Electronic supplementary materials *Mendeleev Commun.*, 2027, **37**, just accepted

The chlorin-chlorin intermolecular interaction in water: an investigation using calorimetry and dynamic light scattering

Andrey V. Kustov and Dmitriy V. Batov

S1. Chemicals in this study

Purification and identification of chlorin e_6 trisodium salt (Chl e_6)

Chl e_6 (see the main text for its chemical formula) was purchased from "RANFARMA" (Russian Federation) as a solid powder mixed with polyvinylpyrrolidone (PVP, M=17000 g/mol). It was reprecipitated from water to obtain a pure solid form. The purification of the PS was carried out as follows. About 50 mg of Chl e_6+PVP (50/50 per weight) was dissolved at efficient stirring in 5-7 ml of bidistilled warm water and then filtered. Then, the solution was cold down to ~273 K, after that about 10 ml of pure cold acetone was added. Then, the system was kept at ~ 253 K for several hours to allow Chl e_6 to precipitate. The precipitate was centrifuged, separated from a liquid phase and washed several times by pure chloroform. The residual solvent was removed using a rotary evaporator under vacuum and then the final product was accurately dried. The NMR spectrum is shown in Figure S1.

^{1}H NMR spectrum (500 MHz, DMSO d_6, *J*, Hz), δ, ppm: 9.75 s (1H, 10-H); 9.60 s (1H, 5-H); 9.08 s (1H, 20-H); 8.33 m (1H, 3-C<u>H</u>=CH_2); 6.43 d (1H, *J* 16.0 Hz, 3-CH=CH<u>H</u> (*trans*)); 6.13 d (1H, *J* 10.5 Hz, 3-CH=C<u>H</u>H (*cis*)); 5.66 br. s. (2H, <u>CH_2</u>$COOCH_3$; 4.54 m (2H, 18-H, 17-H) signals from 4 to 1 ppm seem to be covered by a small amount of residual PVP; -2.06 br.s. (1H, 23-NH); -2.62 br.s. (1H, 21-NH), which is not detected by FTIR-spectroscopy (see Figure S2).

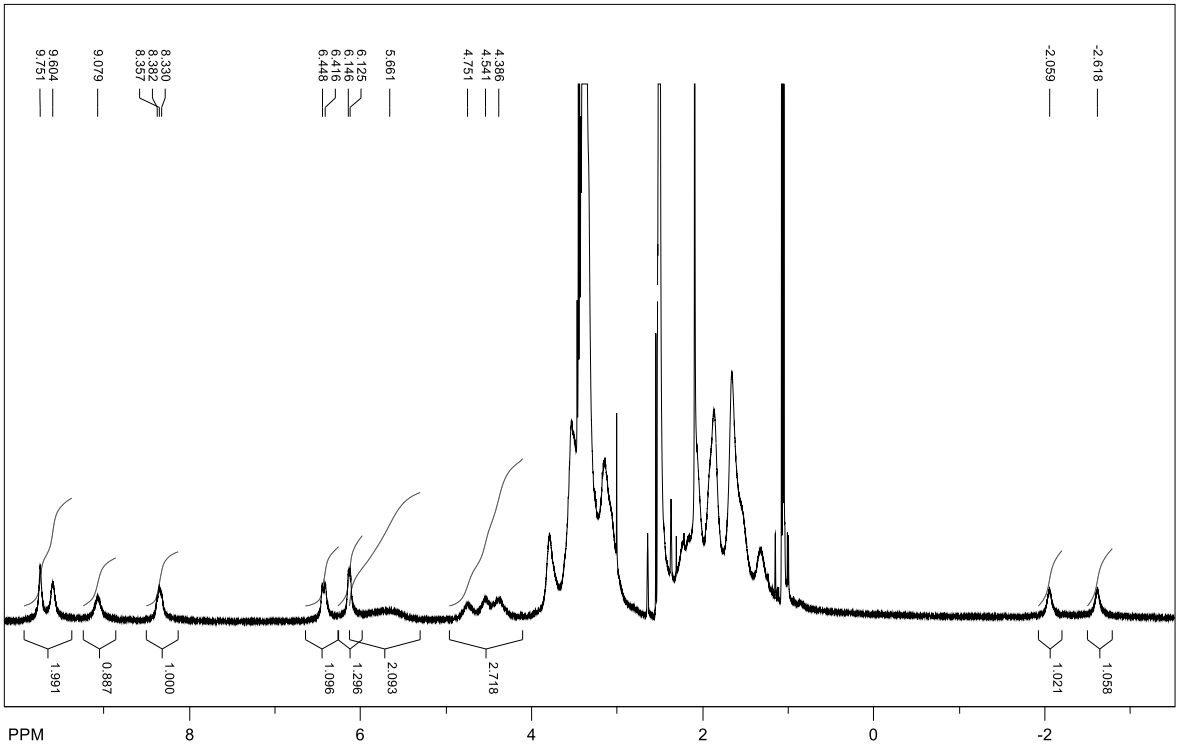


Figure S1. ^{1}H NMR spectrum of Chl e_6 in DMSO d_6.

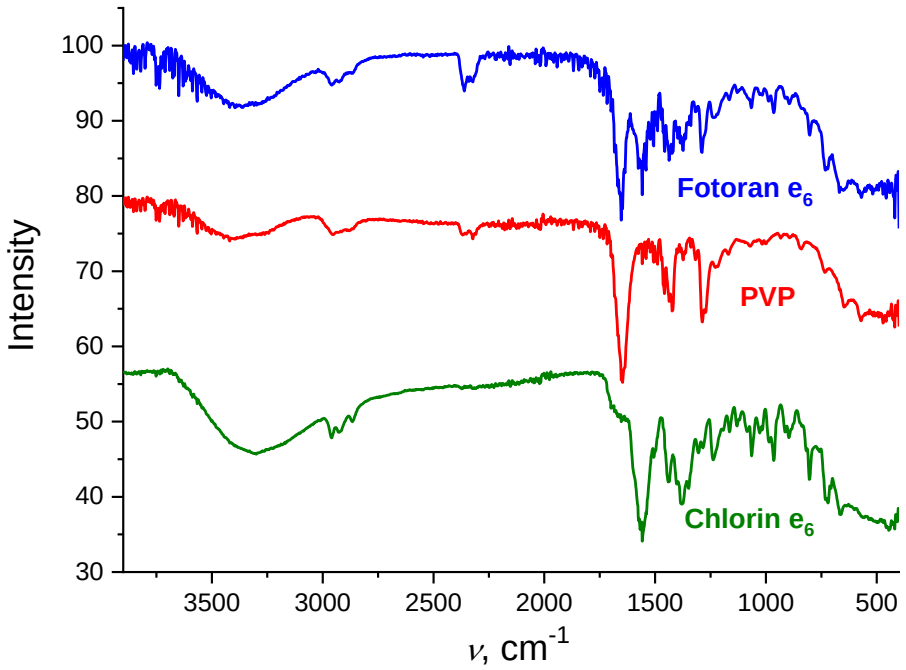


Figure S2. FTIR-spectra of Chl e_6, PVP and Fotoran e_6 (Chl e_6+PVP, 50/50).

S2. Physicochemical studies

Dynamic light scattering (DLS) studies were performed at 298 K using a Zetasizer Nano ZS ZEN3600 instrument (Malvern Instruments, Great Britain) equipped by a 632 nm diode laser. The dynamic viscosity and refractive index of water were taken from the device database.

The enthalpies of dilution were determined with the self-built calorimetric system based on a commercial MS 80 D heat conduction calorimeter (Setaram, France) equipped by two transducers. According to the Calvet principle, two identical self-built titanium calorimetric cells were placed into the transducers inside a calorimetric block which imposed the fixed experimental temperature of 298.15 K. The experimental vessel shown contained a solution to be investigated and the identical reference vessel was usually filled by pure water. Both solutions were usually stirred by a tier propeller stirrer rotated by a computer driven stepper motor (BIC, Belarus). The heat flow was detected by a standard Setaram thermopile containing 1316 thermocouples. The electric signal of the thermopile was registered by an ITEK instrument (BIC, Belarus) with an accuracy of 0.5 nV. The temperature of the calorimetric block was measured by a 100 Ohm platinum thermometer connected to another channel of ITEK. The temperature of the calorimetric block was maintained by a digital PID device also developed in BIC (Belarus). The temperature

instability inside the block was lower than 0.1 mK, and the temperature drift during 12 h did not exceed 2 mK. The calorimeter as well as the measuring and control devises was additionally placed into an air thermostat with the temperature of 293(±2) K.

The titration experiments were performed using a 70 cm stainless-steel capillary permanently connected to a gas tight Hamilton syringe with the volume of 250 μL. The capillary was introduced into the cell using the guide tube and then the first titrant portion of 10 μL was injected into a calorimetric vessel using a SPLab02 precision pump (Baoding Shenchen Precision Pump Co. Ltd., China) and a titration experiment was initiated an hour later. Each injection was performed manually according to the stability of a base line and its volume was varied between 40 – 50 μL. The experimental quantities are given in Table S1.

Table S1. The integral enthalpies of dilution of Chl e_6 aqueous solutions at 298.15 K

m_i, mmol·kg^{-1}	10^3 m_f, mmol·kg^{-1}	$\Delta_{dil}H^m$, J·mol^{-1}	n, mmol
5.12	5.92	-1499	0.00020
5.12	11.82	-1575	0.00041
5.12	17.71	-1507	0.00061
5.12	23.59	-1597	0.00081
5.12	29.45	-1556	0.00102
4.75	5.50	-3025	0.00019
4.75	10.99	-2763	0.00038
4.75	16.47	-2591	0.00057
4.75	21.94	-2519	0.00076
4.75	27.39	-2462	0.00094
3.59	4.15	-7934	0.00014
3.59	8.29	-7934	0.00029
3.59	12.42	-8040	0.00043
3.59	16.54	-8172	0.00057
3.59	20.65	-8124	0.00071
3.59	24.78	-7934	0.00086
2.47	2.86	-14026	0.00010
2.47	5.72	-12672	0.00020
2.47	8.57	-12795	0.00029
2.47	11.41	-12980	0.00039
2.47	14.25	-12746	0.00049
1.50	1.74	-2555	0.00006
1.50	3.48	-2531	0.00012
1.50	5.22	-2617	0.00018
1.50	6.95	-2601	0.00024
1.89	2.18	-3875	0.00008
1.89	4.36	-3990	0.00015
1.89	6.54	-3862	0.00023
1.89	8.71	-3884	0.00030

The calorimeter was calibrated electrically after each series of experiments. The resistance of the heater (R_h) in the cell was obtained using the determination of the heat of dilution of 10 wt %

aqueous 1-propanol which was recommended for the analysis of small heat effects.[S1] The R_h obtained leads to the value of the enthalpy of dilution at m_f<1.4 mg·ml^{-1} equal to 2.565±0.088 mJ·kg^{-1} which is in good agreement with the recommended value of 2.570±0.015 mJ·kg^{-1}.[S2,S3] The densities of the water-1-propanol mixtures were found elsewhere.[S4] Other details can be found in our recent paper (see ref.[19] in the main text).

References

S1. D. Hallén, S.-O. Nilsson and I. Wadsö, *J. Chem. Thermodyn*., 1989, **21**, 529; https://doi.org /10.1016/0021-9614(89)90170-5.

S2. I. Wadsö and R. N. Goldberg, *Pure Appl. Chem*., 2001, **73**, 1625; https://doi.org/10.1351/pac200173101625.

S3. R. Sabbah, An Xu-Wu, J. S. Chickos, M. L. Planas Leitão, M. V. Roux and L. A. Torres, *Thermochim. Acta*, 1999, **331**, 93; https://doi.org/10.1016/S0040-6031(99)00009-X.

S4. L.-E. Briggner and I. Wadso, *J. Biochem. & Biophys. Meth*. 1991, **22**, 101; https://doi.org/10.1016/0165-022X(91)90023-P.