Hydrogen Bond Effect on the Photophysical Properties of 2-Ureido-4[1H]-pyrimidinone Quadruple Hydrogen Bonded Systems

Jun-Sheng Chen,[1, 3, 4] Feng-Jiao Zhao,[1, 4] Yang Yang,[1] Tian-Shu Chu[* 1, 2]

[1]*State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, People's Republic of China*

[2]*Institute for Computational Sciences and Engineering, Laboratory of New Fiber Materials and Modern Textile, the Growing Base for State Key Laboratory, Qingdao University, Qingdao, 266071, People's Republic of China*

[3]*Department of Chemical Physics, Lund University, 22100 Lund, Sweden*

[4]*University of the Chinese Academy of Sciences, Beijing, 100049, People's Republic of China*

[*] Corresponding author, Emails: tschu@dicp.ac.cn; tschu008@163.com

Table S1. Summary of steady-state absorption and fluorescence emission measurements.

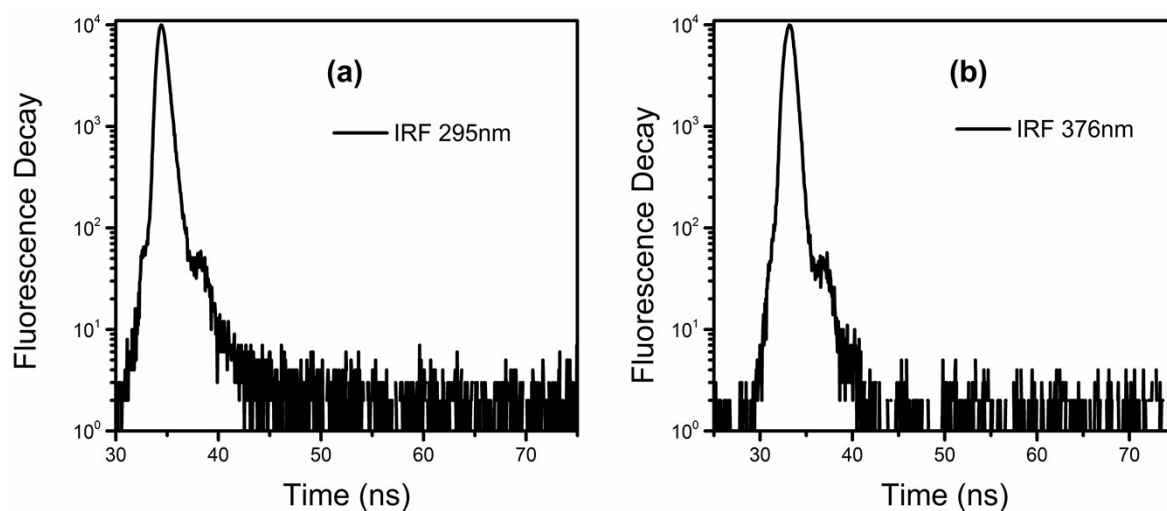| compound	absorption bands λ_{max} / nm [$\varepsilon \times 10^4$ / cm^{-1}·M^{-1}]	λ_{ex} /nm	λ_{emis} /nm
AnUP-DCM	391 [4.59], 370 [4.74], 352 [2.91], 335 [1.34], 259 [62.06]	350	392, 415, 441, 470
AnUP-DMSO	393 [9.11], 372 [9.63], 354 [6.02], 337 [3.05], 287 [12.29], 261 [116.45]	350	395, 418, 443,469
NaUP-DCM	268 [13.88]	280	319, 326, 350, 334
NaUP-DMSO	288 [24.93]	280	319, 335, 350
UPNa-DCM	288 [1.35], 256 [4.08]	280	340, 353
UPNa-DMSO	285 [0.68]	280	358

Figure S1. The instrument response functions (IRFs)

Table S2: Calculated important bond lengths (in Å) and bond angles (in degree) for the fully optimized structure of AnUP-dimer (in DCM) and AnUP-DMSO complex (in DMSO) in ground state (S_0) and first excited state (S_1). The corresponding X-ray data[1] are listed in parentheses.

	AnUP(DCM)[a]	AnUP(DMSO)[a]	AnUP(DCM)[b]	AnUP(DMSO)[b]
N_1-H_1	1.03 (0.86)	1.02	1.04	1.03
N_2-H_2	1.04 (0.86)	1.04	1.04	1.04
N_1'-H_1'	1.03 (0.86)	-	1.04	-
N_2'-H_2'	1.04 (0.86)	-	1.04	-
N_4-H_3	1.03 (0.86)	1.03	1.03	1.03
N_4'-H_3'	1.03 (0.86)	-	1.03	-
$O_1'\cdots H_1$	1.71 (1.90)	1.99	1.71	1.99
$N_3'\cdots H_2$	1.92 (2.12)	-	1.92	-
$N_3\cdots H_2'$	1.92 (2.12)	-	1.92	-
$O_1\cdots H_1'/H_2$	1.71 (1.90)	1.68	1.72	1.68
$O_2\cdots H_3$	1.72 (1.91)	1.83	1.72	1.83
$O_2'\cdots H_3'$	1.72 (1.90)	-	1.72	-
$O_1'\cdots H_1$-N_1	173.19 (168.75)	141.08	173.25	141.06
$N_3'\cdots H_2$-N_2	179.70 (171.39)	-	179.79	-
$N_3\cdots H_2'$- N_2'	179.71 (171.99)	-	179.62	-
$O_1\cdots H_1'/H_2$- N_1'/N_2	173.19 (161.56)	170.67	173.22	170.68
$O_2\cdots H_3$-N_4	136.60 (133.01)	132.68	136.63	132.77
$O_2'\cdots H_3'$-N_4'	136.60 (133.68)	-	136.58	-
C_1-N_1-C_2-N_2	-179.77 (-176.79)	-179.71	-179.87	-179.69
O_2-C_2-N_2-C_3	0.09 (-8.06)	-9.78	0.72	-9.93
H_3-N_4-C_4-C_6	-179.38 (177.42)	179.71	-179.65	179.82
C_5-C_6-C_7-C_8	126.57 (130.37)	-57.78	125.96	-58.08
C_5-C_6-C_8-C_9	-161.30 (-158.78)	-97.56	-160.44	-97.00
C_1'-N_1'-C_2'-N_2'	179.77 (-178.33)	-	179.78	-
O_2'-C_2'-N_2'-C_3'	-0.09 (-0.85)	-	0.14	-
H_3'-N_4'-C_4'-C_6'	179.39 (-179.25)	-	179.57	-
C_5'-C_6'-C_7'-C_8'	-126.57 (-128.67)	-	-126.55	-
C_5'-C_6'-C_8'-C_9'	161.31 (161.46)	-	161.20	-

[a] The geometric parameters of the ground state (S_0). [b] The geometric parameters of the first excited state (S_1)

Table S3: Calculated important bond lengths (in Å) and bond angles (in degree) for the fully optimized structure of NaUP-dimer (in DCM) and NaUP-DMSO complex (in DMSO) in ground state (S_0) and first excited state (S_1).

	NaUP(DCM)[a]	NaUP(DMSO)[a]	NaUP(DCM)[b]	NaUP(DMSO)[b]
N_1-H_1	1.04	1.03	1.04	1.03
N_2-H_2	1.04	1.04	1.04	1.04
N_1'-H_1'	1.04	-	1.04	-
N_2'-H_2'	1.04	-	1.04	-
N_4-H_3	1.03	1.03	1.03	1.03
N_4'-H_3'	1.03	-	1.03	-
$O_1'\cdots H_1$	1.72	1.97	1.72	1.98
$N_3'\cdots H_2$	1.92	-	1.91	-
$N_3\cdots H_2'$	1.92	-	1.92	-
$O_1\cdots H_1'/H_2$	1.72	1.69	1.71	1.69
$O_2\cdots H_3$	1.72	1.83	1.73	1.83
$O_2'\cdots H_3'$	1.72	-	1.72	-
$O_1'\cdots H_1$-N_1	173.12	141.38	173.05	141.47
$N_3'\cdots H_2$-N_2	179.26	-	179.76	-
$N_3\cdots H_2'$-N_2'	179.80	-	179.61	-
$O_1\cdots H_1'/H_2$-N_1'/N_2	173.20	171.27	173.15	171.29
$O_2\cdots H_3$-N_4	136.56	132.71	136.45	132.71
$O_2'\cdots H_3'$-N_4'	136.61	-	136.64	-
C_1-N_1-C_2-N_2	179.70	-179.09	-179.19	-178.96
O_2-C_2-N_2-C_3	0.34	-8.83	0.75	-8.55
H_3-N_4-C_4-C_6	-179.52	-179.94	-179.15	179.95
C_5-C_6-C_7-C_8	**-90.53**	-83.61	**-102.74**	-86.10
C_5-C_6-C_8-C_9	**100.54**	-115.40	**121.76**	-118.59
C_1'-N_1'-C_2'-N_2'	-179.62	-	-179.70	-
O_2'-C_2'-N_2'-C_3'	0.50	-	1.16	-
H_3'-N_4'-C_4'-C_6'	179.59	-	-179.84	-
C_5'-C_6'-C_7'-C_8'	**89.86**	-	**78.69**	-
C_5'-C_6'-C_8'-C_9'	**-99.24**	-	**-17.69**	-

[a] The geometric parameters of the ground state (S_0). [b] The geometric parameters of the first excited state (S_1)

Table S4: Calculated important bond lengths (in Å) and bond angles (in degree) for the fully optimized structure of UPNa-dimer (in DCM) and UPNa-DMSO complex (in DMSO) in ground state (S_0) and first excited state (S_1).

	UPNa (DCM)[a]	UPNa (DMSO)[a]	UPNa (DCM)[b]	UPNa (DMSO)[b]
N_1-H_1	1.04	1.04	1.05	1.05
N_2-H_2	1.04	1.05	1.04	1.05
N_1'-H_1'	1.04	-	1.04	-
N_2'-H_2'	1.04	-	1.04	-
N_4-H_3	1.03	1.03	1.03	1.02
N_4'-H_3'	1.03	-	1.03	-
$O_1'\cdots H_1$	**1.70**	**1.75**	**1.66**	**1.68**
$N_3'\cdots H_2$	**1.92**	-	**1.89**	-
$N3\cdots H2'$	**1.92**	-	**1.90**	-
$O1\cdots H1'/H_2$	1.70	**1.71**	1.70	**1.68**
$O_2\cdots H_3$	**1.74**	**1.84**	**1.76**	**1.86**
$O_2'\cdots H_3'$	**1.74**	-	**1.75**	-
$O1'\cdots H_1$-N_1	171.54	164.38	171.21	167.71
$N_3'\cdots H_2$-N_2	177.59	-	178.26	-
$N_3\cdots H_2'$-N_2'	177.59	-	177.60	-
$O_1\cdots H_1'/H_2$-N_1'/N_2	171.54	172.10	172.12	171.63
$O_2\cdots H_3$-N_4	135.05	131.90	134.10	131.05
$O_2'\cdots H_3'$-N_4'	135.05	-	134.72	-
N_2-C_1-N_1-C_2	-178.32	-172.62	-173.29	-168.38
N_2-C_1-C_2-C_3	**-178.03**	**40.19**	**-164.44**	**26.04**
N_2'-C_1'-N_1'-C_2'	-178.32	-	-177.75	-
N_2'-C_1'-C_2'-C_3'	-178.04	-	-173.58	-

[a] The geometric parameters of the ground state (S_0). [b] The geometric parameters of the first excited state (S_1)

AnUP
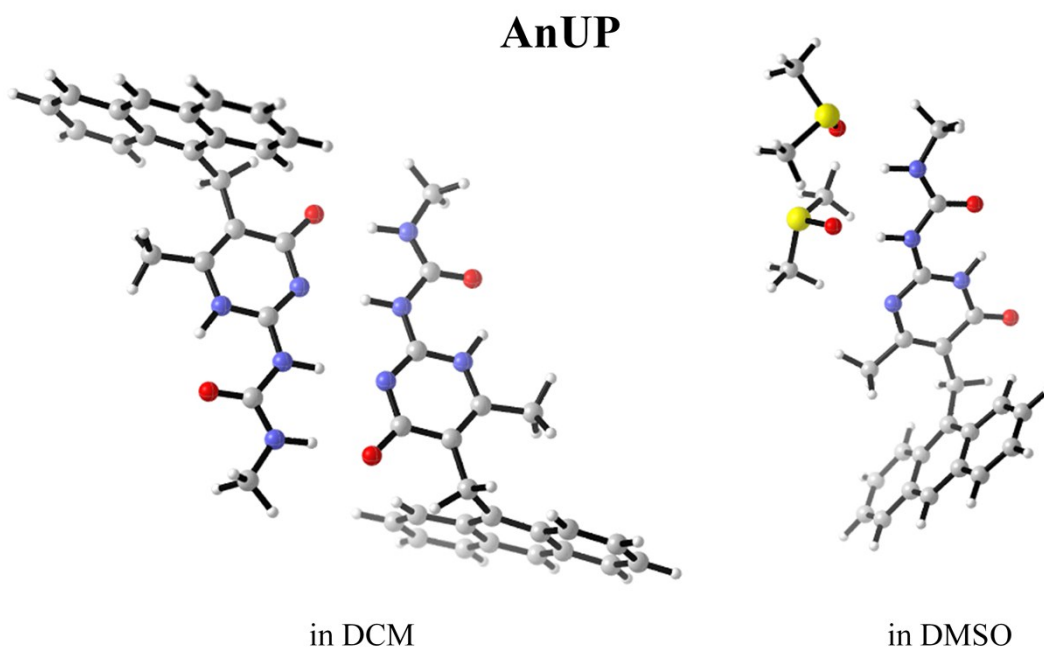

in DCM   in DMSO

Figure S2. Optimized first excited state (S$_1$) structures for AnUP dimer (in DCM) and monomer complexes (in DMSO). Gray: C; red: O; blue: N; yellow: S; white: H.
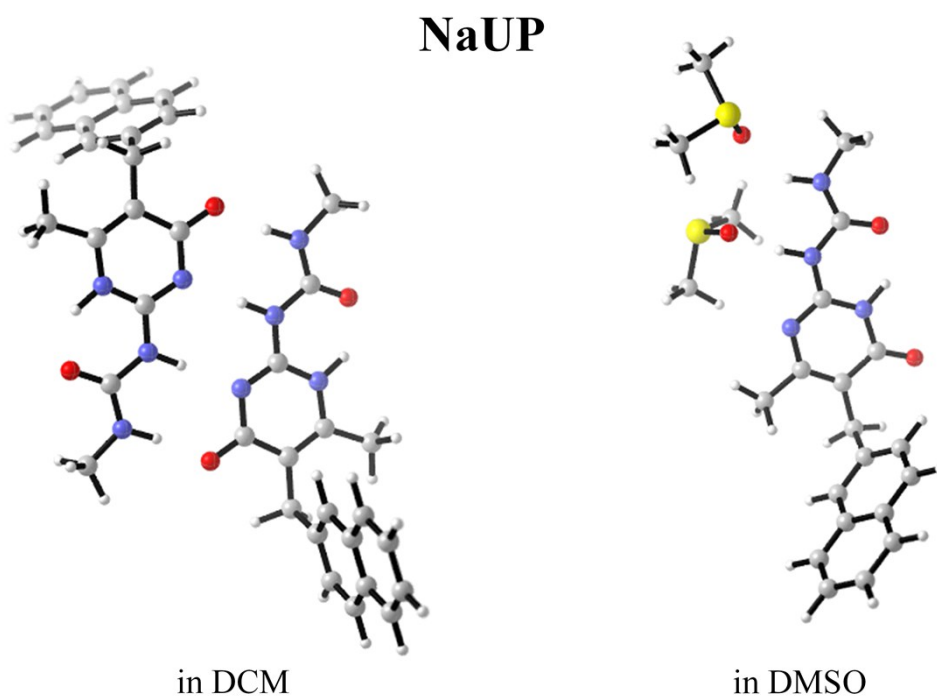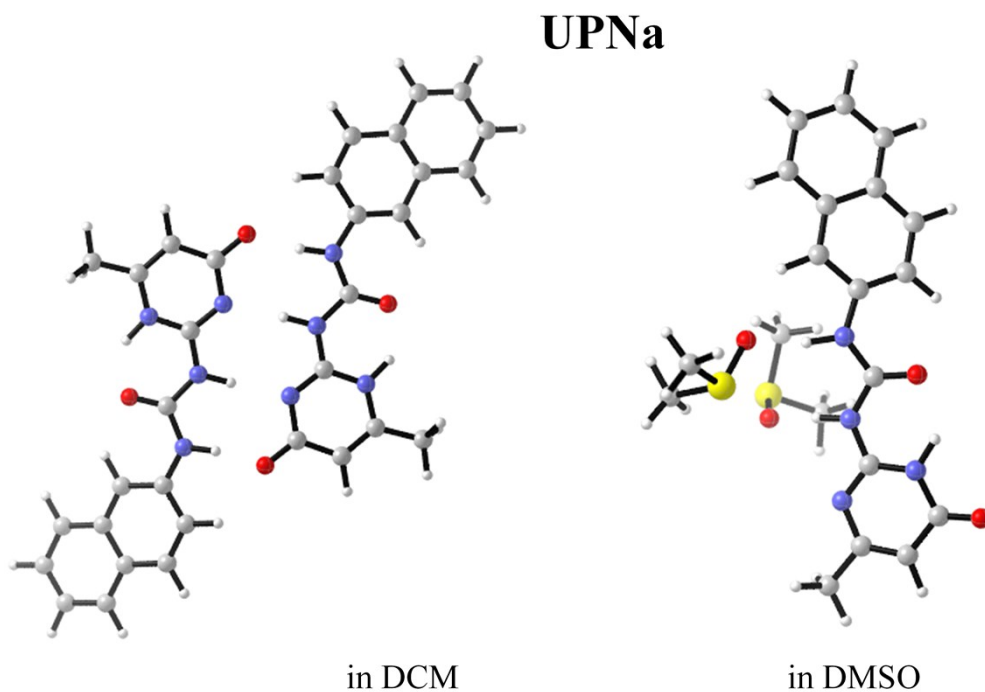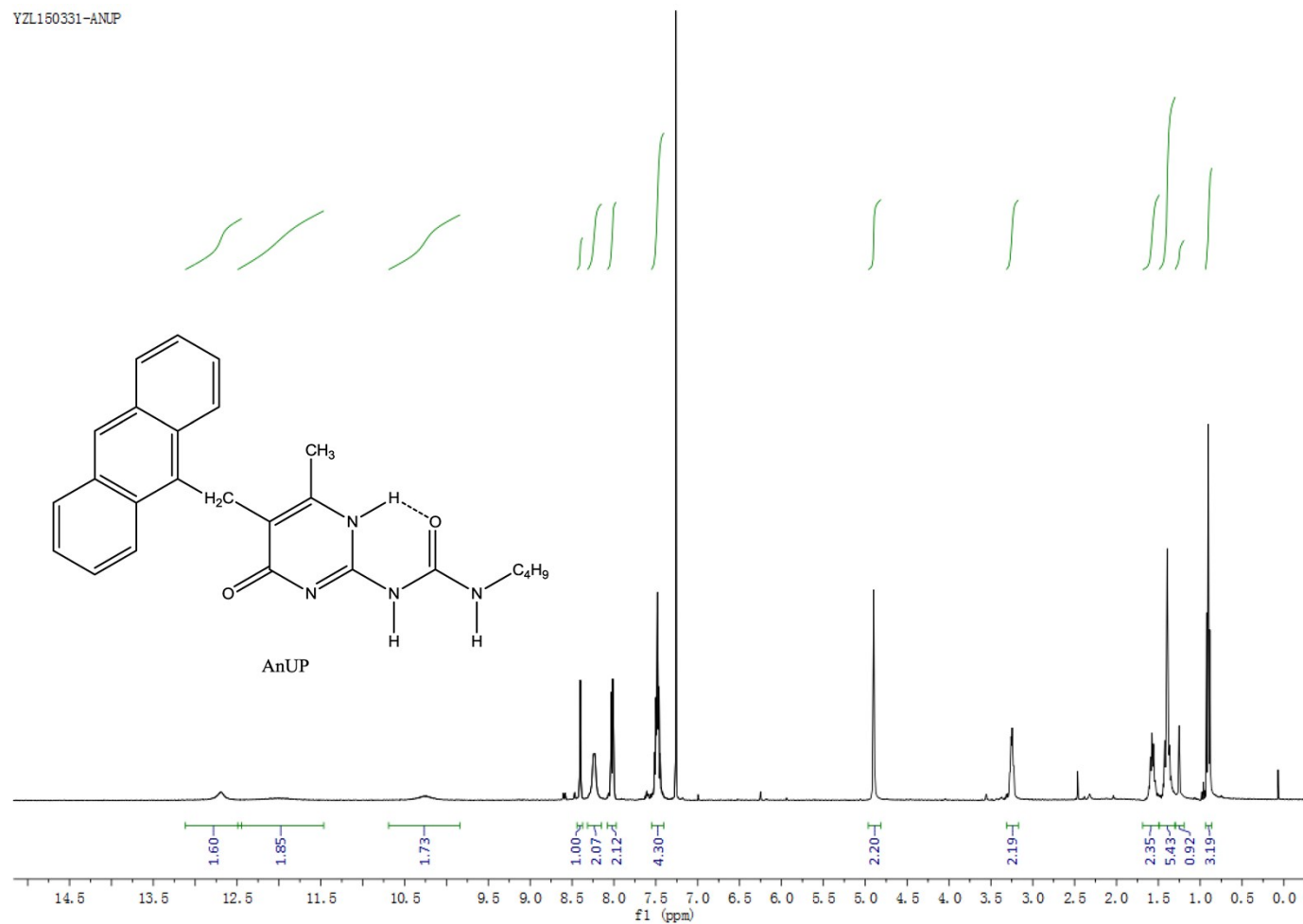
NaUP

in DCM   in DMSO

Figure S3. Optimized first excited state (S$_1$) structures for NaUP dimer (in DCM) and monomer complexes (in DMSO). Gray: C; red: O; blue: N; yellow: S; white: H.

UPNa

in DCM   in DMSO

Figure S4. Optimized first excited state (S$_1$) structures for UPNa dimer (in DCM) and monomer complexes (in DMSO). Gray: C; red: O; blue: N; yellow: S; white: H.
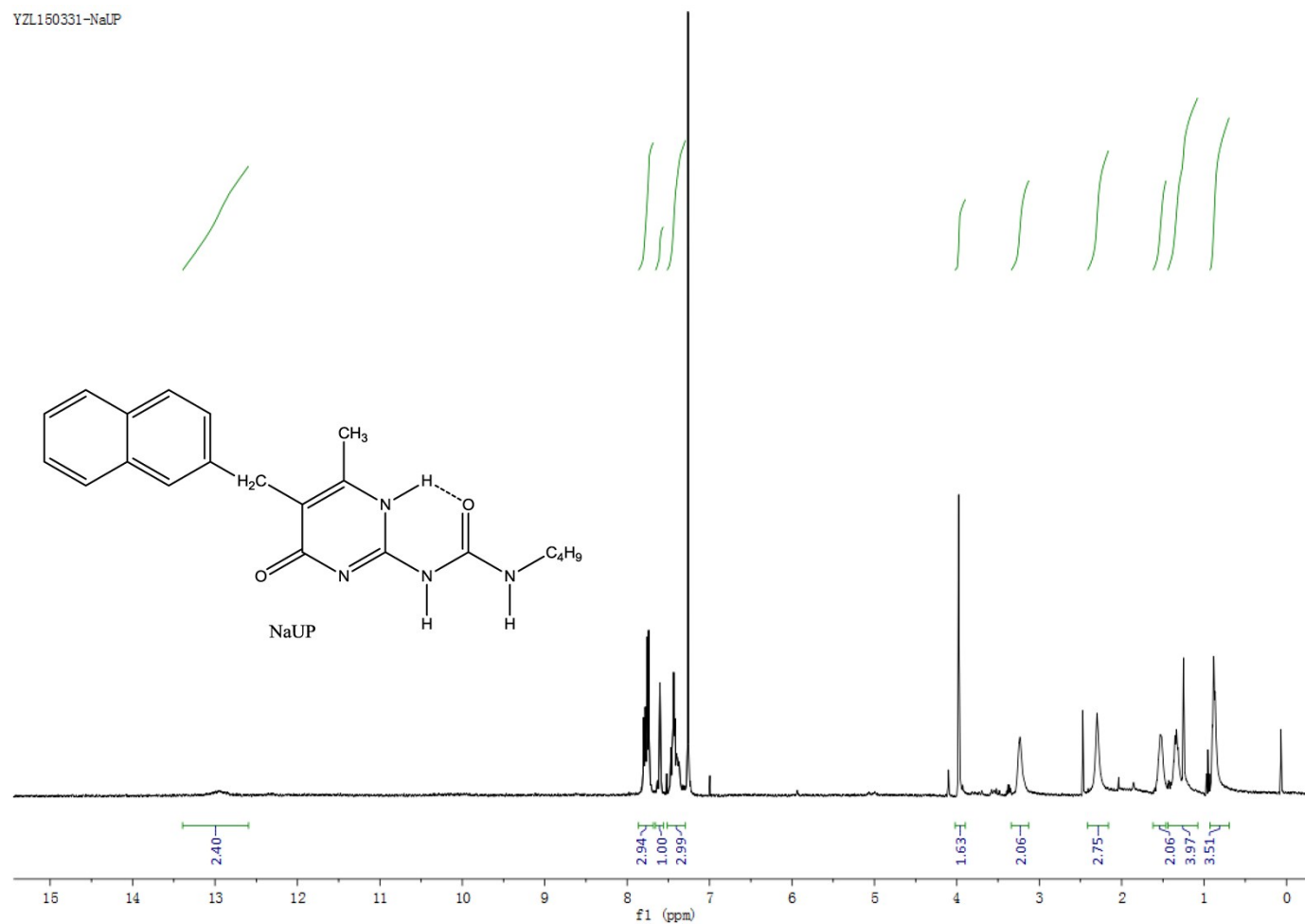
Figure S6. ^{1}H NMR spectrum of AnUP in CDCl$_3$

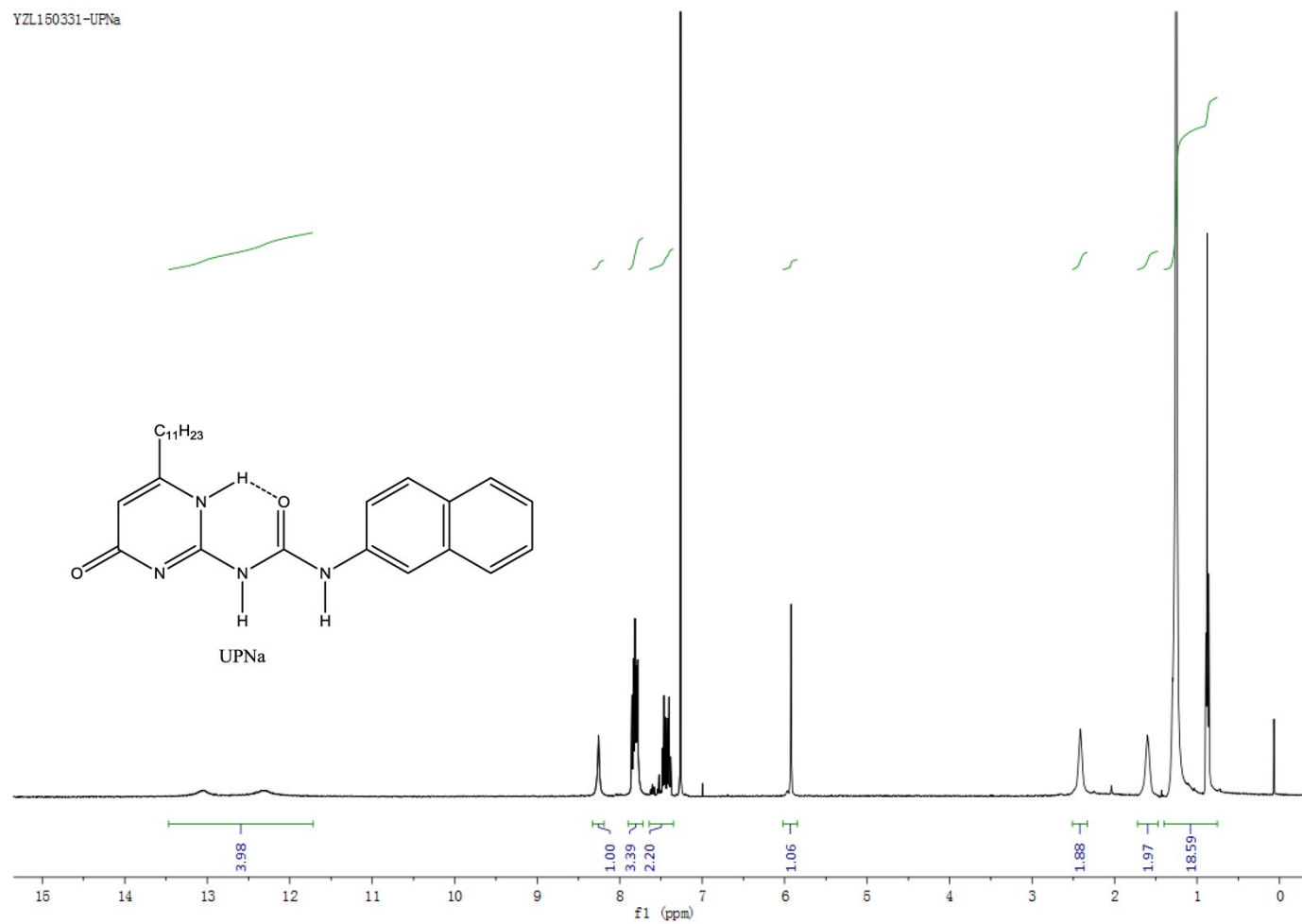**Figure S7.** ^{1}H NMR spectrum of NaUP in CDCl$_3$

Figure S8. ^{1}H NMR spectrum of UPNa in CDCl$_3$

^{1}H NMR spectra were recorded on a Bruker Avance II 400 MHz NMR spectrometers using CDCl$_3$ as solvent. Chemical shifts (δ) are reported to the shift-scale calibrated with the residual NMR solvent as internal standard.

Reference:

1.	Zhao, Y.-p.; Zhao, C.-c.; Wu, L.-z.; Zhang, L.-p.; Tung, C.-h.; Pan, Y.-j., First Fluorescent Sensor for Fluoride Based on 2-Ureido-4 [1H] -pyrimidinone Quadruple Hydrogen-Bonded AADD Supramolecular Assembly. *J Org Chem* **2006,** *71*, 2143-2146.