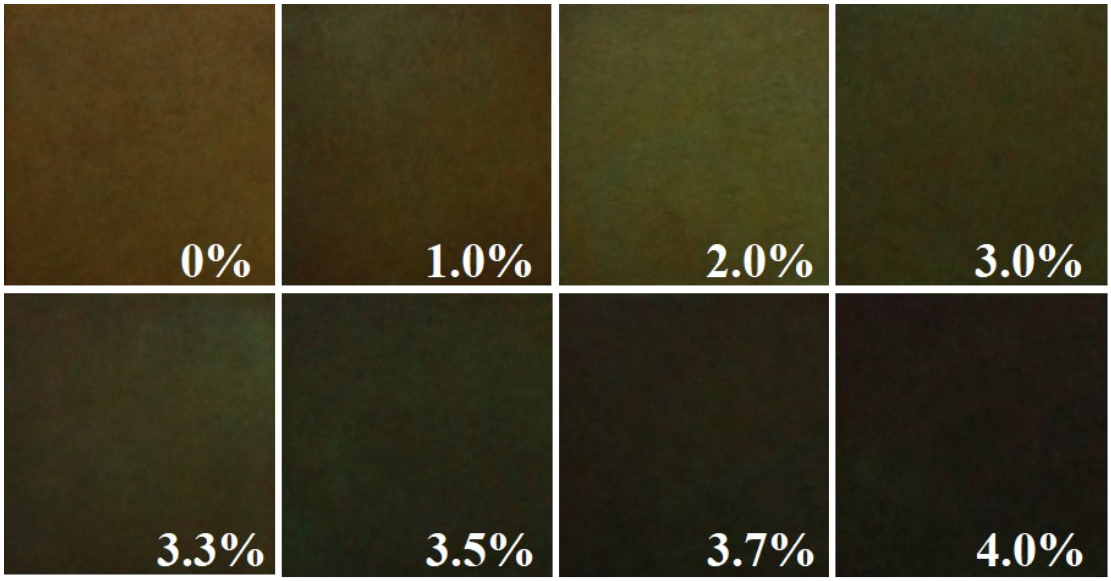


Fig. S11 The fluorescence color changes of **2TPACHO**-coated Whatman paper strips in the presence of DMSO solutions containing different water contents (0, 1.0, 1.1, 1.2, 1.3, 1.5, 1.7, 2.0 %, v/v) under 365 nm lamp.

Table S6 Emission maxima (λem), quantum yields (Φ), and fluorescence lifetime (τ) of **2TPACHO** sample before and after grinding.

2TPACHO	Φ[a]	τ(ns)	k_r[b](×10^8 s^{-1})	k_{nr}[c](×10^8 s^{-1})
pristine	0.62	2.56	2.44	1.46
ground	0.22	1.11	2.04	6.97

[a] Absolute quantum yields were determined by using an integration sphere. [b] k_r = radiative decay rate (Φ/τ). [c] k_{nr} = nonradiative decay rate (1/τ - k_r).

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