Supporting Information (SI) for

A Flexible Molecular Organic Crystals with π−π Bonding for the Highly Selective Recognition of Hydrogen Isotopes

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Content

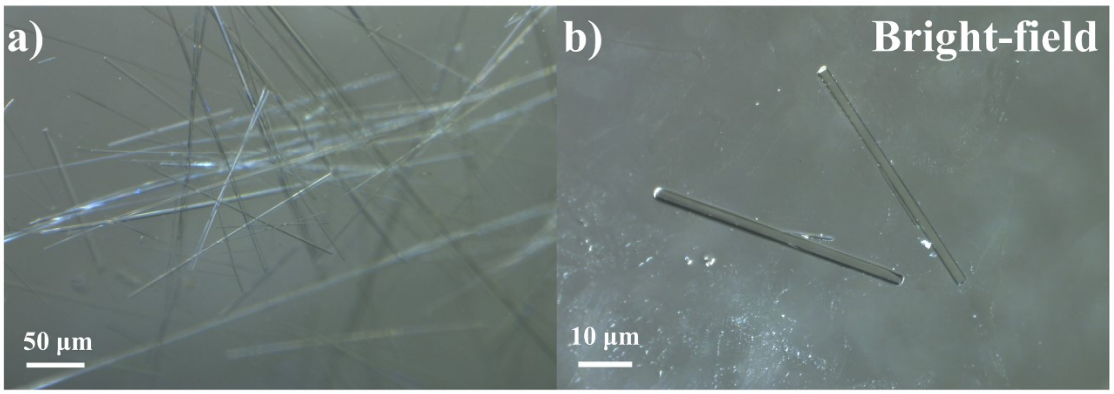

Figure S1. Microscopic images of crystals of ASP−101.

Measurement of the fresh crystal of ASP-101 by Single Crystal X-ray Diffraction: The prepared crystals of ASP−101 were transferred from the mother liquor onto the slide. With the aid of a microscope, a rod−shaped crystal, that exhibited no grain or cracks, was selected and mounted on a cryoloop using silicon oil. The corresponding crystallographic data (CCDC: 2381082) are shown in Table S1.

Table S1. Crystallographic data of the fresh crystal of ASP-101.

Compound	**ASP-101(fresh)**
Empirical formula	$C_{38}H_{41}O_{12}S_4$
Mr [g·mol^{-1}]	817.95
Crystal system	monoclinic
Space group	*C 2/c*
a(Å)	20.809(3)
b(Å)	18.499(2)
c(Å)	10.0983(12)
α(°)	90
β(°)	95.989(6)
γ(°)	90
Volume(Å^3)	3866.1(8)

Z	4
D_c (g·cm^{-3})	1.405
μ(mm^{-1})	0.308
F(000)	1716
Temperature(K)	150(2)
GOF on F^2	1.117
R_{int}	3.3%
R_1[a]/wR_2[b][$I > 2\sigma(I)$]	0.0772/0.1755
R_1[a]/wR_2[b] (all data)	0.1062/0.1910

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2=[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

Measurement of dried crystal of ASP-101 by Single Crystal X-ray Diffraction: Fresh crystals of ASP-101 are prone to absorb water in the air, which may affect the accurate identification of trace water molecules in high-purity heavy water. Thus, fresh crystals of ASP-101 were dried at 65℃ for 20 minutes and then measured using a single crystal X-ray diffractometer. The corresponding crystallographic data (Table S2) is almost same to the data in Table S1, indicating that the structure of ASP-101 doesn't change after the dry treatment. Therefore, dried crystals were used in subsequent other tests and experiments.

Table S2. Crystallographic data of the dried crystal of ASP-101.

Compound	**ASP-101(dry)**
Empirical formula	$C_{38}H_{42}O_{12}S_4$
Mr [g·mol^{-1}]	818.95
Crystal system	monoclinic
Space group	*C 2/c*
a(Å)	20.819(4)
b(Å)	18.462(4)

c(Å)	10.101(2)
α(°)	90
β(°)	96.203(8)
γ(°)	90
Volume(Å^3)	3859.6(14)
Z	4
D_c (g·cm^{-3})	1.409
μ(mm^{-1})	0.309
F(000)	1720
Temperature(K)	150
GOF on F^2	1.039
R_{int}	16.26 %
R_1[a]/wR_2[b][$I>2\sigma(I)$]	0.1144 / 0.2638
R_1[a]/wR_2[b] (all data)	0.1631 / 0.2998

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b]$wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S3. The bond lengths and bond angles of hydrogen bonds in the structures of fresh and dried crystals of ASP-101.

	D-H-A Bonds	**Bond length(Å)**	**Bond angle**
ASP-101(fresh)	O2-H1--O5	2.6416	165.264°
	O1-H2--O3	2.6053	144.359°
ASP-101(dry)	O9-H9--O57	2.8172	146.659°
	O18-H18--O4	2.6438	163.204°

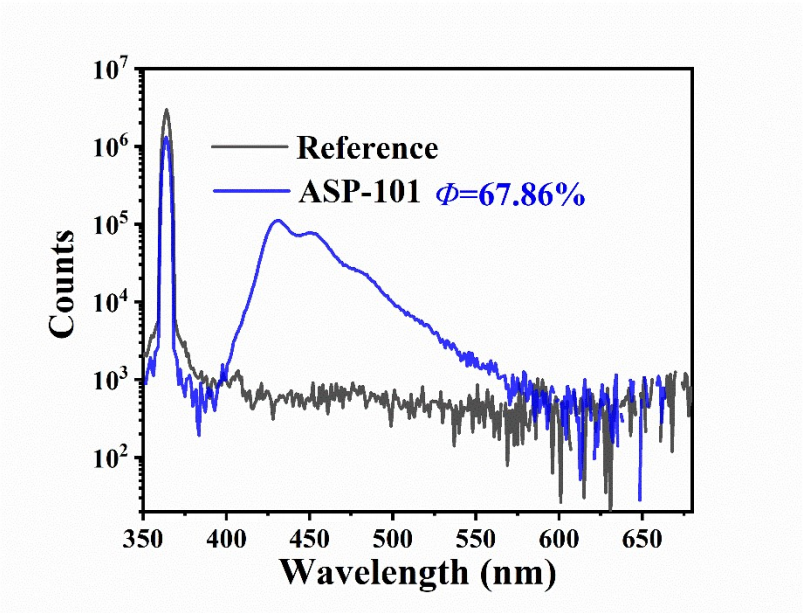

Figure S2. Quantum yield of ASP−101.

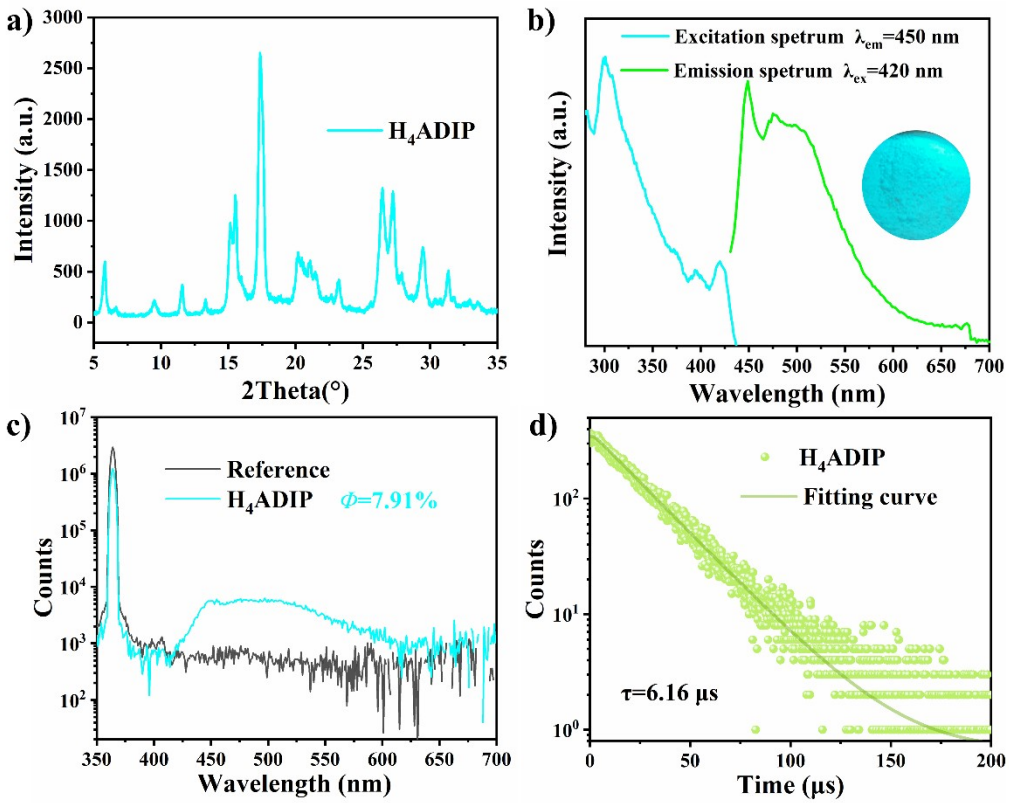

Figure S3. a) The powder X-ray diffraction pattern of H_4ADIP; b) Excitation and emission spectra of H_4ADIP, inset is its fluorescent photograph under 365 nm UV; c, d) Quantum yield and fluorescence lifetime of H_4ADIP.

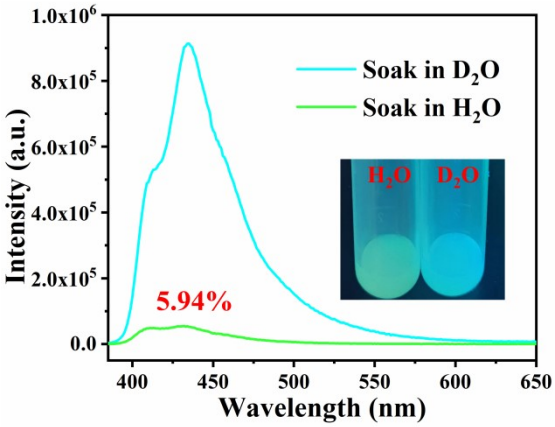

Figure S4. The emission spectra of ASP−101 in H_2O and D_2O.

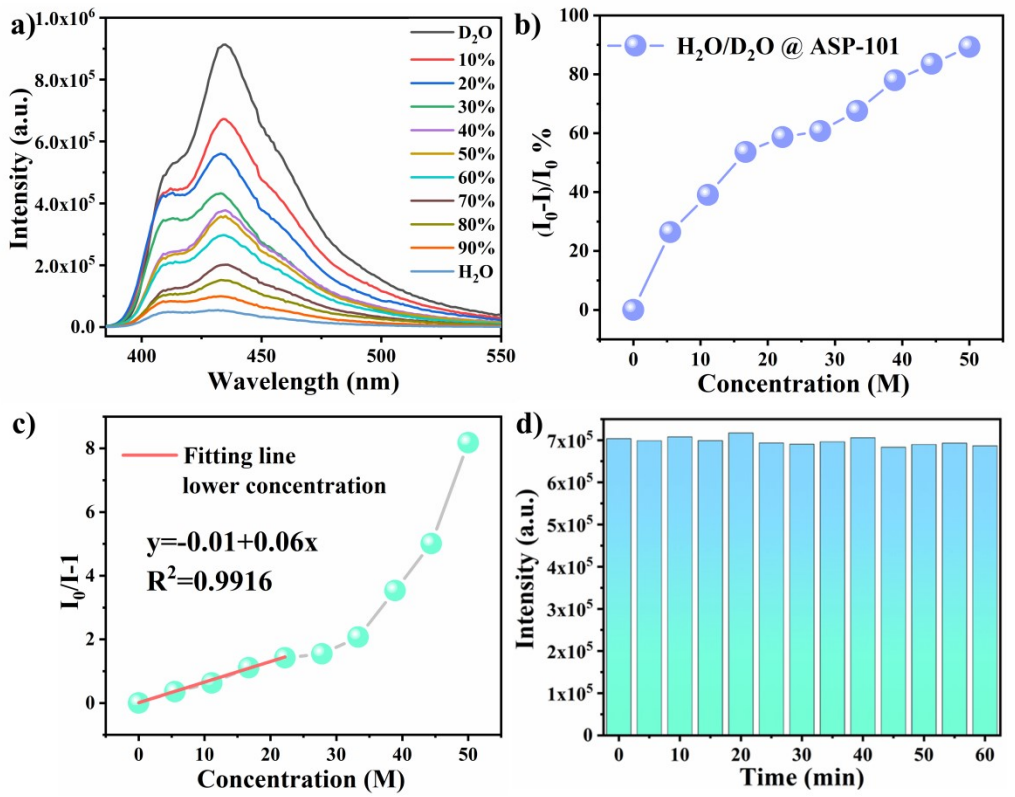

Figure S5. a) Luminescence spectra of ASP−101 soaked in the mixed solutions of H_2O and D_2O containing different amount of H_2O (vol.%). b) The correlation between the quenching ratio $(I_0-I)/I_0$ and concentration. c) Relationship between $I_0/I-1$ and the concentration of H_2O. I_0 and I refer to the luminescence intensity of ASP−101 soaked in D_2O and the mixed solutions of H_2O and D_2O, respectively. The volume concentrations of 0 to 90% correspond to molar concentrations of 0 to 50 M. d) Variation in the luminescence intensity of ASP-101 immersed in a mixed solution of H_2O and D_2O (1:10 ratio) over time.

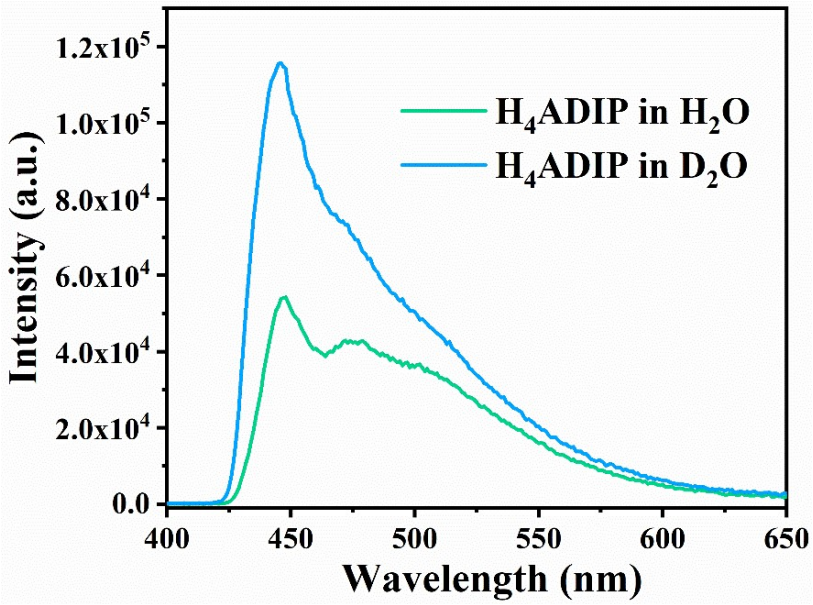

Figure S6. The emission spectra of H_4ADIP in H_2O and D_2O.

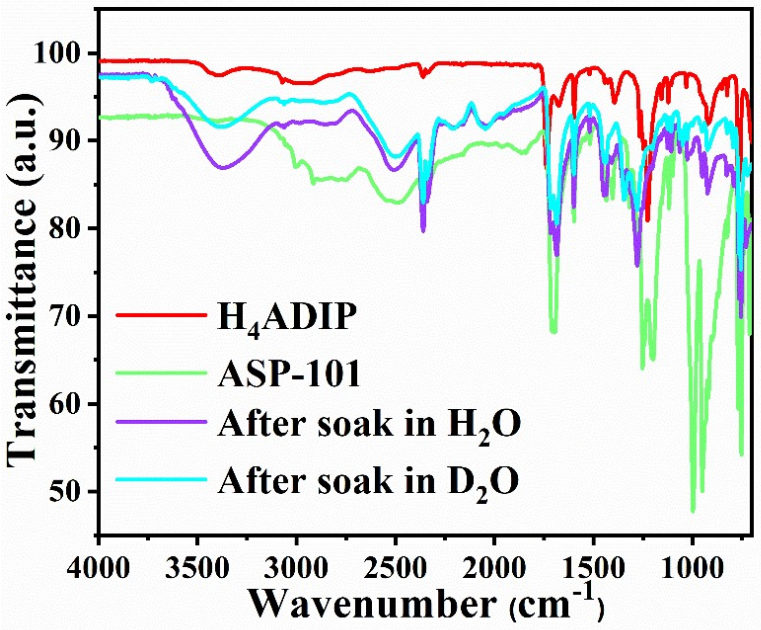

Figure S7. Fourier transform infrared spectra of H_4ADIP and ASP-101, and the spectra of ASP-101 after being soaked in H_2O and D_2O.

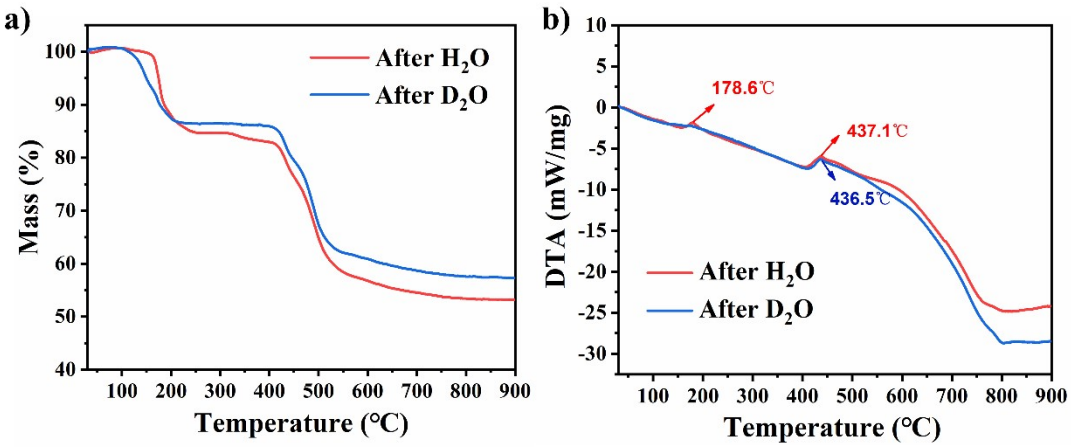

Figure S8. Thermogravimetric curves of ASP−101 after being soaked in H_2O and D_2O, respectively. a) Mass loss curves; b) Differential thermal analysis (DTA) curves.

Table S4. Elemental analysis results of ASP−101 before and after being soaked in H_2O and D_2O, respectively.

Sample	C area	H area	S area	C %	H %	S %
ASP−101	34106	6830	2250	62.17	4.426	9.308
After D_2O	33 853	4 837	264	69.01	3.653	1.160
After H_2O	41159	5939	239	69.61	3.619	0.869

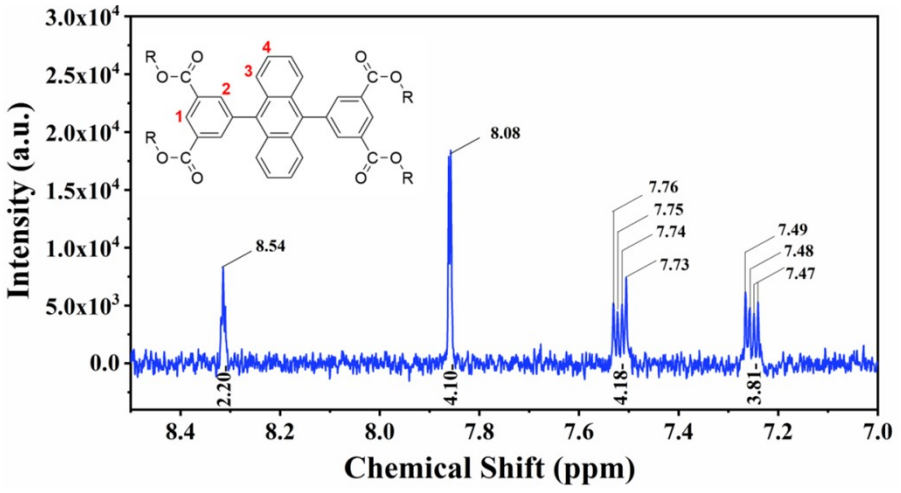

Figure S9. The 7.0 to 8.5 ppm region of ^{1}H-NMR spectrum of ASP-101 after its partial dissolution in D_2O.