Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The structural properties of $ZnCl_2$-ethylene glycol binary system and the peculiarities at the eutectic composition

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A submission to Physical Chemistry Chemical Physics

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Table S1. The interaction energies (kJ/mol) of the optimized structures considered for this study using the three methods B3LYP, B3LYP-D3 and M06-2X.

Complex	B3LYP	B3LYP-D3	M06-2X	Complex	B3LYP	B3LYP-D3	M06-2X
$ZnCl_2$-EG	-53.00			$ZnCl_2$-6EG	-232.54		
	-63.03				-269.72		
	-70.33				**-309.25**	**-457.54**	**-507.20**
	-77.31	**-103.09**	**-129.64**	EG dimer	-20.09		
$ZnCl_2$-2EG	-97.23				-33.75		
	-110.04				**-36.25**	**-52.92**	**-42.13**
	-124.12	-165.98	-199.27	EG trimer	-56.55		
	-138.52	**-185.44**	**-211.17**		**-81.13**	**-118.82**	**-103.52**
$ZnCl_2$-3EG	-89.12			EG tetramer	-54.45		
	-157.77	-163.15	-190.44		-69.06		
	-166.45				**-116.75**	**-173.06**	**-159.83**
	-189.32	**-250.20**	**-270.98**	EG pentamer	-81.33		
$ZnCl_2$-4EG	-108.30				-136.43	-205.94	-192.14
	-121.93			EG hexamer	-145.95	-226.50	-205.39
	-130.18			$2ZnCl_2$-3EG	-225.72	-259.05	-299.03
	-155.49				-354.44		
	-155.66				-383.19		
	-199.86			$2ZnCl_2$-4EG	-191.57	-323.93	
	-204.91				-206.51	-379.87	-441.35
	-222.05	-190.77	-216.56	$3ZnCl_2$-2EG	-278.60	-409.89	-511.56
	-236.97	**-216.54**	**-240.93**	$3ZnCl_2$-3EG	-229.93	-349.04	-403.40
	-242.22	**-344.64**	**-381.87**		-297.41	-434.29	
$ZnCl_2$-5EG	-214.91			$3ZnCl_2$-EG	-222.07	-315.85	-372.80
	-229.76			$5ZnCl_2$-EG	-321.01	-529.91	
	-270.17	**-415.63**	**-432.20**				

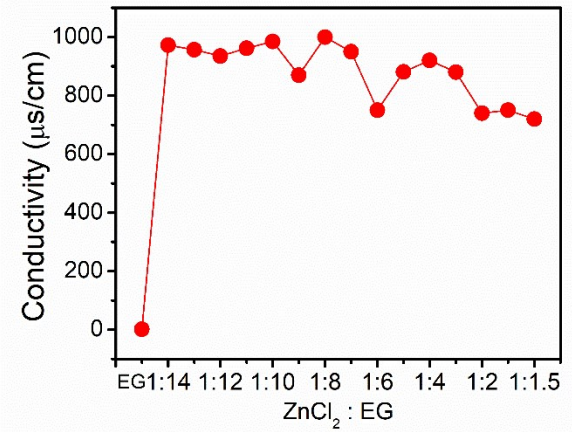

Figure S1. Conductivity values of pure ethylene glycol (EG) and $ZnCl_2$-EG mixtures.

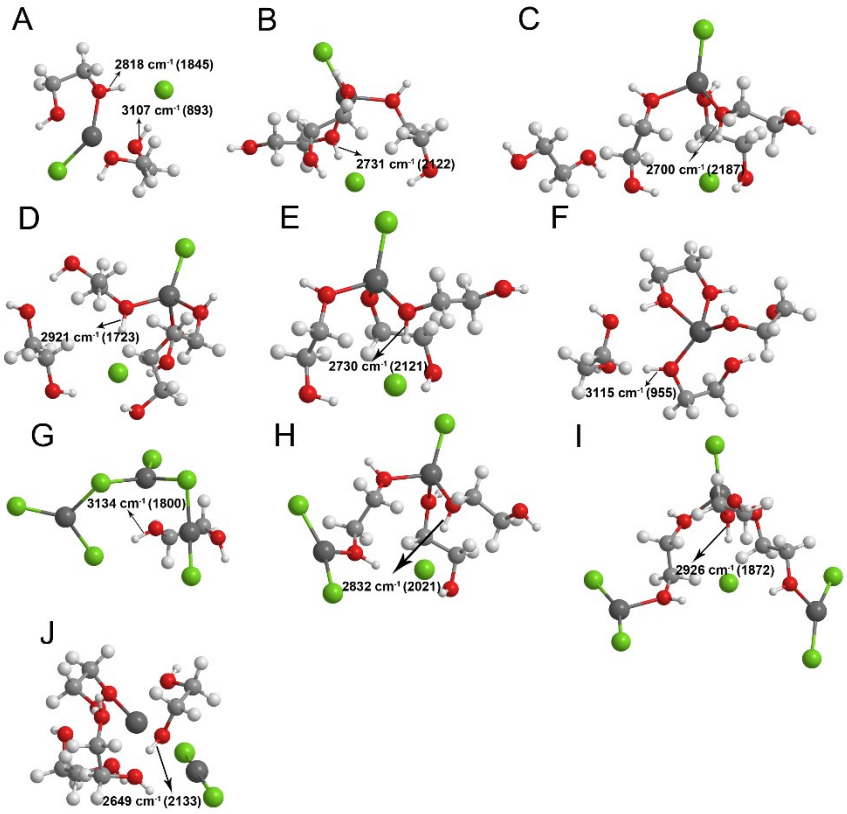

Figure S2. Optimized geometries of different complexes involving EG molecules and $ZnCl_2$ or its components. The complexes all contain largely red-shifted hydroxyl(s) which are indicated. The values in parenthesis are the intensities. The optimization was at the M06-2X/6-311++G(d,p) level of theory.

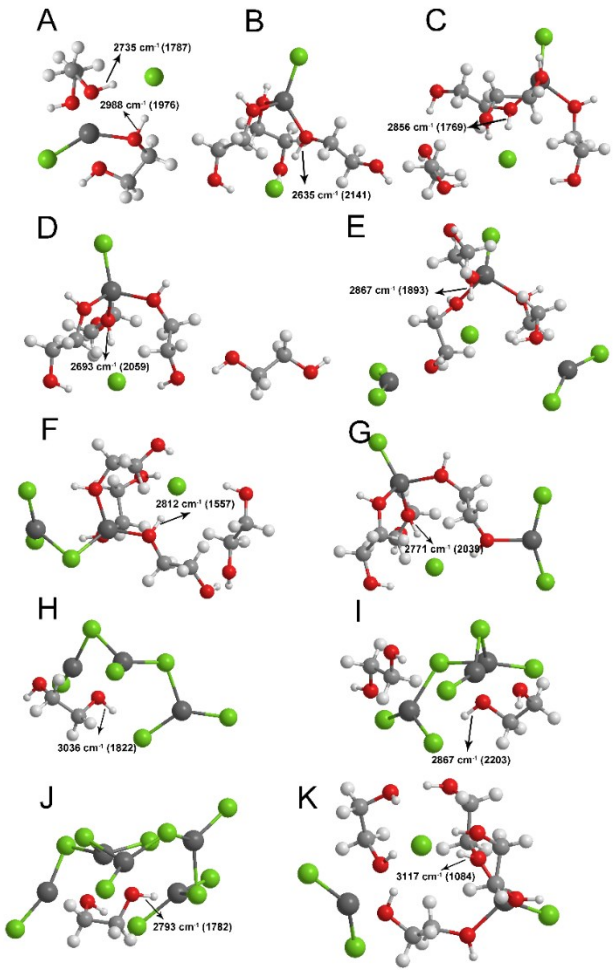

Figure S3. Optimized geometries of different complexes involving EG molecules and $ZnCl_2$ or its components. The complexes all contain largely red-shifted hydroxyl(s). The values in parenthesis are the intensities. The optimization was at the B3LYP-D3/6-311++G(d,p) level of theory.

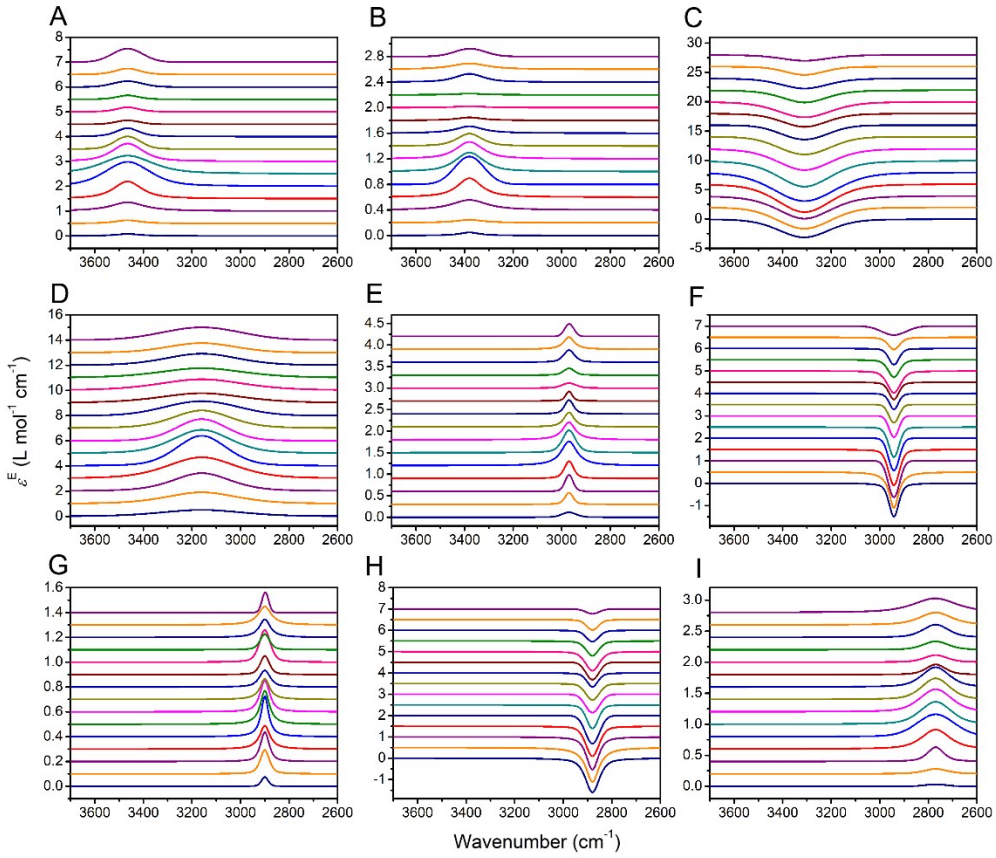

Figure S4. Deconvolution results of the excess IR spectra in υ(O–H) and υ(C–H) regions for $ZnCl_2$:EG mixtures in 1:1.5 to 1:14 molar ratios. The peaks are at (A) 3465 cm^{-1}, (B) 3380 cm^{-1}, (C) 3310 cm^{-1}, (D) 3160 cm^{-1}, (E) 2970 cm^{-1}, (F) 2942 cm^{-1}, (G) 2900 cm^{-1}, (H) 2880 cm^{-1} and (I) 2770 cm^{-1}.

Table S2. Natural charges (q/e) on selected atoms and molecules. The data in the parentheses represent the charge changes of the corresponding species upon complexation. Positive and negative values mean decrease and increase in charge, respectively.

atom/group	monomer	$ZnCl_2$:EG complex					
		1:1	1:2	1:3	1:4	1:5	1:6
$ZnCl_2$	0	-0.167	-0.199	-0.187	-0.235	-0.235	-0.246
		(-0.167)	(-0.199)	(-0.187)	(-0.235)	(-0.235)	(-0.246)
Zn	1.077	1.037	1.040	1.066	1.098	1.125	1.116
		(-0.040)	(-0.037)	(-0.011)	(0.021)	(0.048)	(0.039)
2Cl	-1.077	-1.204	-1.240	-1.253	-1.333	-1.360	-1.362
		(-0.127)	(-0.163)	(-0.176)	(-0.256)	(-0.283)	(-0.285)
EG	0	0.167	0.199	0.187	0.235	0.235	0.246
		(0.167)	(0.199)	(0.187)	(0.235)	(0.235)	(0.246)
CH_2	0.563	0.652	1.262	1.830	2.471	3.056	3.640
		(0.089)	(0.699)	(1.267)	(1.908)	(2.493)	(3.077)
OH	-0.563	-0.485	-1.062	-1.643	-2.236	-2.821	-3.394
		(0.078)	(-0.499)	(-1.080)	(-1.673)	(-2.258)	(-2.831)

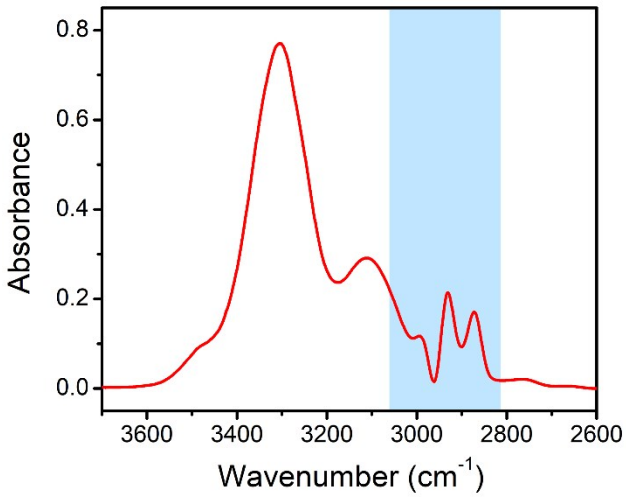

Figure S5. Power spectrum representing the diagonal wavenumbers of the synchronous map in υ(O–H) and υ(C–H) regions. The υ(C–H) region is highlighted.