Dichotomous Behavior of Water in Binary Mixtures with Turning Point between 40 and 60 °C

Amiya Atahar[a], Noushaba Nusrat Mafy[a], Mohammad Hossain[ab], and Md. Abu Bin Hasan Susan[*ac]

[a]*Department of Chemistry, University of Dhaka, Dhaka 1000, Bangladesh;*
[b]*Department of Chemistry, Bangladesh University of Engineering and Technology (BUET), Dhaka 1000, Bangladesh;*
[c]*Dhaka University Nanotechnology Center (DUNC), University of Dhaka, Dhaka 1000, Bangladesh*

*Corresponding authors. E-mails: susan@du.ac.bd

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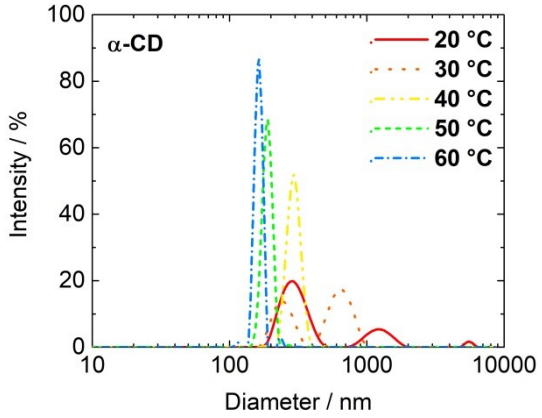

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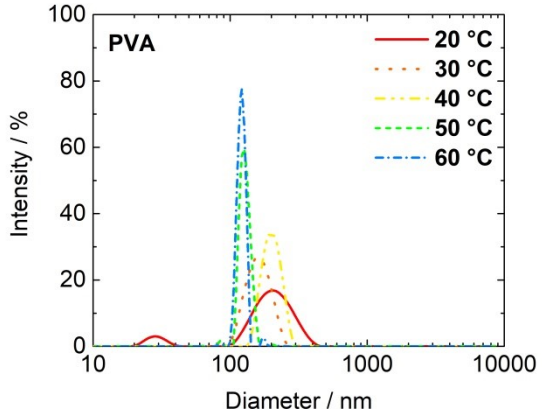

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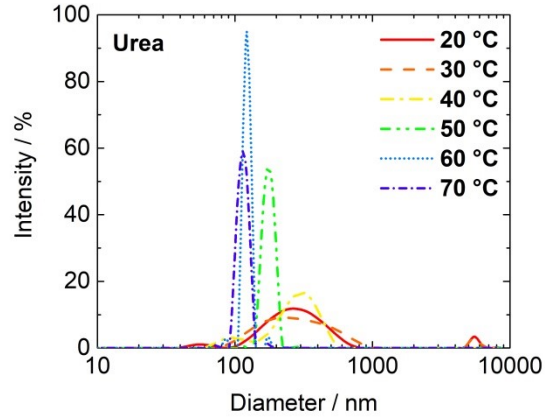
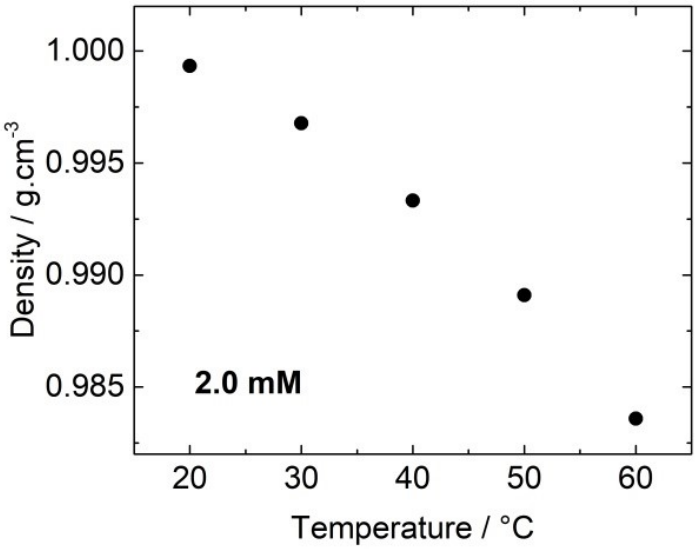
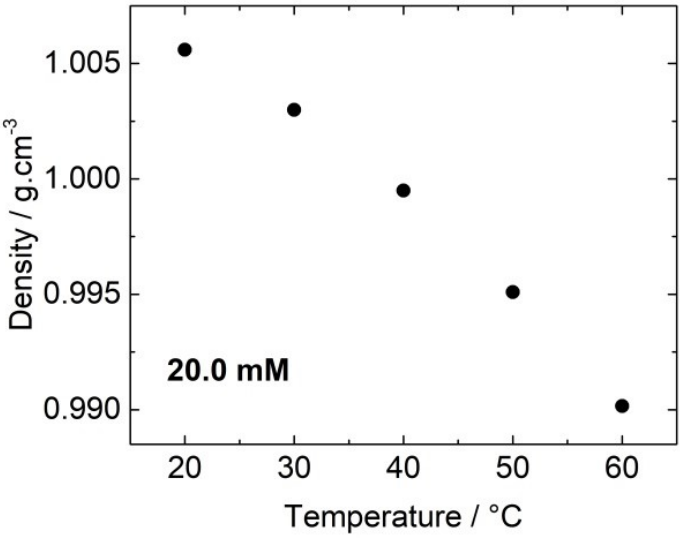


(c)

Fig. S1 Size distribution of (a) 2.0 mM α-CD, (b) aqueous PVA, and (c) 2.0 M urea at different temperatures.



(a)



(b)

Fig. S2 Density of (a) 2.0 mM and (b) 20.0 mM α-CD at different temperatures.

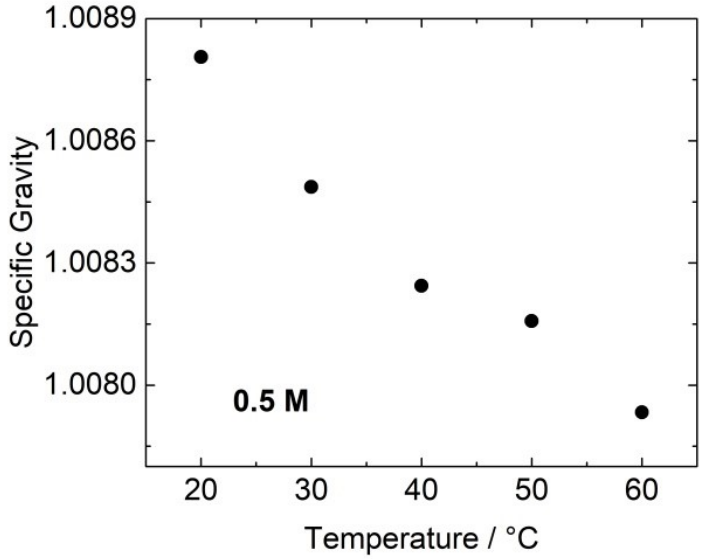


Fig. S3 Specific gravity of 0.5 M urea at different temperatures.

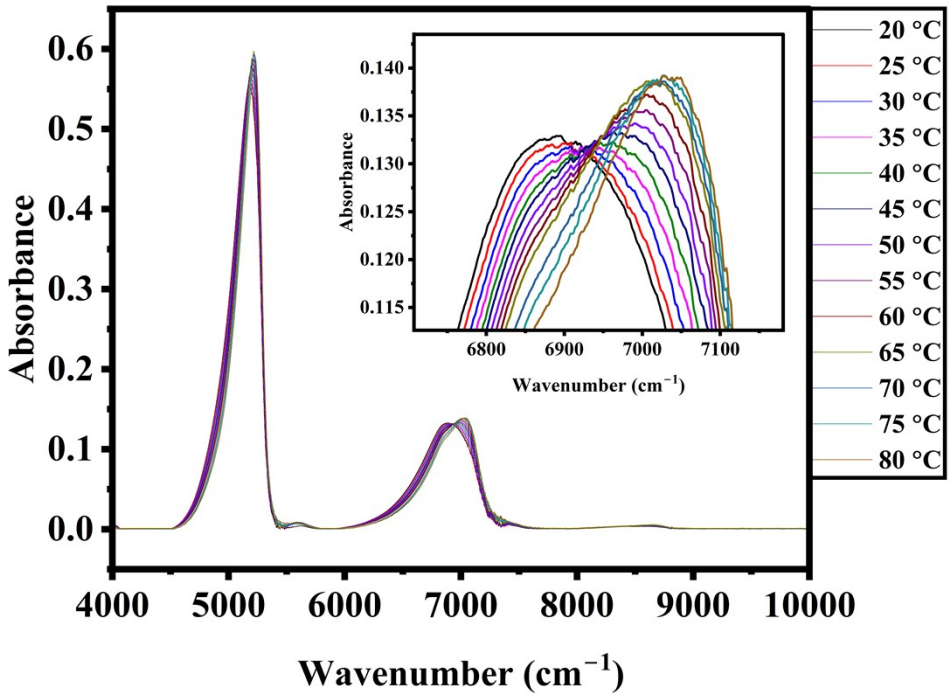
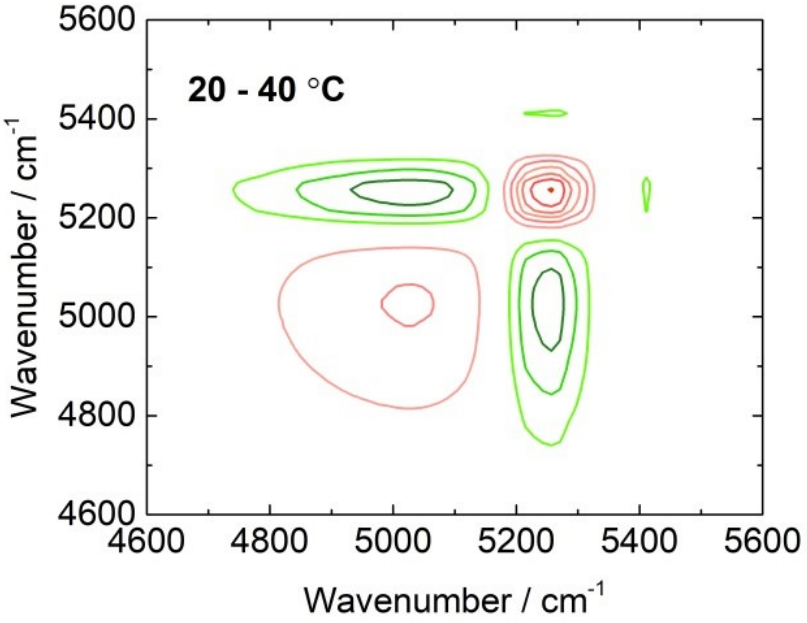
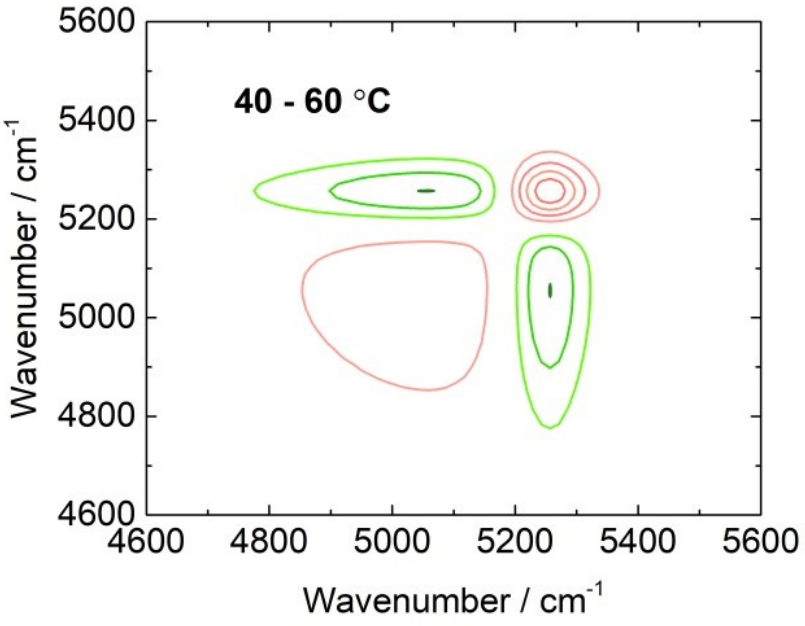


Fig. S4 NIR spectra of a 2.0 mM aqueous solution of α-CD from 20 ℃ to 80 ℃ at an interval of 5 ℃.



(a)



(b)

Fig. S5 Synchronous spectra of 2DCoS of 2.0 mM α-CD in different temperature ranges.

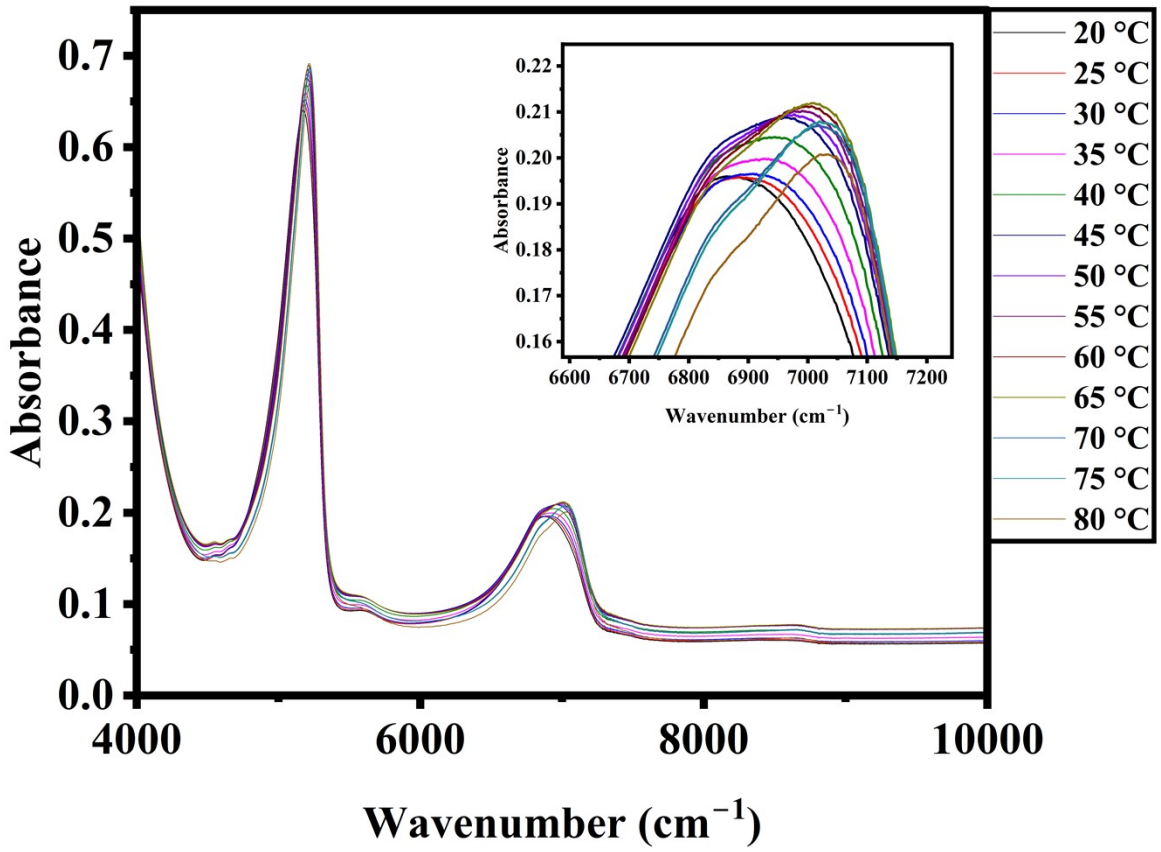
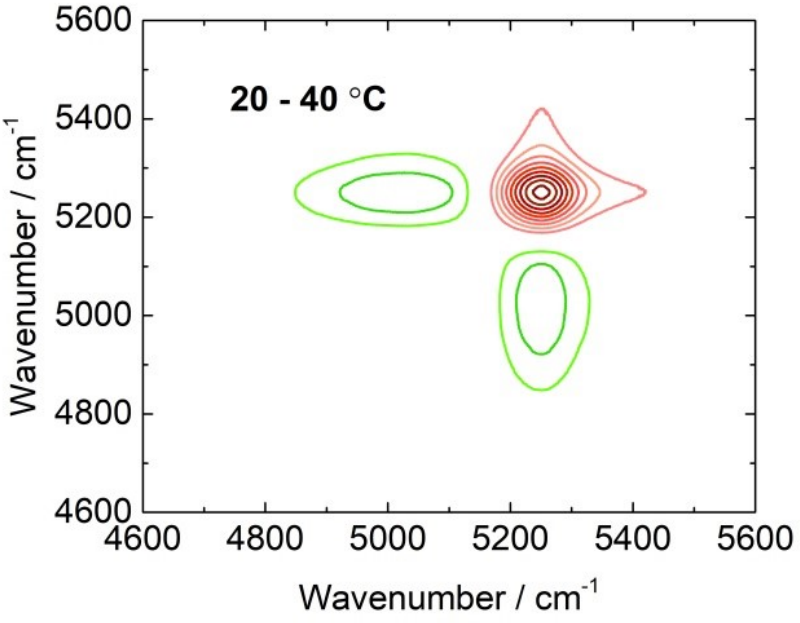
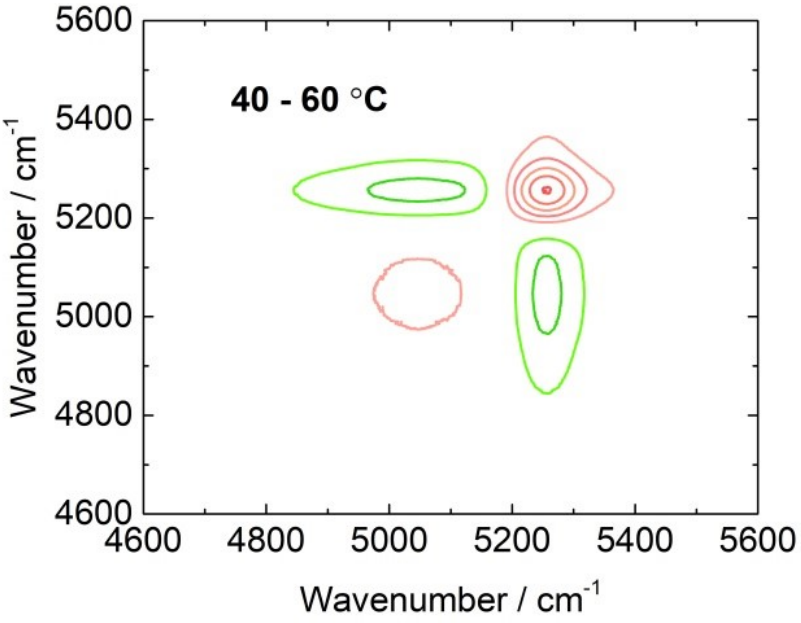


Fig. S6 NIR spectra of aqueous solution of 0.5 M urea from 20 ℃ to 80 ℃ at the interval of 5 ℃.



(a)



(b)

Fig. S7 Synchronous spectra of 2DCoS of 0.5 M urea in different temperature ranges.

Table S1. Structural anomalies of liquid water and aqueous systems near 40−60 ℃

Temperature (℃)	Observed Anomaly	Reference
~46 ℃	Low-density and high-density water remain in the liquid state, and with increasing temperature, the former converts to the latter.[1]	Ref 16
50 ± 10 ℃	A bilinear behavior of liquid water exists, having a crossover temperature for thermal conductivity at 64 ℃, proton spin-lattice relaxation time at 50 ℃, refractive index at 50 ℃, conductance at 53 ℃, and surface tension at 57 ℃.[2]	Ref 19
~60 ℃	A significant dielectric anomaly remains in liquid water around linked to a transition in the average dipole moment from a low-temperature configuration (~2.17 D) to a high-temperature configuration (~1.87 D), resembling that of water vapor.[3]	Ref 21
~43 ℃	Liquid water changes its structure at 43 ℃. Bilinear behavior of polarizability at 45 ℃, dipolarity at 45 ℃, and hydrogen bond acceptor basicity at 43 ℃ exist in water.	Ref 23
~45 ℃	A more extensive hydrogen-bonded low-density water and a less extensive hydrogen-bonded high-density water remain in equilibrium.	Ref 24
35 ℃−45 ℃	The crossover temperature observed in the luminescence of europium trisbipyridine cryptate shifts from 45 ℃ to 35 ℃ with decreasing pH.	Ref 25
40 ℃−60 ℃	The dichotomous behavior of water exists in the presence of four different additives, such as **α**-cyclodextrin, urea, poly (vinyl alcohol), and the inclusion complex of **β**-cyclodextrin and an ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim]PF_6$).	This work

Table S2 Size distribution of 2.0 mM aqueous solution of α-CD from 20 ℃ to 60 ℃ at an interval of 10 ℃

Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %
0.2000	0.0	2.8070	0.0	39.4100	0.0	553.2000	1.6
0.2316	0.0	3.2510	0.0	45.6400	0.0	640.7000	1.7
0.2682	0.0	3.7650	0.0	52.8500	0.0	741.9000	0.7
0.3106	0.0	4.3600	0.0	61.2100	0.0	859.2000	0.0
0.3597	0.4	5.0500	0.0	70.8900	0.0	995.1000	0.0
0.4166	0.5	5.8480	0.0	82.0900	0.0	1152.0000	0.0
0.4825	0.2	6.7720	0.0	95.0700	0.4	1335.0000	0.0
0.5587	0.4	7.8430	0.0	110.100	9.7	1545.0000	0.0
0.647	0.1	9.0830	0.0	127.5000	13.5	1790.0000	0.0
0.7493	0.5	10.5200	0.0	147.7000	5.0	2073.0000	0.0
0.8678	0.4	12.1800	4.2	171.0000	7.2	2400.0000	0.0
1.0050	0.2	14.1100	11.6	198.0000	7.6	2780.0000	0.0
1.1640	0.4	16.3400	7.4	229.3000	6.6	3219.0000	0.0
1.3480	0.0	18.9200	10.1	265.6000	2.0	3728.0000	0.0
1.5610	0.0	21.9100	0.0	307.6000	0.3	4317.0000	0.0
1.8080	0.0	25.3700	5.8	356.2000	0.0	5000.0000	0.0
2.0930	0.0	29.3900	0.8	412.5000	0.0		
2.4240	0.0	34.0300	0.0	477.7000	0.6		

Table S3 Size distribution of aqueous PVA from 20 ℃ to 60 ℃ at an interval of 10 ℃

Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %
0.2000	0.0	2.8070	0.0	39.4100	0.4	553.2000	0.2
0.2316	0.0	3.2510	0.0	45.6400	1.3	640.7000	0.2
0.2682	0.0	3.7650	0.1	52.8500	3.4	741.9000	0.1
0.3106	0.6	4.3600	0.2	61.2100	14.5	859.2000	0.0
0.3597	0.0	5.0500	0.3	70.8900	17.1	995.1000	0.0
0.4166	0.6	5.8480	0.9	82.0900	15.7	1152.0000	0.0
0.4825	0.0	6.7720	0.7	95.0700	13.5	1335.0000	0.0
0.5587	0.0	7.8430	0.8	110.100	10.7	1545.0000	0.0
0.647	0.0	9.0830	0.1	127.5000	8.1	1790.0000	0.0
0.7493	0.2	10.5200	0.1	147.7000	4.7	2073.0000	0.0
0.8678	0.6	12.1800	0.9	171.0000	1.8	2400.0000	0.1
1.0050	0.0	14.1100	0.2	198.0000	0.6	2780.0000	0.3
1.1640	0.1	16.3400	0.1	229.3000	0.1	3219.0000	0.0
1.3480	0.3	18.9200	0.0	265.6000	0.0	3728.0000	0.0
1.5610	0.0	21.9100	0.0	307.6000	0.0	4317.0000	0.0
1.8080	0.0	25.3700	0.0	356.2000	0.0	5000.0000	0.0
2.0930	0.0	29.3900	0.0	412.5000	0.1		
2.4240	0.0	34.0300	0.0	477.7000	0.2		

Table S4 Size distribution of aqueous 2.0 M urea from 20 ℃ to 70 ℃ at an interval of 10 ℃

Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %
0.2000	0.0	2.8070	0.0	39.4100	0.4	553.2000	0.0
0.2316	0.0	3.2510	0.0	45.6400	0.9	640.7000	0.0
0.2682	0.0	3.7650	0.0	52.8500	6.1	741.9000	0.0
0.3106	0.0	4.3600	0.0	61.2100	22.3	859.2000	0.0
0.3597	0.0	5.0500	0.0	70.8900	13	995.1000	0.0
0.4166	0.0	5.8480	0.0	82.0900	11.2	1152.0000	0.0
0.4825	0.0	6.7720	0.0	95.0700	9.7	1335.0000	0.0
0.5587	0.0	7.8430	0.0	110.100	5.0	1545.0000	0.1
0.647	0.0	9.0830	0.0	127.5000	4.4	1790.0000	0.1
0.7493	0.0	10.5200	0.0	147.7000	4.7	2073.0000	0.2
0.8678	0.0	12.1800	0.0	171.0000	4.8	2400.0000	0.4
1.0050	0.0	14.1100	0.0	198.0000	4.6	2780.0000	1.2
1.1640	0.0	16.3400	0.0	229.3000	4.0	3219.0000	0.0
1.3480	0.0	18.9200	0.0	265.6000	3.0	3728.0000	0.0
1.5610	0.0	21.9100	0.0	307.6000	2.0	4317.0000	0.0
1.8080	0.0	25.3700	0.1	356.2000	1.1	5000.0000	0.0
2.0930	0.0	29.3900	0.1	412.5000	0.4		
2.4240	0.0	34.0300	0.2	477.7000	0.1		

Table S5 Size distribution of β-CD-[C_4mim]PF_6 inclusion complex in water from 20 ℃ to 70 ℃ at an interval of 10 ℃

Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %	Diameter/ nm	Intensity/ %
0.2000	0.0	2.8070	0.0	39.4100	0.0	553.2000	1.5
0.2316	0.0	3.2510	0.0	45.6400	0.0	640.7000	0.2
0.2682	0.0	3.7650	0.0	52.8500	0.0	741.9000	0.9
0.3106	1.0	4.3600	0.0	61.2100	0.9	859.2000	0.9
0.3597	0.2	5.0500	0.0	70.8900	0.2	995.1000	0.2
0.4166	0.2	5.8480	0.0	82.0900	4.0	1152.0000	0.0
0.4825	2.6	6.7720	0.0	95.0700	0.2	1335.0000	0.0
0.5587	3.0	7.8430	0.0	110.100	2.5	1545.0000	0.0
0.647	2.8	9.0830	0.0	127.5000	0.0	1790.0000	0.0
0.7493	2.6	10.5200	0.0	147.7000	1.3	2073.0000	0.2
0.8678	2.1	12.1800	0.8	171.0000	3.7	2400.0000	0.4
1.0050	0.3	14.1100	0.8	198.0000	0.0	2780.0000	0.7
1.1640	0.0	16.3400	1.8	229.3000	0.0	3219.0000	0.0
1.3480	0.0	18.9200	0.0	265.6000	2.6	3728.0000	0.0
1.5610	0.0	21.9100	0.0	307.6000	13.8	4317.0000	0.0
1.8080	0.0	25.3700	0.0	356.2000	17.2	5000.0000	0.0
2.0930	0.0	29.3900	0.0	412.5000	16.9		
2.4240	0.0	34.0300	0.0	477.7000	13.7		