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Supplementary Information

Effect of Polyethyleneglycols (PEG) on Solubility of Co^{III} 5,10,15,20-Tetra(4-carboxyphenyl)porphyrin and Methylimidazolyl Axial Complex at 298.2 K: Experiment and Modeling

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Methods

UV-Vis spectra were recorded using a UV-Vis spectrophotometer Varian Cary-50. Infrared spectra were recorded using a spectrophotometer Avatar 360 FT-IR-ESP. Nuclear magnetic resonance (NMR) spectra were recorded using a Bruker VC-500 spectrometer at 500.7 MHz.

Co^{III} 5,10,15,20-Tetrakis-(4-carboxyphenyl)porphyrin (**1**)

UV-Vis λ / nm 422 (5.01), 439 (4.24); IR (KBr) ν / cm^{-1} 2948, 2927, 2869, 2917, 2849, 1712, 1694, 1599, 1480, 1437, 1406, 1350, 1150,1073, 1004, 930, 796, 752, 702, 470; ^{1}H NMR (400 MHz, D_2O) δ 10.14 (br s, 8H, pyrrole ring), 13.24 (br s, 8H, ortho-Ph), 8.11 (d, 8H, meta-Ph), 3.28 (br s, 4H, COOH); for $C_{48}H_{30}CoN_4O_9$ anal. calcd. (%) C 66.59, H 3.47, N 6.82; found (%): C 67.31, H 3.34, N 6.79.

Co^{III} Tetra(4-carboxyphenyl)porphyrin complex with *N*-methylimidazole (**2**)

UV-Vis λ / nm 427 (4.74), 442 (4.16); IR (KBr) ν / cm^{-1} 2948, 2927, 2869, 2917, 2849, 2817-2721, 2582-2188, 1712, 1694, 1599, 1480, 1550, 1497, 1444, 1437, 1406, 1362, 1324, 1350, 1150, 1073, 1004, 930, 796, 750, 700, 472; ^{1}H NMR (400 MHz, D_2O) δ 10.15 (br s, 8H, pyrrole ring), 13.25 (br s, 8H, ortho-Ph), 8.11 (d, 8H, meta-Ph), 6.34 (d, 2H, Im), 5.27 (d, 2H, Im), 4.94 (s, 2H, Im), 3.64 (s, 6H, Im), 3.29 (s, 4H, COOH).

Table S1. Experimental molar solubilities (S) of porphyrins **1** and **2** in saturated solutions at 298.2 K, p = 0.1 MPa

Volume fraction, $f_{3\text{-PEG}}$[b]	Molar fraction, $f_{3\text{-PEG}}$[b]	S^a / (mol L^{-1})		Volume fraction, $f_{4\text{-PEG}}$[b]	Molar fraction, $f_{4\text{-PEG}}$[b]	S^a / (mol L^{-1})	
		1	**2**			**1**	**2**
0	0	4.37×10^{-4}	7.10×10^{-4}	0	0	4.37×10^{-4}	7.10×10^{-4}
0.015	0.002	5.20×10^{-4}	7.20×10^{-4}	0.015	0.0016	5.80×10^{-4}	8.43×10^{-4}
0.100	0.015	2.60×10^{-3}	2.57×10^{-3}	0.100	0.011	1.01×10^{-3}	2.11×10^{-3}
0.240	0.040	2.17×10^{-2}	1.91×10^{-2}	0.237	0.031	4.70×10^{-3}	9.68×10^{-3}
0.300	0.054	2.90×10^{-2}	2.55×10^{-2}	0.300	0.042	7.68×10^{-3}	1.60×10^{-2}
0.375	0.074	4.33×10^{-2}	2.62×10^{-2}	0.385	0.061	8.47×10^{-3}	1.77×10^{-2}
0.492	0.114	4.14×10^{-2}	2.50×10^{-2}	0.491	0.090	9.63×10^{-3}	2.01×10^{-2}
0.600	0.166	2.90×10^{-2}	1.75×10^{-2}	0.600	0.134	8.15×10^{-3}	1.70×10^{-2}
0.700	0.237	2.02×10^{-2}	1.22×10^{-2}	0.700	0.194	4.10×10^{-3}	8.56×10^{-3}
0.822	0.380	1.21×10^{-2}	7.31×10^{-3}	0.763	0.249	1.45×10^{-3}	3.03×10^{-3}
0.900	0.545	8.46×10^{-3}	5.11×10^{-3}	0.900	0.481	1.68×10^{-4}	3.51×10^{-4}
1	1	1.86×10^{-4}	6.91×10^{-5}	1	1	1.68×10^{-5}	4.90×10^{-5}

[a]S: experimental molar solubilities, relative standard uncertainty $u_r(S) = 0.04$; standard uncertainties are u(T) = 0.1 K and u(p) = 0.03 kPa; [b]PEG: polyethyleneglycol.

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Table S2. Geometrical parameters of the molecules for individual components

Parameter	**1**	**2**	Water	3-PEG[a]	4-PEG[a]
r[b]	21.75	23.49	0.73	5.53	7.14
q[b]	17.60	18.99	0.79	4.62	5.91

[a]PEG: polyethyleneglycols; [b]r, q: geometrical parameters.

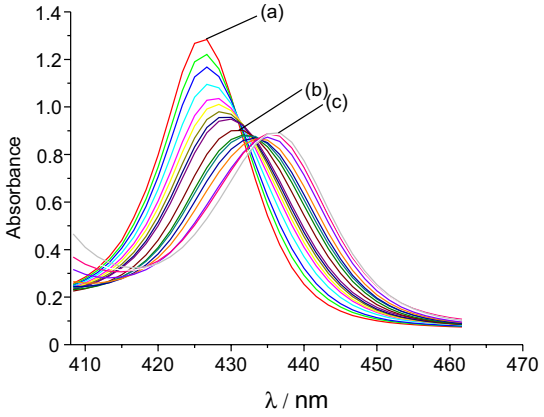

Figure S1. Absorption spectra in the Soret region for: (a) porphyrin **1** (6.6×10^{-6} mol L^{-1}); (b) porphyrin **1** plus MeIm, [MeIm]: (2.2×10^{-6} mol L^{-1}); (c) 2.6×10^{-5} mol L^{-1}. pH 7.4, 25 ºC.

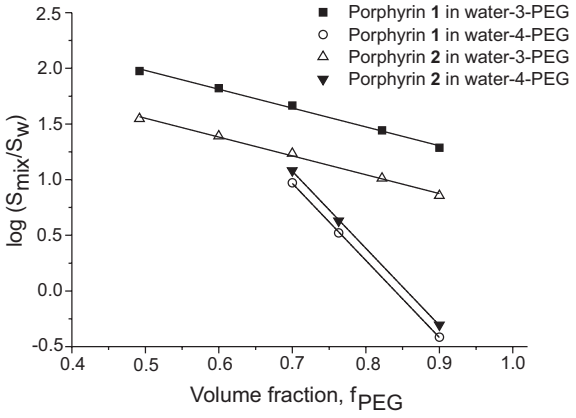

Figure S2. Desolubization profiles of porphyrins **1** and **2** in water-PEG mixtures (ranges of PEGs: $0.5 \le f_{3\text{-PEG}} \le 0.9$ and $0.7 \le f_{4\text{-PEG}} \le 0.9$).

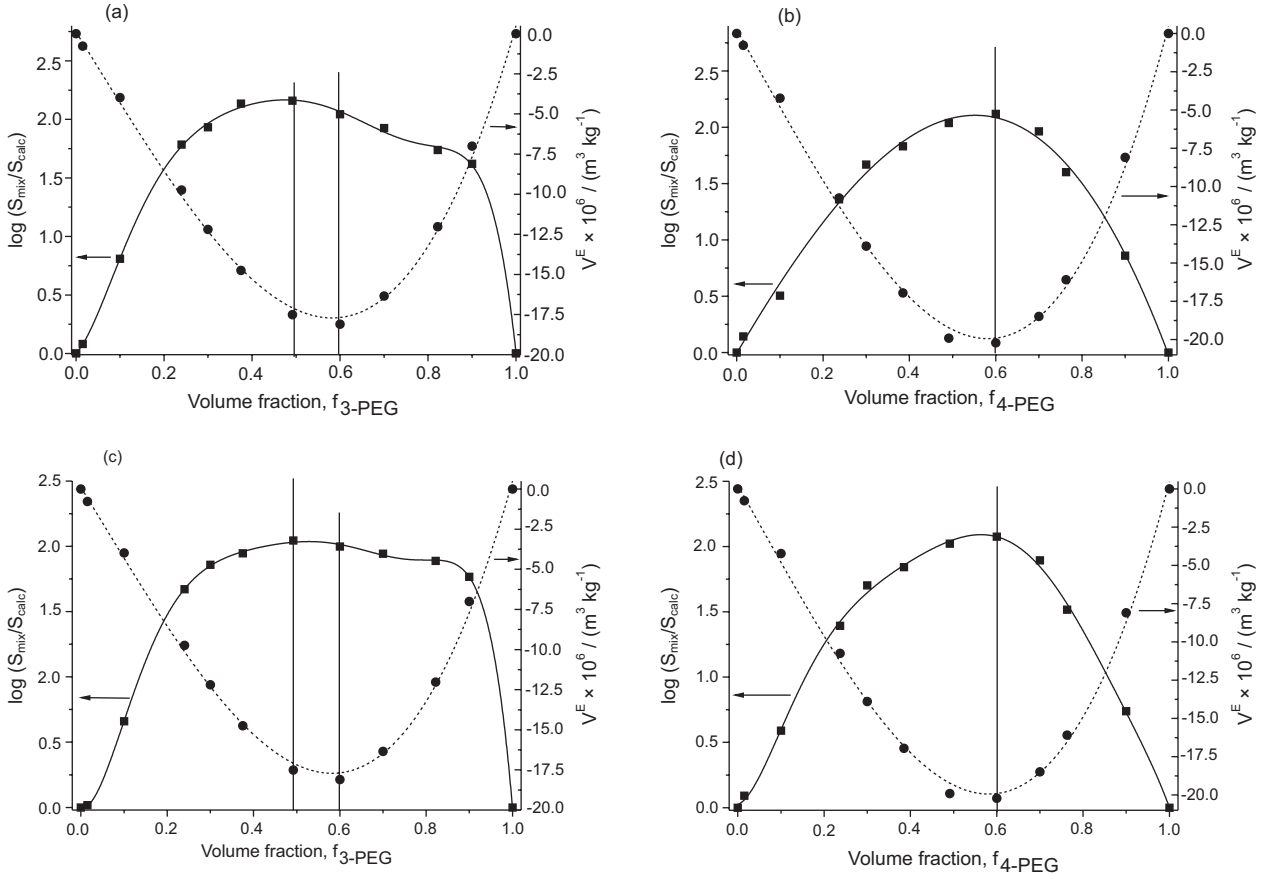

Figure S3. Comparison of excess solubilities and excess volumes (V^E) of porphyrins **1**-**2** in PEG-water mixtures: (a) porphyrin **1** in water-3-PEG; (b) porphyrin **1** in water-4-PEG; (c) porphyrin **2** in water-3-PEG; (d) porphyrin **2** in water-4-PEG.

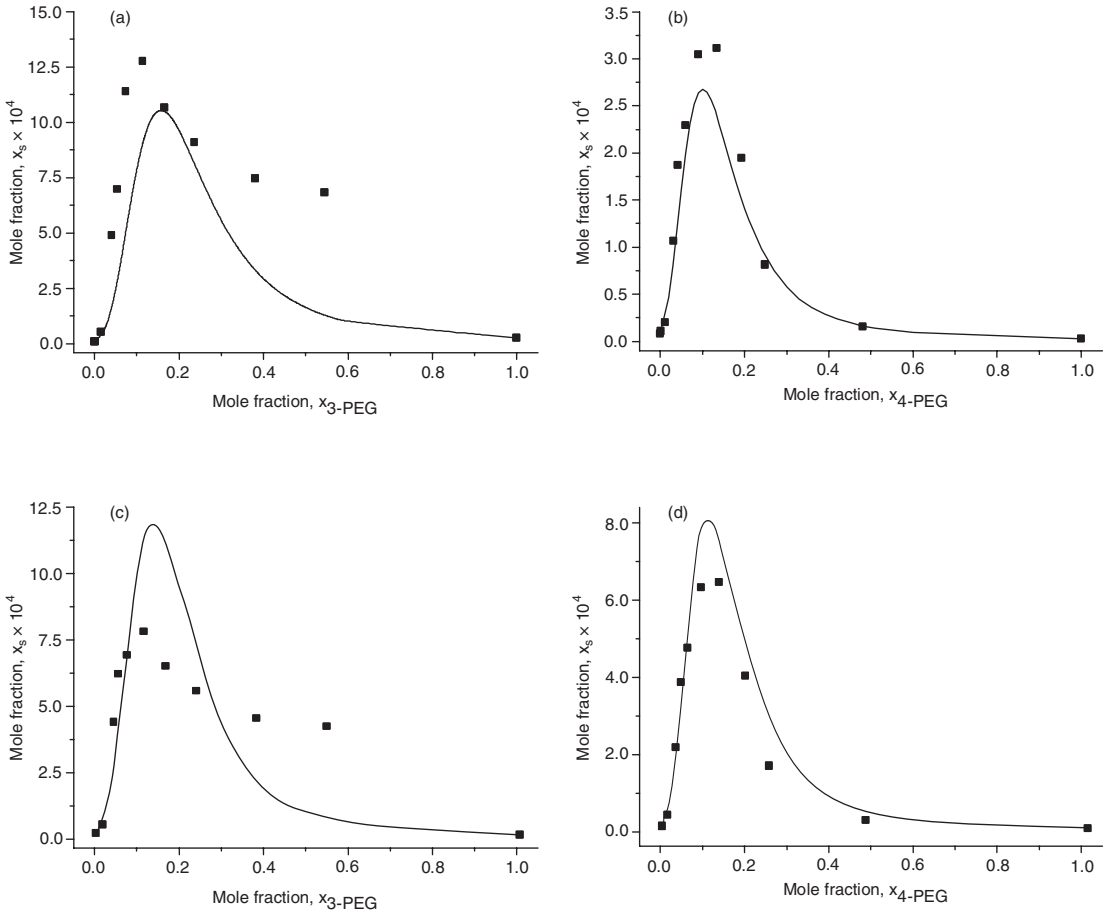

Figure S4. Mole fraction solubility profiles of porphyrins **1** and **2** in PEG-water mixtures. Comparison of predicted by ASL-model (solid line) and experimental (symbols) data: (a, b) porphyrin **1**; (c, d) porphyrin **2**.