Supplementary Material

Rational Design of a 1,8-Naphthalimide-Based Fluorescent Probe for Water Detection in Organic Solvents

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1. Instrumentation and materials

2. Photon-physical properties

3. Characterization

1. Instrumentation and materials

All organic solvents, chemicals, and various consumables were purchased from Energy Chemical or Shanghai Aladdin Biochemical Technology Co., Ltd.. All chemicals were of analytical grade and all organic solvents were not pretreated unless otherwise specified. The silica gel (200-300 mesh, China Qingdao Haiyang Chemical Co.) was used for the compound purification. NMR ^{1}H and ^{13}C spectral data of the compounds were measured on an AVANCE III HD 600 MHz (Bruker). Mass data of the compounds were obtained on a Q-Exactive HR-MS (Bruker). The UV-vis absorption and fluorescence emission data of the solution and solid were conducted on a T9CS spectrophotometer (Beijing Puxi General Instrument Co., LTD) and an F-7000 spectrofluorometer (HITACHI), respectively. The quantum yield was measured using an Edinburgh FLS1000 spectrometer.

2. Photon-physical properties

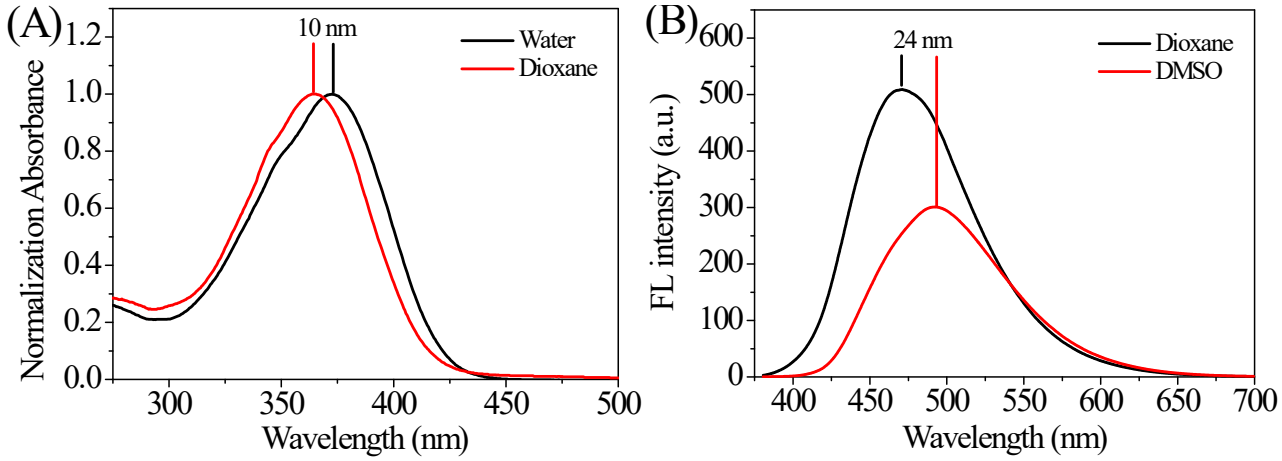
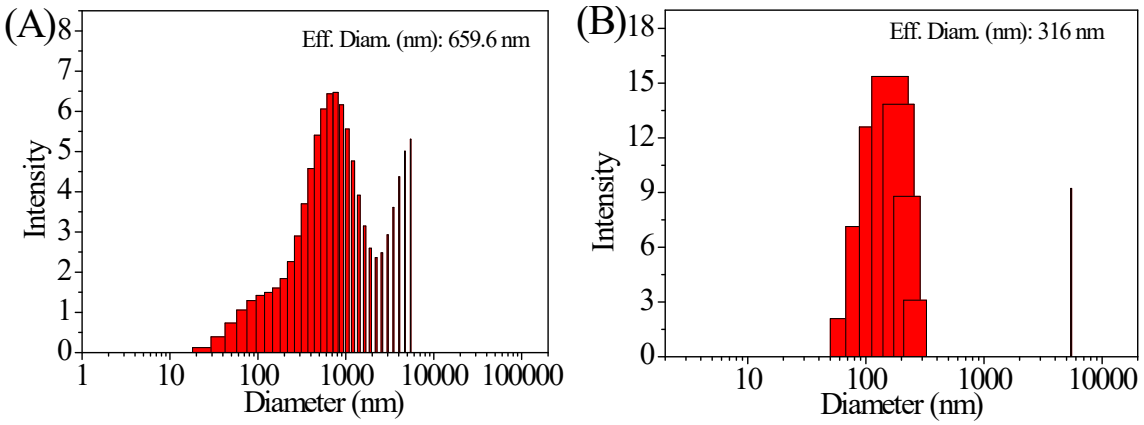


Fig. S1. (A) Normalization absorption spectra of **NPP-N+** (20 μM) in Dio (365 nm) and DMSO (375 nm); (B) FL maxima and intensity of **NPP-N+** (20 μM) in Dio (470 nm) and DMSO (494 nm) under excitation wavelength λ_{ex} = 366 nm.



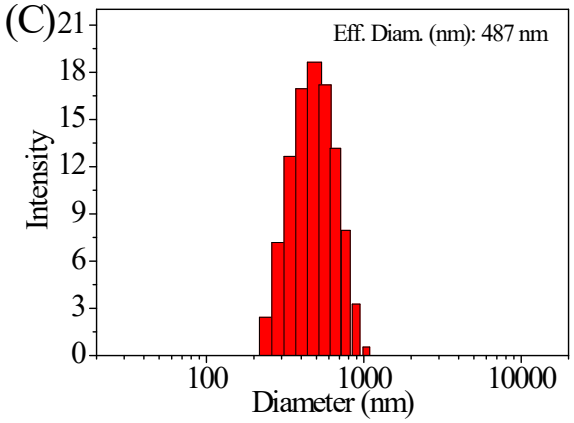


Fig. S2. Particle size distribution of **NPP-N+** (20 μM) in water (A), DMSO (B) and Dio (C).

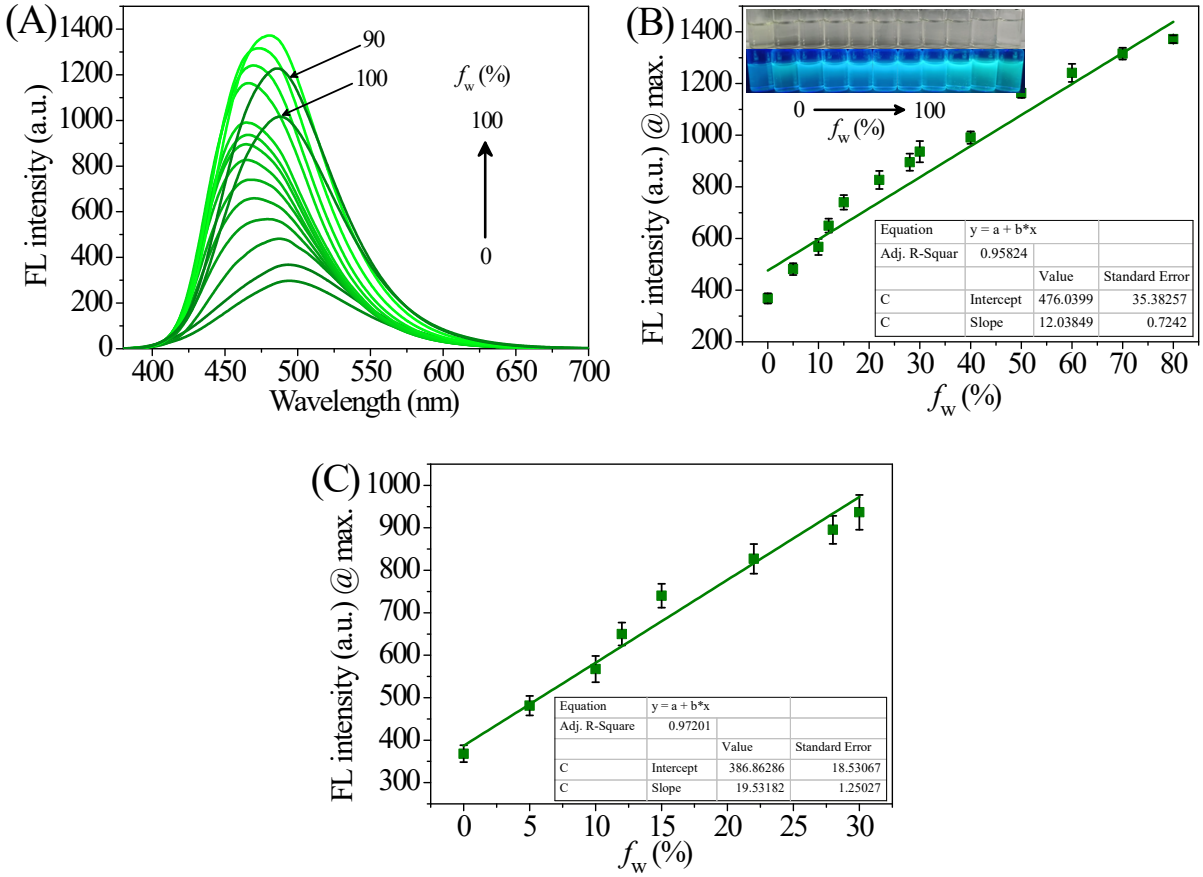


Fig. S3. (A) FL spectra of **NPP-N+** (20 μM) in THF/H_2O mixtures with different water fractions; (B and C) Linear relationship between the maximum FL intensity and the water contents in THF.

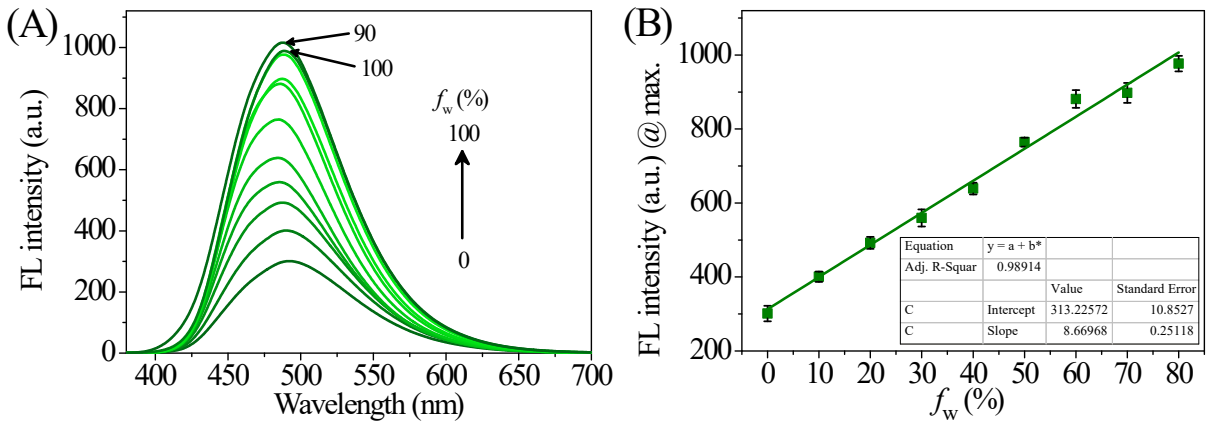


Fig. S5. (A) FL spectra of **NPP-N+** (20 μM) in DMSO/H_2O mixtures with different water fractions; (B) Linear relationship between the maximum FL intensity and the water contents in DMSO.

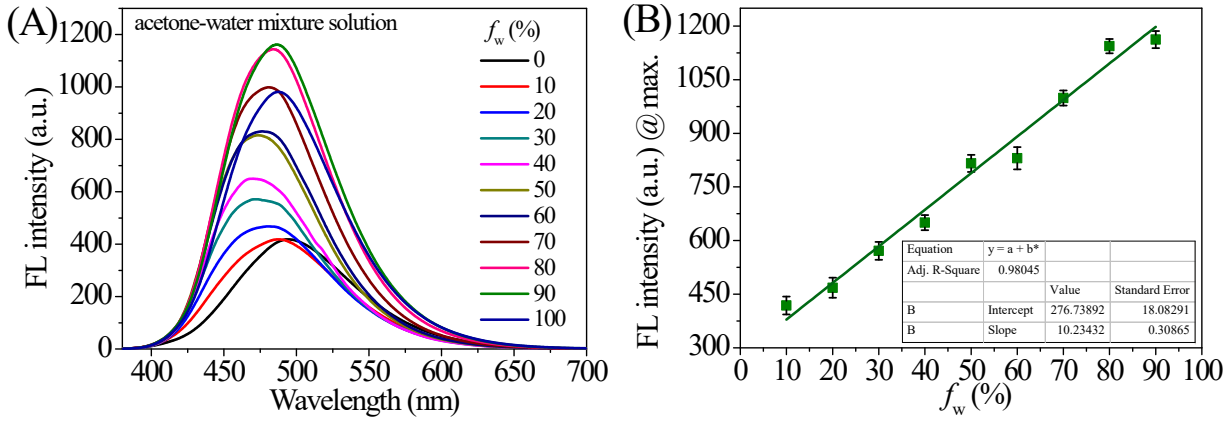


Fig. S6. (A) FL spectra of **NPP-N+** (20 μM) in ACE/H_2O mixtures with different water fractions; (B) Linear relationship between the maximum FL intensity and the water contents in ACE.

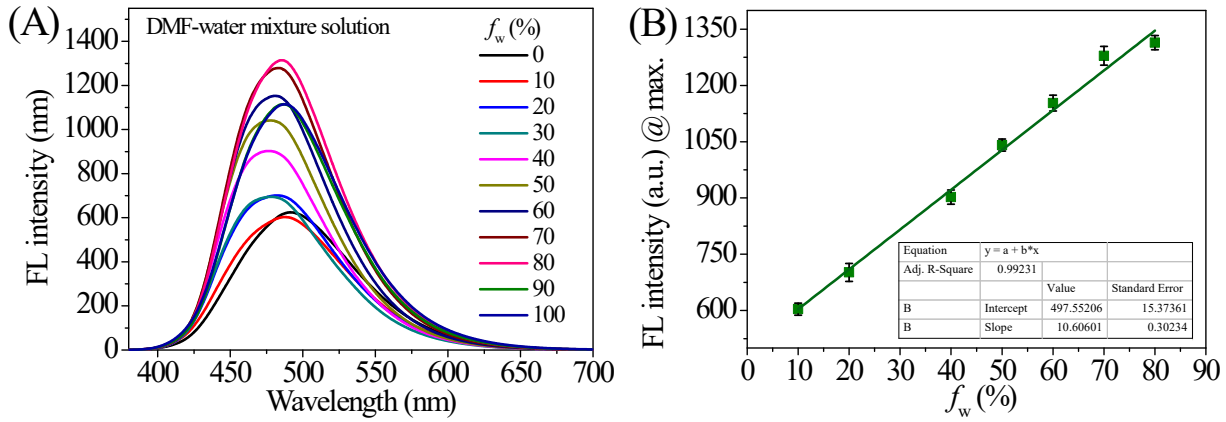


Fig. S6. (A) FL spectra of **NPP-N+** (20 μM) in DMF/H_2O mixtures with different water fractions; (B) Linear relationship between the maximum FL intensity and the water contents in DMF.

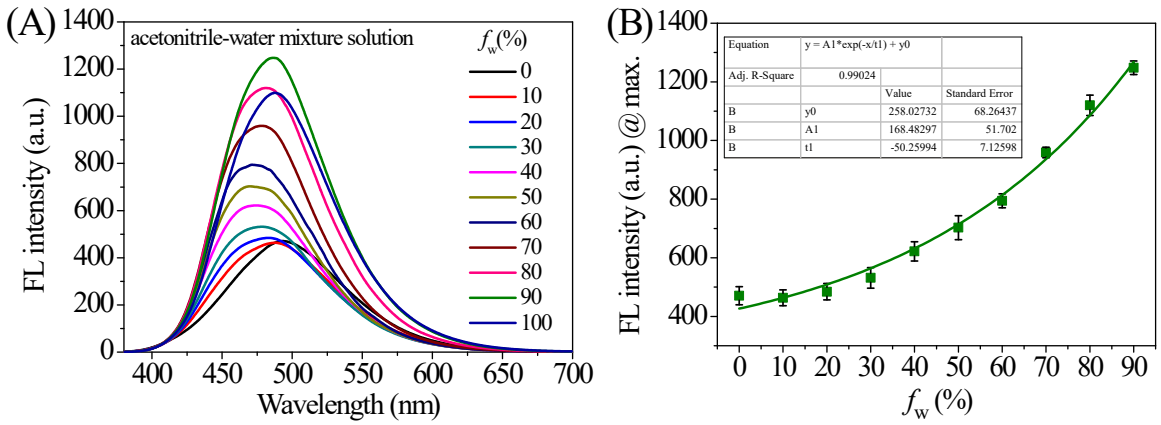


Fig. S7. (A) FL spectra of **NPP-N+** (20 μM) in MeCN/H_2O mixtures with different water fractions; (B) Linear relationship between the maximum FL intensity and the water contents in MeCN.

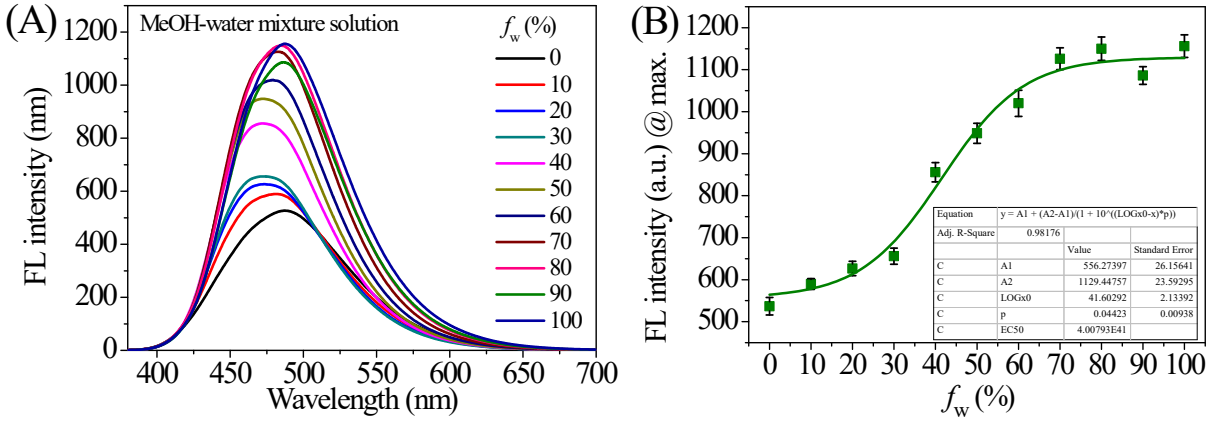


Fig. S8. (A) FL spectra of **NPP-N+** (20 μM) in MeOH/H_2O mixtures with different water fractions; (B) Linear relationship between the maximum FL intensity and the water contents in MeOH.

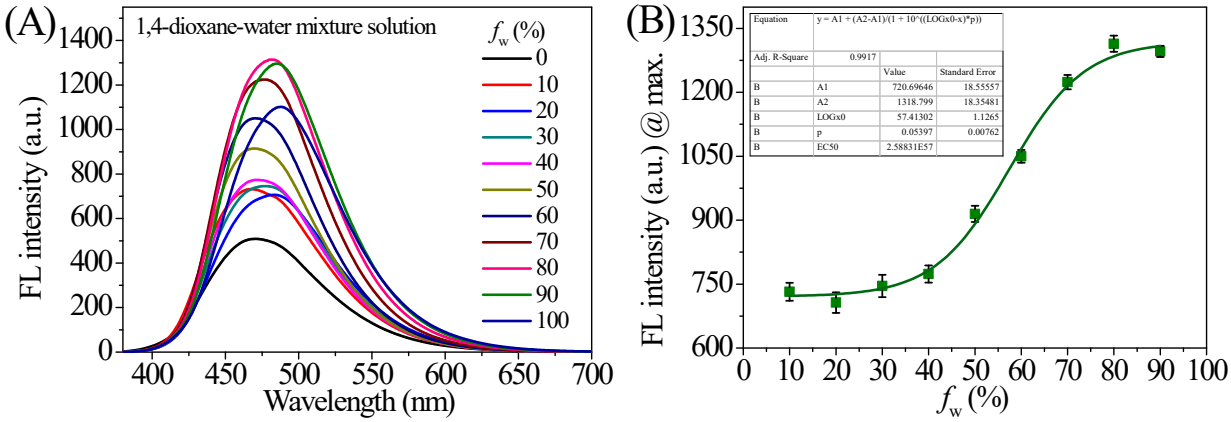


Fig. S9. (A) FL spectra of **NPP-N+** (20 μM) in Diox/H_2O mixtures with different water fractions; (B) Linear relationship between the maximum FL intensity and the water contents in Diox.

Table S1. The linear response ranges and the calibration curves for determination of water by **NPP-N+** in different solvents.

Solvent	Calibration curve	R^2	Response range (f_w)	LOD
EtOH	F = 11.4868f_w + 399.2368	0.9827	0 - 80	0.99
THF	F = 19.5318f_w + 386.8628	0.9720	0 - 30	0.75
DMSO	F = 8.6697f_w + 313.2257	0.9891	0 - 80	0.50
ACE	F = 10.2343f_w + 276.7389	0.9805	10 - 90	1.77
DMF	F = 10.6060f_w + 497.5521	0.9923	10 - 80	0.35
MeCN	F = 168.4380exp(-f_w/-50.2599)+258.0273	0.9902	0 - 90	-
MeOH	F = 556.2340 + 573.2136(1+10^((41.6029-f_w)*0.04423))	0.9818	0 - 100	-
Diox	F = 720.6964 + 598.1025(1+10^((57.4130-f_w)*0.05397))	0.9917	0 - 100	-

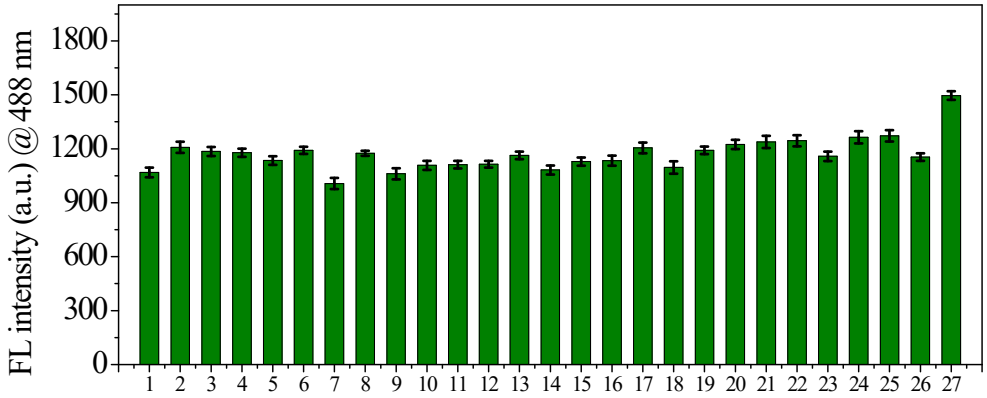
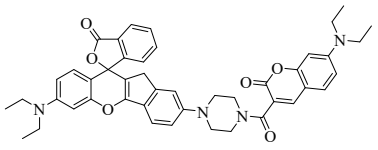
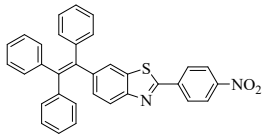
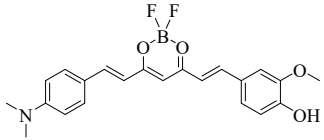
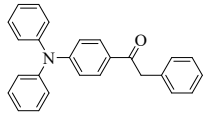
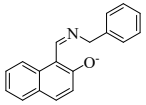
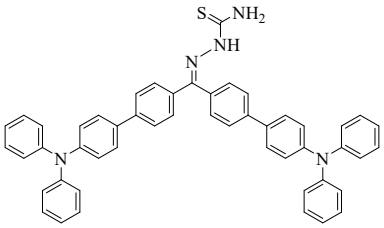
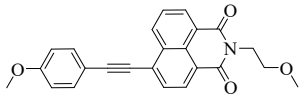
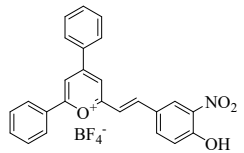
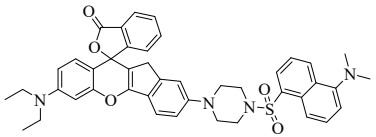
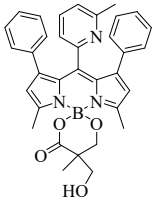
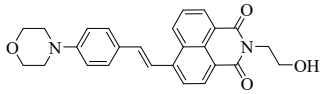
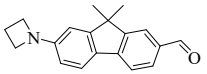
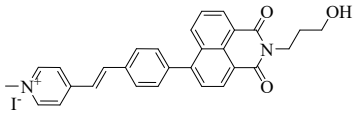


Fig. S10. The FL intensity of **NPP-N+** (20 μM) toward different analytes (100 μM) in H_2O solution (λem = 488 nm, 1: Li^+, 2: K^+, 3: Ca^{2+}, 4: Fe^{2+}, 5: Cr^{3+}, 6: Co^{2+}, 7: Zn^{2+}, 8: Cd^{2+}, 9: Hg^{2+}, 10: Ni^{2+}, 11: Pb^{2+}, 12: Ba^{2+}, 13: Sr^{2+}, 14: Cs^{2+}, 15: Br^-, 16: F^-, 17: HCO_3^-, 18: I^-, 19: NO_2^-, 20: S^{2-}, 21: $S_23_3^{2-}$, 22: SO_4^{2-}, 23: Glycine, 24: Glutamic acid, 25: Serine, 26: Blank, 27: Glycerol);

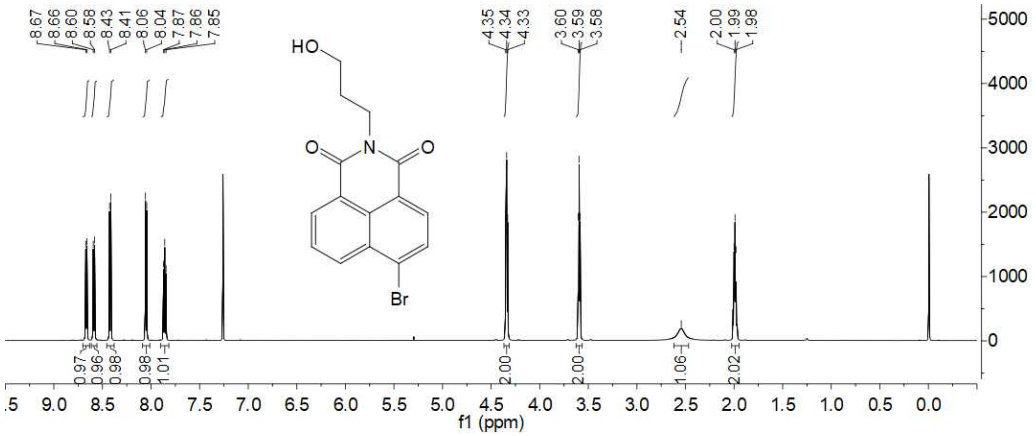
Table S2. Organic small molecule fluorescent probes for the detection of water content in water-soluble organic solvents.

Probe structure	Response type	Type of solvent	Solvent	LOD (v/v%)	Response range (v/v%)	Application situation	Ref.
	Turn ON	2	MeCN	0.011	0–1.8	-	[1]
	Turn OFF	4	THF	0.019	0.1-0.3	Conventional solvents	[2]
	Turn OFF	1	Dioxane	0.016	0-1	Conventional solvents	[3]
	Turn OFF	2	THF	0.0032	≤0.5 1-5	-	[4]
	Turn OFF	1	MeCN	0.0011	0-0.05	Inorganic salts	[5]
	Turn OFF	8	MeCN	0.0071	0-5.33	Raw food materials	[6]
	Turn OFF	5	THF	0.0523	0-30	Conventional solvents	[7]

	Turn OFF	2	Acetone	0.003	0.005-0.5	-	[8]
	Turn ON	3	DMF	0.026	0-8	-	[9]
	Turn ON	1	MeCN	-	0-10 40-90	-	[10]
	Turn OFF	3	Dioxane	54 ppm	0-1.4	Conventional solvents	[11]
	Turn OFF	3	DMSO	0.13	0-98	-	[12]
	Turn ON	8	DMSO	0.5	0-80	Medical alcohol and DMSO with natural water absorption	This work

3. Characterization

^{1}H NMR spectrum of compound 2:



^{1}H NMR (600 MHz, $CDCl_3$, δ):

8.67 (d, J=7.0 Hz, 1H), 8.59 (d, J=8.4 Hz, 1H), 8.42 (d, J=7.8 Hz, 1H), 8.05 (d, J=7.8 Hz, 1H), 7.90–7.82 (m, 1H): Aromatic protons on the 1,8-naphthalimide ring (C4, C5, C7, C8, C6 protons, respectively, numbered per the naphthalimide core structure).

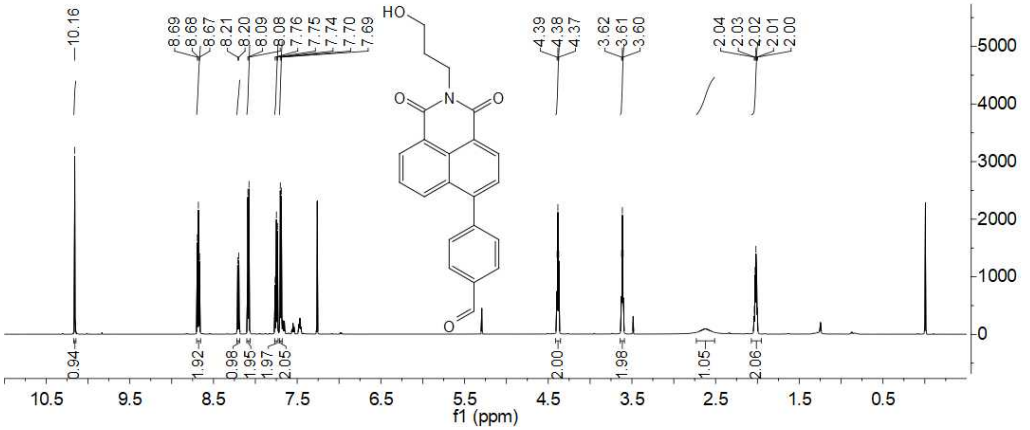
4.34 (t, J=6.2 Hz, 2H): Methylene protons (-N-CH_2-CH_2-CH_2-OH, C2' protons adjacent to the imide nitrogen).

3.63–3.56 (m, 2H): Methylene protons (-CH_2-OH, C4' protons adjacent to the hydroxyl group).

2.54 (s, 1H): Hydroxyl proton (-OH, exchangeable with $CDCl_3$).

2.02–1.95 (m, 2H): Methylene protons (-CH_2-CH_2-OH, C3' protons between C2' and C4').

^{1}H NMR spectrum of compound 3:



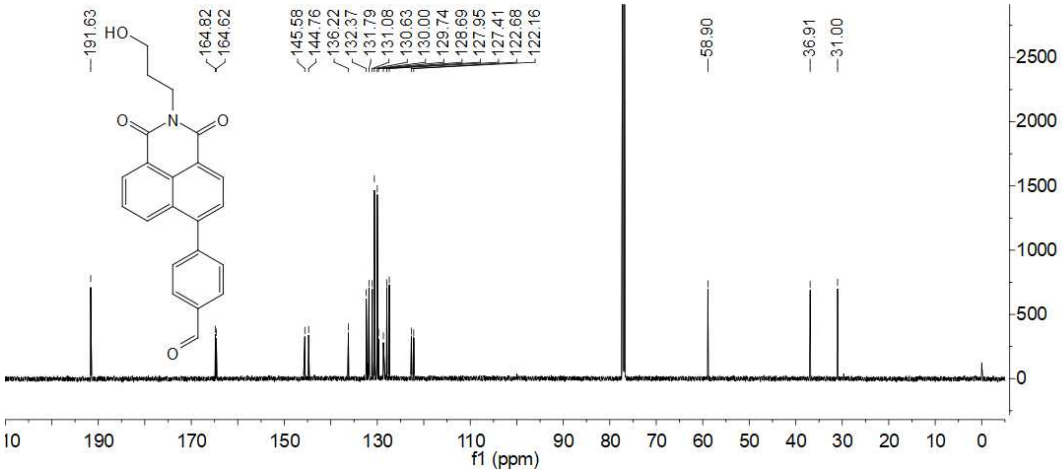
^{1}H NMR (600 MHz, $CDCl_3$, δ):

10.16 (s, 1H): Aldehyde proton (-CHO, C10 proton).

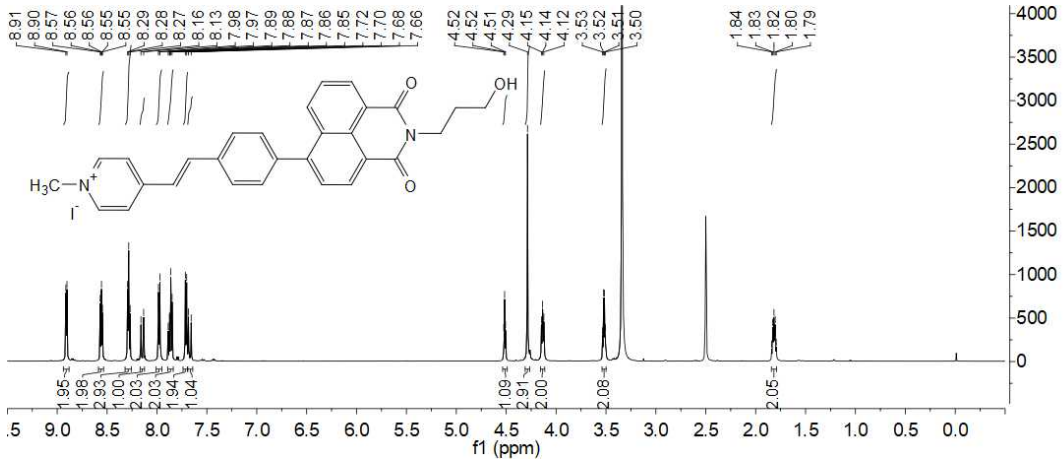
8.68 (t, J=8.1 Hz, 2H), 8.20 (d, J=8.4 Hz, 1H), 7.75 (t, J=8.5 Hz, 2H): Aromatic protons on the 1,8-naphthalimide ring (C4, C5, C7, C8 protons) and the benzene linker (C8, C9 protons adjacent to the aldehyde group).

4.38 (t, J=6.2 Hz, 2H), 3.61 (t, J=5.6 Hz, 2H), 2.62 (s, 1H), 2.07–1.95 (m, 2H): Same as Compound 2, corresponding to the 3-hydroxypropyl chain (-N-CH_2-CH_2-CH_2-OH).

^{13}C NMR spectrum of compound 3:



^{1}H NMR spectrum of NPP-N+:



^{1}H NMR (600 MHz, DMSO, δ):

8.91 (d, J=6.7 Hz, 2H): Aromatic protons on the pyridinium ring (C12, C15 protons adjacent to the positively charged nitrogen).

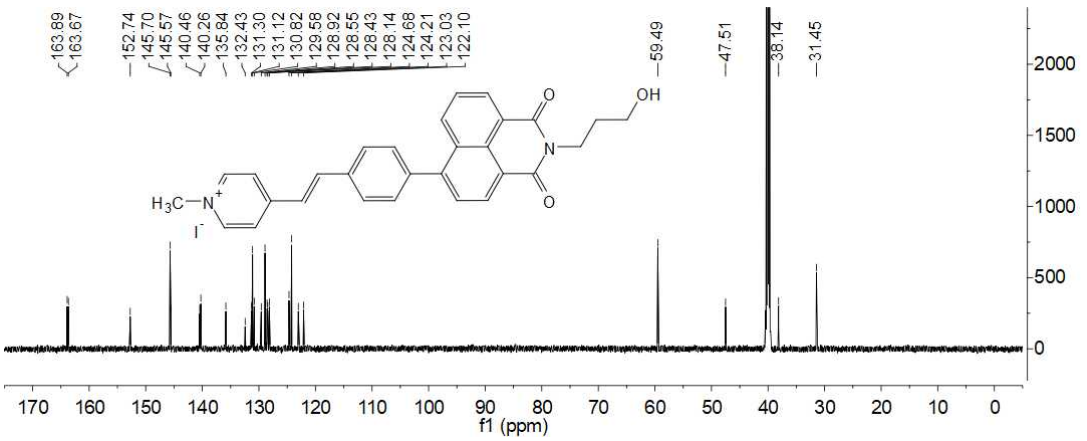
8.59–8.54 (m, 2H), 8.28 (t, J=7.6 Hz, 3H): Aromatic protons on the 1,8-naphthalimide ring (C4, C5, C7, C8 protons) and the styryl benzene ring (C8, C9 protons).

8.15 (d, J=16.4 Hz, 1H), 7.67 (d, J=16.4 Hz, 1H): trans-Stilbene protons (-CH=CH-, C10, C11 protons, large J value confirms trans configuration).

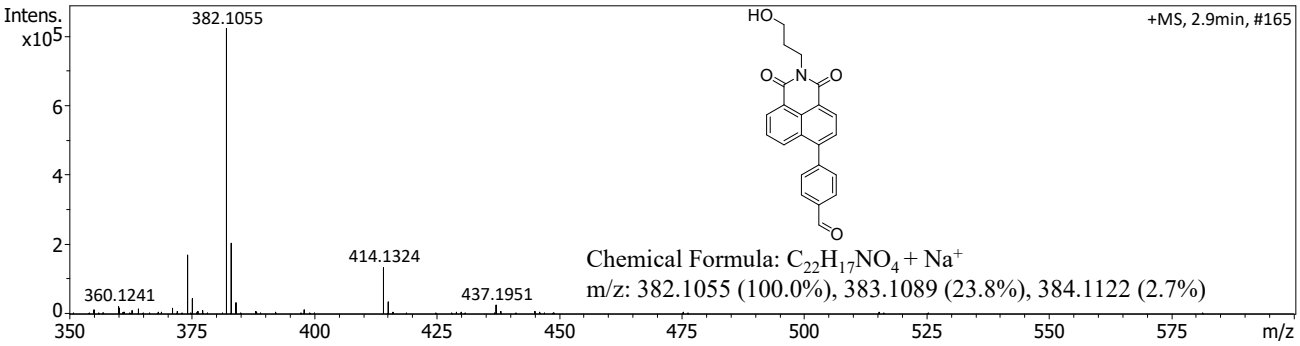
4.29 (s, 3H): Methyl protons on the pyridinium ring (-N^+-CH_3, C16 protons).

4.16–4.11 (m, 2H), 3.52 (dd, J=11.6, 6.2 Hz, 2H), 1.84–1.79 (m, 2H): 3-hydroxypropyl chain protons (-N-CH_2-CH_2-CH_2-OH), consistent with intermediates.

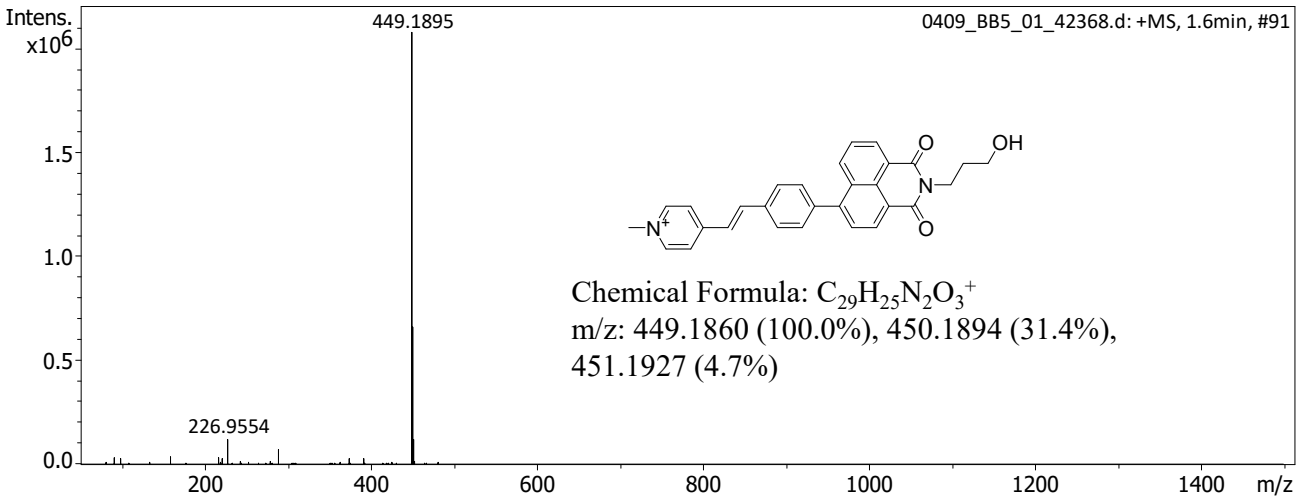
^{13}C NMR spectrum of NPP-N+:



HRMS spectrum of compound 3:



HRMS spectrum of NPP-N+:



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