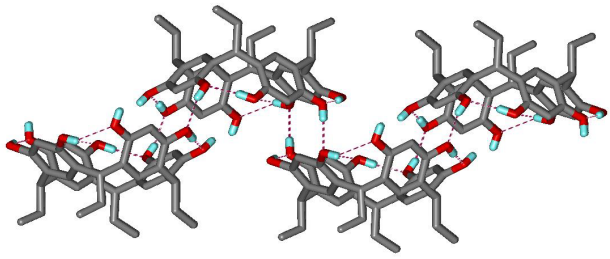
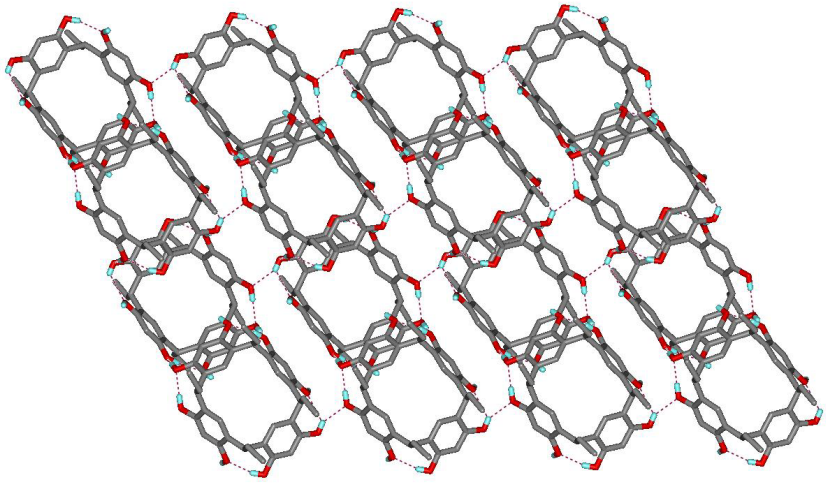
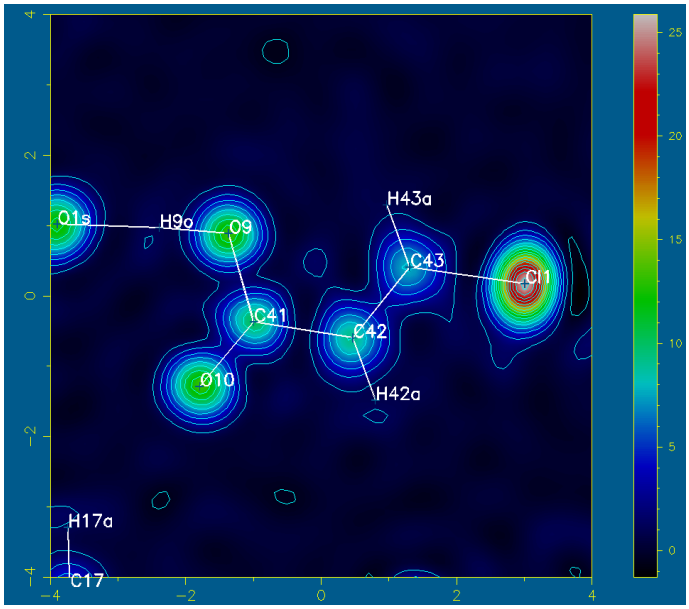


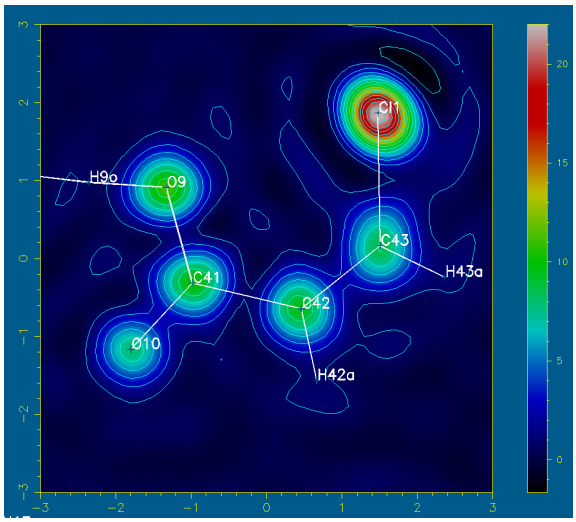
(a)



(b)

Figure S1. The hydrogen-bonded layer in **1-*E*** viewed (a) on the side and (b) from above.





(a) (b)

Figure S2. The Fourier maps for (a) *E* and (b) *Z*- HClA in 1-*E* and 1-*Z* (contour lever: 1.5 e Å^{-3}).

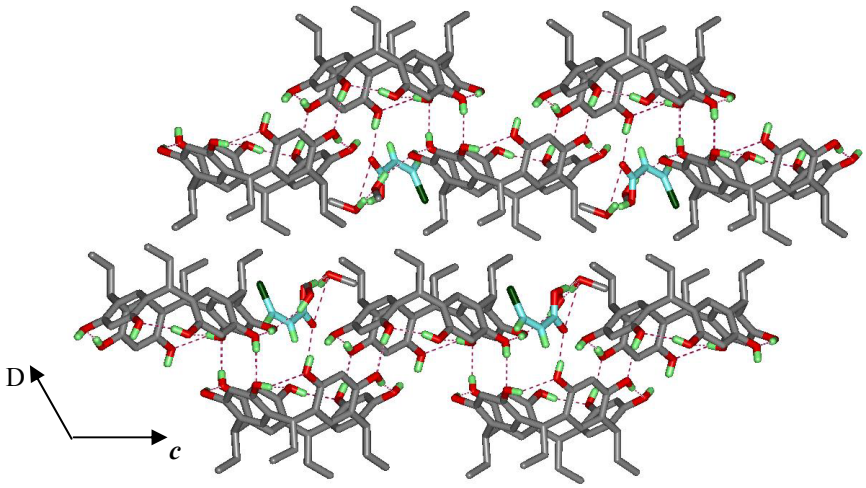
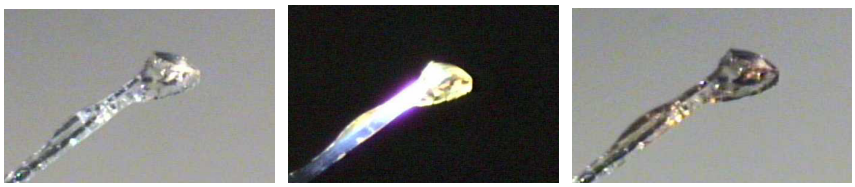
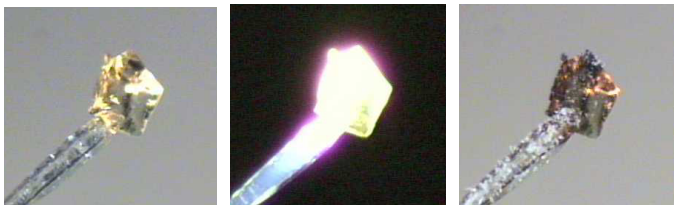


Figure S3. Three-dimensional architecture of **1-*Z*** viewed along the *a*-axis direction.



(a)



(b)

Figure S4. The crystals used in the experiments (a) **1-*E*** and (b) **1-*Z*** (left: before; center: during exposure; right: after exposure).

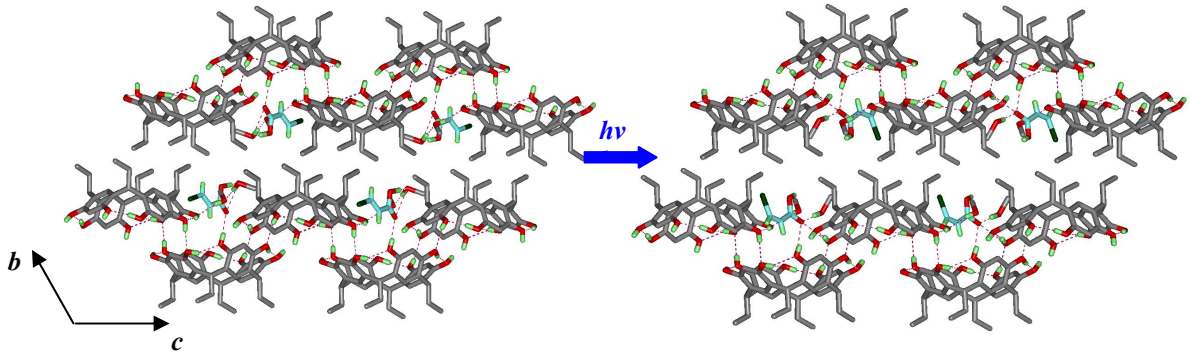


Figure S5. Three-dimensional architecture of **1-*Z*** viewed along the *a*-axis direction and the change of the guests on exposure.

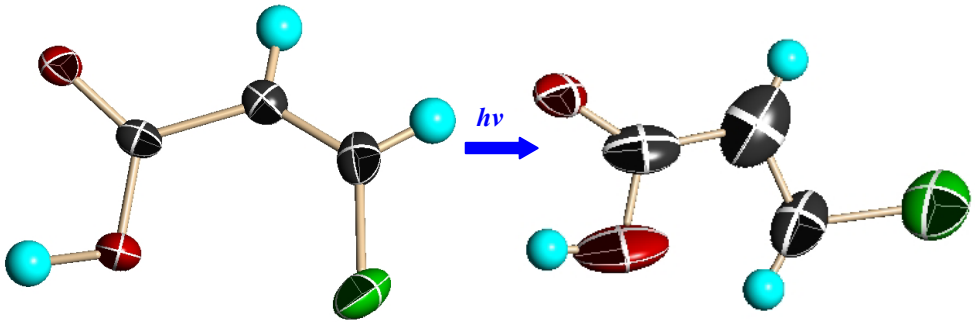


Figure S6. Change in structure of HClA in **1-*Z*** on 1 hour exposure (50% probability ellipsoids).

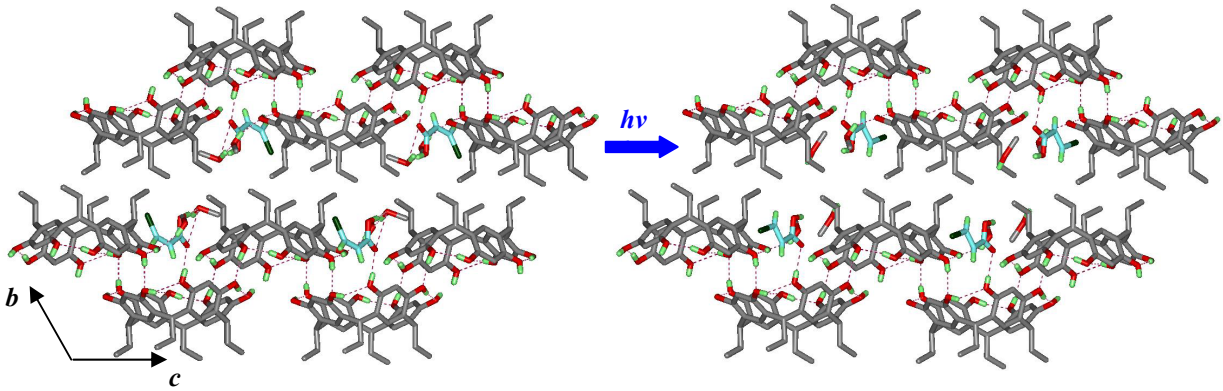


Figure S7. Three-dimensional architecture of **1-*E*** viewed along the *a*-axis direction.

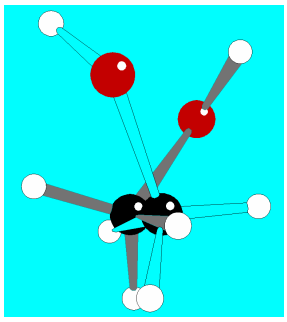


Figure S8. Shift in position and orientation of the methanol molecule in **1-*Z*** on 1 hour exposure.

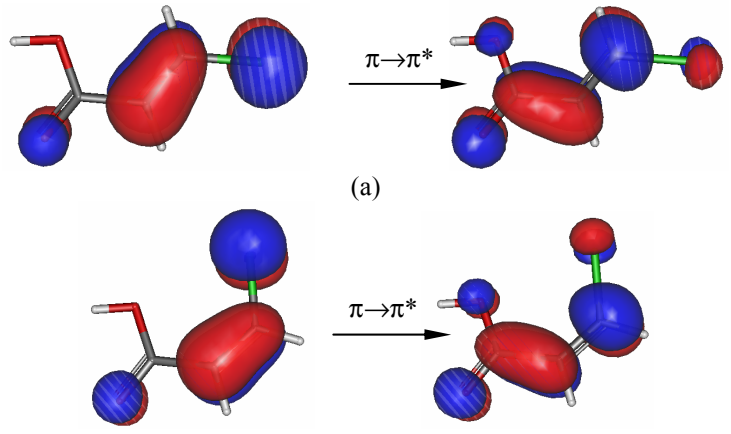


Figure S9. The contour plots (isosurfaces at ±0.05 au) of the HOMO (π) of S_0 and the π* orbital of S_2(π, π*)of (a) *E*-HClA and (b) *Z*-HClA based on TDDFT energy level and molecular orbitals analyses.

Table S1. Crystal data and structure refinement of **1.***

	1-*E*@200K before exposure	**1-*E*@**90K before exposure	**1-*E*@**90K-1h-exposure
Chemical formula	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$
M_r	798.29	798.29	798.29
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	11.4557 (9)	11.3821 (5)	11.3771(5)
b (Å)	13.3257 (11)	13.2720 (5)	13.3223 (7)
c (Å)	14.6792 (12)	14.5631 (6)	14.6324 (6)
α (°)	98.972 (2)	99.0020 (12)	99.0998 (15)
β (°)	109.090 (2)	108.7610 (11)	109.2728 (13)
γ (°)	95.411 (2)	95.1928 (12)	95.2633 (15)
V (Å^3)	2066.2 (3)	2033.94 (14)	2042.38 (16)
Z	2	2	2
D_x (Mg m^{-3})	1.283	1.303	1.298
μ (mm^{-1})	0.157	0.159	0.159
Reflections collected	10648	26025	9715
Independent reflections	7221	7170,	6944
R_{int}	0.024	0.026	0.0162
Goodness-of-fit on F^2	1.028	1.061	1.150
$R_1[I > 2\sigma(F^2)]$	0.0603	0.0491	0.062
wR_2	0.1897	0.1422	0.173
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.585, –0.577	0.768, –0.784	0.573, –0.720

	1-*E*@90K-2h-exposure	**1-*E*@**90K-6h-exposure	**1-*E*@**90K-10h-exposure
Chemical formula	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$
M_r	798.29	798.29	798.29
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	11.3717(4)	11.3799(5)	11.3847(5)
b (Å)	13.3231(5)	13.3742(6)	13.3860(7)
c (Å)	14.6367(5)	14.6526(6)	14.6572(6)
α (°)	99.0890(11)	99.0913(14)	99.1048(16)
β (°)	109.3441(10)	109.7794(13)	109.8419(13)
γ (°)	95.2480(11)	95.1761(14)	95.1665(15)
V (Å^3)	2041.34(13)	2047.22(15)	2049.61(16)
Z	2	2	2
D_x (Mg m^{-3})	1.303	1.295	1.294

μ (mm^{-1})	0.159	0.158	0.158
Reflections collected	14686	12241	9151
Independent reflections	7191,	7091	6788
R_{int}	0.0189	0.0175	0.0132
Goodness-of-fit on F^2	1.181	1.200	1.212
$R_1[I > 2\sigma(F^2)]$	0.0621	0.0676	0.0685
wR_2	0.1753	0.1882	0.1732
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.654, –0.774	0.881, –0.520	0.898, –0.454

	1-*Z*@200K	**1-*Z*@**90K	**1-*Z*@**90K-1h-exposure
Chemical formula	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$
M_r	798.29	798.29	798.29
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	11.3681(4)	11.2946(4)	11.3657(3)
b (Å)	13.4995(5)	13.4660(5)	13.3996(3)
c (Å)	14.7379(6)	14.6284(5)	14.6514(4)
α (°)	98.6833(11)	98.6809(10)	98.9111(8)
β (°)	111.0001(10)	111.1014(9)	110.2197(8)
γ (°)	95.1494(11)	94.8602(10)	95.1864(8)
V ($Å^3$)	2061.79(13)	2028.45(13)	2043.48(9)
Z	2	2	2
D_x (Mg m^{-3})	1.286	1.307	1.297
μ (mm^{-1})	0.157	0.160	0.159
Reflections collected	7979	22694	16516
Independent reflections	6255	7140	7178
R_{int}	0.0147	0.0208	0.0192
Goodness-of-fit on F^2	1.017	1.023	1.169
$R_1[I > 2\sigma(F^2)]$	0.0529	0.0455	0.0631
wR_2	0.1502	0.1279	0.1695
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.611, –0.696	0.691, –0.702	0.840, –0.438

	1-*Z*@90K-2h-exposure	**1-*Z*@**90K-4h-exposure	**1-*Z*@**90K-8h-exposure
Chemical formula	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$	$C_{41}H_{54}ClO_{13.50}$
M_r	798.29	798.29	798.29
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a (Å)	11.3736(4)	11.3794(4)	11.3833(4)

b (Å)	13.3966(4)	13.3976(5)	13.4042(5)
c (Å)	14.6486(5)	14.6461(5)	14.6333(5)
α (°)	98.9479(10)	99.0222(10)	99.0088(11)
β (°)	110.1919(10)	110.2090(10)	110.2459(11)
γ (°)	95.1444(10)	95.0382(11)	94.9955(11)
V (Å^3)	2044.42(12)	2045.08 (13)	2044.83(13)
Z	2	2	2
D_x (Mg m^{-3})	1.297	1.296	1.297
μ (mm^{-1})	0.159	0.159	0.159
Reflections collected	14724	14949	15027
Independent reflections	7186	7180	7182
R_{int}	0.0216	0.0211	0.0222
Goodness-of-fit on F^2	1.209	1.217	1.197
$R_1[I > 2\sigma(F^2)]$	0.0657	0.0675	0.0662
wR_2	0.1800	0.1825	0.1814
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.941, –0.467	0.979, –0.417	0.58, –0.78

	1-*Z*@90K-12h-exposure
Chemical formula	$C_{41}H_{54}ClO_{13.50}$
M_r	798.29
Cell setting, space group	Triclinic, $P\bar{1}$
a (Å)	11.3796(7)
b (Å)	13.4055(8)
c (Å)	14.6244(8)
α (°)	98.9840(17)
β (°)	110.2775(16)
γ (°)	94.9880(18)
V (Å^3)	2042.9(2)
Z	2
D_x (Mg m^{-3})	1.298
μ (mm^{-1})	0.159
Reflections collected	15802
Independent reflections	7179
R_{int}	0.0339
Goodness-of-fit on F^2	1.141
$R_1[I > 2\sigma(F^2)]$	0.0652
wR_2	0.1852

$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3}) 0.555, –0.452

- There are some artificially shorter than normal H···H separations involving the disordered water H atoms, as the water position are only partially occupied.

Table S2. Hydrogen bonds distances in 1 at 90 K.

D–H···A	d(D···A)/Å	<DHA/°	D–H···A	d(D···A)/Å	<DHA/°
1-*E*					
O(1)-H(1O)···O(7a)	2.678(2)	162(3)	O(7)-H(7O)···O(6)	2.877(2)	128(3)
O(2)-H(2O)···O(3)	2.746(2)	170(3)	O(8)-H(8O)···O(1)	2.730(2)	164(3)
O(3)-H(3O)···O(5b)	2.707(2)	162(3)	O(9)-H(9O)···O(1S)	2.539(3)	177(3)
O(5)-H(5O)···O(4)	2.934(2)	166(3)	O(1S)-H(1S)···O(2S)	2.655(3)	177.3
O(6)-H(6O)···O(10)	2.705(2)	170(3)	O(2S)-H(2S)···O(8a)	2.749(3)	169.6
O(7)-H(7O)···O(2c)	2.768(2)	141(3)			
a) -x+2, -y+1, -z+1; b) -x+1, -y+1, -z; c) x+1, y, z.					
1-*Z*					
O(1)-H(1O)···O(7a)	2.772(2)	171(3)	O(7)-H(7O)···O(2c)	2.773(2)	142(3)
O(2)-H(2O)···O(3)	2.731(2)	170(3)	O(7)-H(7O)···O(6)	2.863(2)	129(3)
O(3)-H(3O)···O(5b)	2.709(2)	162(3)	O(8)-H(8O)···O(1)	2.729(2)	164(3)
O(5)-H(5O)···O(4)	2.752(2)	164(3)	O(9)-H(9O)···O(1S)	2.581(3)	175(4)
O(6)-H(6O)···O(10)	2.670(2)	173(3)	O(1S)-H(1S)···O(2S)	2.657(3)	169.1
a) -x+2,-y+1,-z+1; b) -x+1,-y+1,-z; c) x+1,y,z					

Table S3. Volume (Å^3) of the channels in **1**.

	Crystal volume (Å^3)	Volume (Å^3) of the channels, % of crystal volume	Cavity volume per HClA molecule (Å^3)
1-*E*	2034.0	686.6 (33.8%)	150.6
1-*Z*	2028.4	669.1 (33.0%)	147.4
1-*E*-1h-exposure	2042.4	688.8 (33.7%)	151.5
1-*Z*-1h-exposure	2043.5	688.4 (33.6%)	160.5

Table S4. Unit cells of **1-*E*** and**1-*Z*** before and after irradiation for specific time periods.

State	*a* (Å)	*b* (Å)	*c* (Å)	α(°)	β(°)	γ(°)	*V* (Å^3)	Conver. /%
1-*E*								
200 K 0h	**11.4557(9)**	**13.326(1)**	**14.679(1)**	**98.972(2)**	**109.090(2)**	**95.411(2)**	**2066.2(3)**	
90 K 0h	**11.3821(5)**	**13.2720(5)**	**14.5631(6)**	**99.002(1)**	**108.761(1)**	**95.193(1)**	**2033.9(1)**	
1h	**11.3771(5)**	**13.3223(7)**	**14.6324(6)**	**99.100(2)**	**109.273(1)**	**95.263(2)**	**2042.4(3)**	**29.1(3)**
2h	**11.3717(4)**	**13.3231(5)**	**14.6367(5)**	**99.089(1)**	**109.344(1)**	**95.248(1)**	**2041.3(3)**	**32.0(3)**
6h	**11.3799(5)**	**13.3742(6)**	**14.6526(6)**	**99.091(1)**	**109.779(1)**	**95.176(1)**	**2047.2(3)**	**40.3(4)**
10h	**11.3847(5)**	**13.3860(6)**	**14.6572(6)**	**99.105(1)**	**109.842(1)**	**95.165(1)**	**2049.6(3)**	**41.1(4)**
1-*Z*								
200 K 0h	**11.3681(4)**	**13.4995(5)**	**14.7379(6)**	**98.683(2)**	**110.000(1)**	**95.149(1)**	**2061.8(2)**	
90 K 0h	**11.2946(4)**	**13.4660(5)**	**14.6284(6)**	**98.681(1)**	**111.101(1)**	**94.860(1)**	**2028.5(2)**	
1h	**11.3657(3)**	**13.3996(5)**	**14.6514(6)**	**98.911(1)**	**110.220(1)**	**95.186(1)**	**2043.5(2)**	**39.7(3)**
2h	**11.3736(4)**	**13.3966(4)**	**14.6486(5)**	**98.948(1)**	**110.192(1)**	**95.144(1)**	**2044.4(2)**	**44.3(3)**
4h	**11.3794(4)**	**13.3976(5)**	**14.6461(5)**	**99.022(1)**	**110.209(1)**	**95.038(1)**	**2045.1(2)**	**48.9(3)**
8h	**11.3833(4)**	**13.4042(5)**	**14.6333(5)**	**99.009(1)**	**110.246(1)**	**94.995(1)**	**2044.8(2)**	**50.5(3)**
12h	**11.3796(7)**	**13.4055(8)**	**14.6244(8)**	**98.984(2)**	**110.278(2)**	**94.988(1)**	**2042.9(2)**	**51.4(3)**