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Electronic Supplementary Information (ESI)

Phthalocyanine Blue in Aqueous Solutions

Mark Staniford,[a] Marina M. Lezhnina,[a,b] Ulrich H. Kynast[a]*

[a]Muenster University of Applied Sciences, Institute for Optical Technologies,
Stegerwald-Str. 39, 48565 Steinfurt, Germany
[b]On leave from Volga State University of Technology, Department of Physics, Lenin-pl.3,
Yoshkar-Ola, 424000, Russia

*corresponding author:
Prof. Dr. Ulrich H. Kynast
Stegerwaldstraße 39, 48565 Steinfurt, Germany
e-mail: uk@fh-muenster.de

Electronic Supplementary Information (ESI):

Experimental details and methods

Figures S1-S6

Table S1.

Reference to the ESI

Experimental details and methods

The starting materials Laponite RD (Rockwood) and CuPc (Aldrich) were used as received without further purification.

Solutions (1). The following procedure was used for the preparation of CuPc-laponite carrying nominally 10 mpd (4.97 mg CuPc/g laponite), of which 0.89 mpd (0.32 mg CuPC/g laponite) were found in the solution. The same procedure was applied for all other samples by adjusting the amount of CuPc, albeit the eventual amounts mobilized by the laponite, i.e. the "loading efficiencies", varied considerably (see Figure S5). Thus, 5 mg of CuPc (8.5 x 10^{-6} mol) were thoroughly mortared with 1 g of laponite (5.2 x 10^{18} disks) and added to a mixture of CH_3CN (50 ml) and water (50 ml) in a round bottom flask. The mixture was refluxed for 48 hrs and subsequently filtered via a Büchner funnel applying a 602 H filter paper with a particle retention of < 2 μm to yield a deep blue solution.

Recovery of intermediade powders. In order to obtain crystallographic and spectral information, the volumes of solutions (1) were reduced to approximately 50 ml. From these, the precipitation of the solid materials was accomplished by the addition ethanol. The precipates were settled by centrifugation and decanting of the supernatant solvent. The remaining gels were dried in a vacuum drying chamber at 60 °C for 24 hrs to give deep blue powders.

Solutions (2). 1 g each of the intermediate powders was re-dispersed in water at r.t. using a magnetic stirrer. The re-dispersion was immediate for all samples, but to ensure equilibration, stirring was continued for approximately 2 hrs.

Molecules per disk (mpd) and recalculation of the solution concentrations of α-CuPc and monomeric CuPc. It sometimes seemed more convenient to express the dye concentration as dye molecules per disk as a more intuitively comprehensible unit:

$$mpd = \frac{n_{CuPc} * N_A}{5{,}2 * 10^{17}\,[\frac{disks}{g}] * m_{Laponite}} \qquad \text{(eq. S1)}$$

("mpd"; N_A = Avogadro constant, n_{CuPc} = number of CuPc molecules, $m_{Laponite}$ = mass of the laponite clay)

Determination of the extinction coefficient ε_{673} of monomeric CuPc. In order to obtain extinction coefficients of monomeric CuPc-laponite hybrids, and α-CuPc eventually, indirect routes were pursued to determine the contents of CuPc in the hybrid samples prepared. This route essentially consists of the preparation of aqueous hybrid samples with purely monomeric CuPc, which was accomplished by jointly dispersing thorough mixtures of laponite and native CuPc in water, followed by filtration and centrifuging steps, until clear solutions were obtained and their absorption spectra showed no bands due to α-CuPc and background due to scatter. In the course of these measurements, it had turned out that the temperature during every step of preparation and filtration was a decisive factor. At temperatures above ca. 60 °C an increasing amount of protonated species and turbidity (agglomeration of the clay platelets) in the H_2O dispersions was observed. The temperature of the dispersed samples should therefore be kept at no more than 60 °C during all handling steps. The absorbance of the aqueous dispersions was measured, the solvent evaporated at moderate temperatures and the residue dissolved in concentrated sulfuric acid, from which the absorbance of the protonated phthalocyanines at 790 nm was measured once again. The corresponding absorbance was evaluated against a calibration curve of pure CuPc in H_2SO_4 (see Fig. S1) to give the absolute concentration of protonated Pc. This in turn then allows the concentration recalculation of the aqueous parent solution, and the extinction coefficient of monomeric CuPc eventually. The temperature considerations above hold true of course also, when H_2SO_4 is added to CuPc-clay hybrids, which inevitably contain water in the interlayers, or vice versa. The H_2SO_4 was consequently cooled, i.e. frozen, and the hybrids added. The mixture was thawed slowly under stirring, such that room temperature was not exceeded. Absorption spectra of the H_2SO_4 solutions were taken within thirty minutes after dissolution of the CuPc, because we noticed that prolonged storage (days) altered the analytical data.

a) determination by subtraction of undissolved residues:
Samples of CuPc (11.0 mg) and laponite clay (2 g) were thorougly mortared (over 30 min.) and dispersed in water (200 ml) under vigorous stirring (2.5 hrs). The resulting dispersion was then filtered four times through a G4 frit (porosity 12 µm) and the residue washed three times with water (giving a RE1 residue and a mother liquor ML1). IR spectra had previously shown that the residue RE1 contained only minute amounts of laponite (< 5 %). Residue RE1 in the frit was extracted three times with conc. H_2SO_4 (110 ml), after which all of the precipitate was dissolved. From the evaluation of the absorption spectra of the (diluted) H_2SO_4 filtrate against the CuPc/H_2SO_4 calibration curve (ε_{790} = 157 762 L x mol^{-1} x cm^{-1}), we found that between 76.4 % and 78.2 % of the CuPc systematically remained unreacted (three independent measurements).
The aqueous mother liquor ML1 (containing between 23.6 % and 21.8 % of the original CuPc) was then vacuum evaporated at 60 °C to a viscous gel and dried further overnight in a vacuum drying furnace (60 °C) to obtain a blue powder of CuPc-laponite. Fractions of this powder were redispersed in H_2O to yield dispersions with 1 wt % of laponite (300.3 mg CuPc-laponite in a total volume of 30.0137 g H_2O). The dispersions were analysed spectroscopically, but still revealed considerable amounts of scattering particles. Only after cenrifugation (3000 rpm, 35 min.) we obtained CuPc-monomer solutions free of scatter. The sediment was then dissolved in H_2SO_4 and the Pc- content determined spectroscopically as described above.
Three samples obtained and measured in this manner had absorbances within a maximum error of 2.9 % (standard deviation 0.75 %). The amount of monomeric CuPc eventually obtained in the solution can now be calculated as the difference between the CuPc weighed out in the beginning minus all filtered and centrifuged fractions. However, the determination of the final, absolute amounts of CuPc by this

method by consecutively subtracting the amount of removed solids is somewhat hampered, among others, by the limited precision of weighing out the small initial amounts of native CuPc.

b) “direct” determination from solutions containing only monomeric CuPc:
To cope for errors in the weighing-out of the CuPc in the very first step of the preparation, we went through the same procedure as described above, but refrained from intermediate isolations and redispersion steps and corresponding analyses. Instead, the absorbance of a final, scatter-free solution of known volume, with monomeric CuPc as the only constituent, was measured. Consecutively, the solution was vacuum evaporated under mild conditions (T =50 °C) to a highly viscous gel. The gel was re-dissolved in a given amount of H_2SO_4, and the concentration of protonated Pc determined by aid of the calbration curve. Finally, the amount thus found can be correlated to the previous aqueous monomer solution. In this method the determination of the extinction coefficient is completely independent of errors made during preceding steps, as it solely relies on the absorbance of the protonated CuPc which unambiguously resulted from a solution exclusively containing monomer. A slight turbidity after H_2SO_4 addition due to insoluble colloidal remnants of the clay could fortunately be taken care of, as the baseline was elevated but straight throughout the measured range between 500 and 900 nm, such that scatter could simply be corrected by subtraction. In any case, the results from a) and b) coincide within 0.11 absorbance units at 0.48 total absorbance. Although b) is probably more reliable, we therefore concede an experimental error of about 23 %.

The extinction coefficient $\varepsilon_{mono,673}$ of monomeric CuPc obtained of 102 777 (± 23 %) L x mol^{-1} x cm^{-1} was used for all subsequent calculations.

The value is lower than previously reported for other solvents, however, it may be owed to the fact that monomeric CuPc has never before been observed in a solvent of as high a polarity or dielectric constant. The absorbance may furthermore be compared to extinction data obtained for tetrasulfonated zinc pthalocyanine ($ZnPcS_4$) for an example, which has recently been reported[R1] for a solution in DMSO to be 114 000 L x mol^{-1} x cm^{-1}. Interestingly, aggregates reported for other solvents had extinction coefficients in the same order of magnitude (ca. 25 000 L x mol^{-1} x cm^{-1}) as the α-CuPc reported in our work (ca. 20 000 L x mol^{-1} x cm^{-1}).

*Concentration of samples in Figures 3a and 3b.*The basis for the calculation of concentrations the samples in Figures 3a and 3b is the extinction coefficient of monomeric CuPc, given in the previous section (102 777(± 23 %) L x mol^{-1} x cm^{-1}) and the sample, which unambiguously contained monomeric CuPc exclusively (Figure 3b, red curve). In this sample, we thus calculate the concentration of CuPc to be 7.68 x 10^{-6} mol x L^{-1}, or 0.89 mpd. The approximate monomer concentrations in solutions (2) (Figure 3b) were recalculated in the same manner, except that in samples containing both, α-CuPc and monomer, the 673 nm monomer absorbance was obtained by subtracting the value of a bridging line connecting the α-CuPc curves in the range between 660 and 690 nm at 673 nm.

Furthermore, a comparison of the spectra of aqueous monomer (0.89 mpd, red curve in Figure 3b) and α-CuPc (Figure 3a) reveals that monomeric CuPc has practically no absorbance at 616 nm, while the absorption of α-CuPc has its maximum at this very wavelength. Given the history of the 0.89 mpd monomer sample, the concentration of α-CuPc in the H_2O/CH_3CN solution was exactly the same 7.68×10^{-6} mol x L^{-1}, as it originated from a filtered, corresponding α-CuPc dispersion, to which no matter but solvents, to give identical total volumes for solutions (1) and (2), had been added or lost. Therefore, the extinction coefficient of α-CuPc at 7.68×10^{-6} mol x L^{-1} could be recalculated, giving a value of 2.1×10^4 L x mol^{-1} x cm^{-1} at 616 nm for α-CuPc. Based on this value, the concentrations of the other samples of the solutions (1) were recalculated.

X-Ray powder diffraction. X-ray powder data of powders and intermediately isolated powders prior to dissolution to solutions (2) were obtained with a Rigaku MiniFlexII by scanning in the 2Θ range between 2° and 60°. Apart from the broad reflexes of the nano-clay, no signals due to CuPc were detected (see Figure S1).

Absorption spectra. The absorption spectra of all samples were recorded using an Ocean Optics HR4000 fiber spectrometer with a 5 µm slit and a 20 W Halogen light source in the range between 300 and 900 nm.

IR-spectroscopy. IR spectra of the residues of the first filtration and the intermediates prior to dissolution to solutions (2) were recorded on a Perkin-Elmer Spectrum One in the range between 4000 and 400 cm^{-1}. Typically, the spectra of the hybrids are by far dominated by the clay absorptions (see Figure S3 for an example). The residue of the first filtration consisted of CuPc almost exclusively, indicating that no clay had precipitated.

Thermogravimetrical analysis (TG / DTG / DTA). For pure laponite and samples containing nominally 54 and 108 mpd (7.2×10^{-4} and 1.44×10^{-3} mol x L^{-1}, respectively), differential thermogravimetry (DTA) was carried out on a Netzsch STA 409 in purified air at a heating rate of 1°/min in the range between r.t. and 600 °C (Figure S2).

Carbon determination. All samples reported here were exposed to a carbon analysis using a CS 800 Carbon Sulphur Determinator (Eltra, Germany). The strong deviations between theory and experiment are discussed in the text.

Nitrogen determination. The nitrogen content was evaluated using a LECO TC 400 nitrogen and oxygen determinator. The settings were done using the program TCWin Analysis Software LECO 4.03 supplied from LECO cooperation.

Supplementary Figures S1-S6 and Table 1

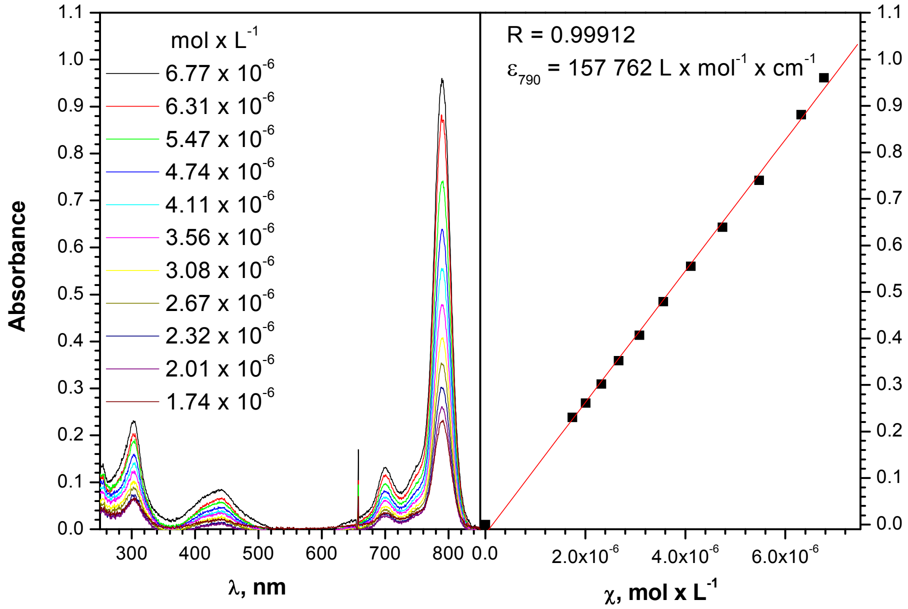

Figure S1. Left panel: Absorption spectra and concentrations of CuPc in conc. H_2SO_4 of the samples used for calibration. Right panel: calibration curve for spectroscopic determination of CuPc in conc. H_2SO_4.

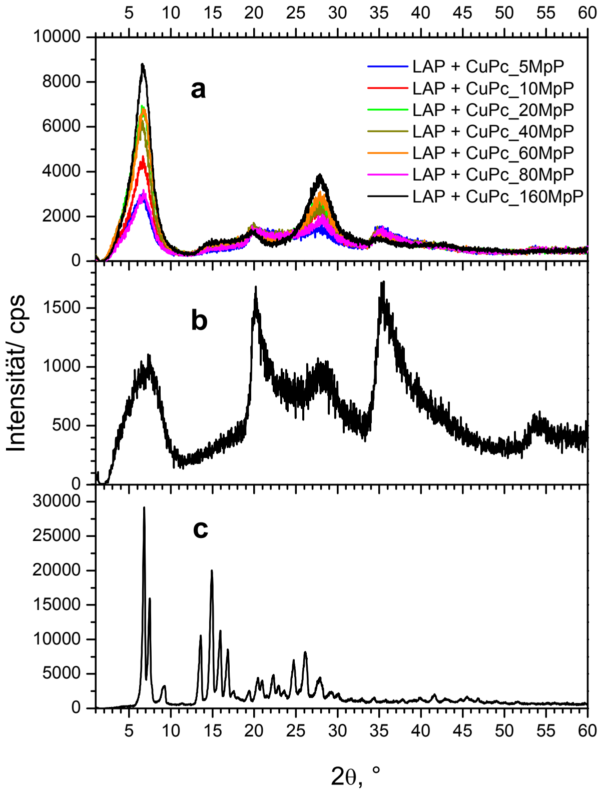

Figure S2. X-ray diffraction data of CuPc-laponite hybrids (a), pure laponite (b) and commercial CuPc (c).

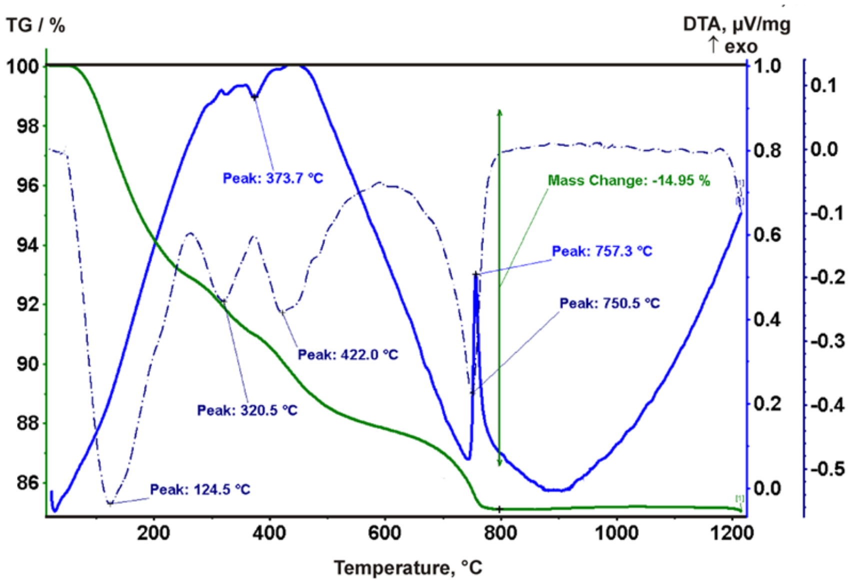

Figure S3. The thermogravimetric measurement of a nominally 20 mpd sample (from a H_2O/CH_3CN [50/50] solution with 2.67 x 10^{-4} mol x L^{-1} CuPc) shows a mass loss of 7.1 % up to 200 °C, however, the corresponding TG curve merges into a very shallow, long tail, which terminates at 780 °C. Measurements of samples with nominally 54 and 108 mpd (7.2 x 10^{-4} and 1.44 x 10^{-3} mol x L^{-1}) revealed mass losses of 6.5 % and 5.9 %, respectively, at temperatures of up to 200 °C.

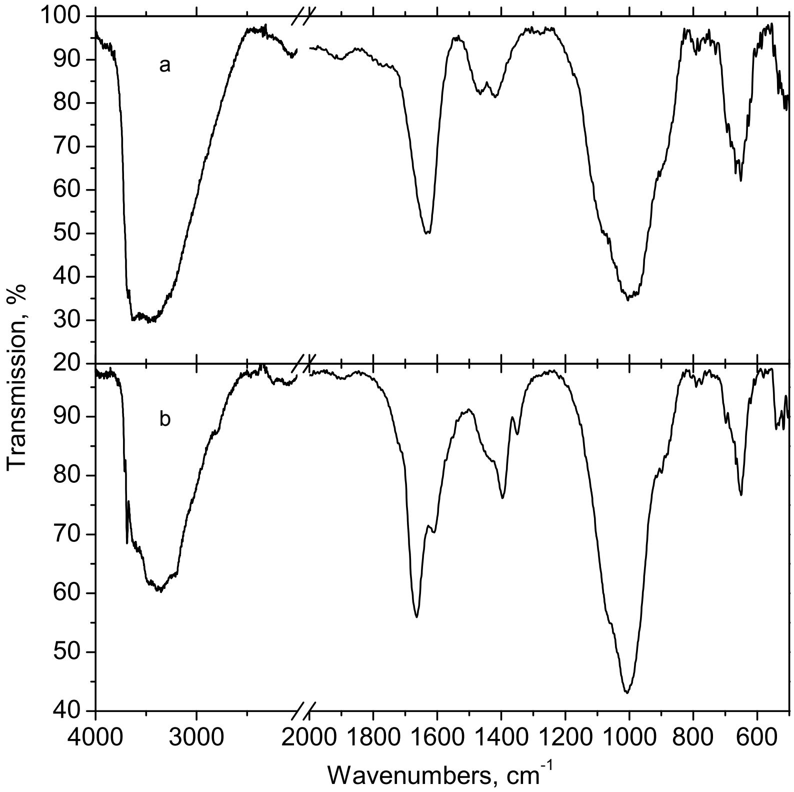

Figure S4. FTIR spectra of pure laponite (a) and a CuPc-laponite hybrid (1.4 mpd, b)

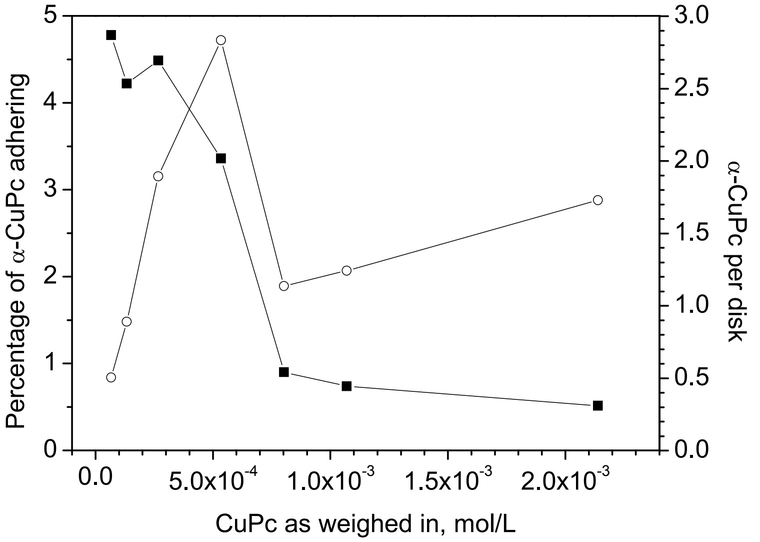

Figure S5. "Loading efficiencies" of the laponites. The figure depicts the percentage of CuPc found in the resulting hybrid materials (solid black squares) and the respective mpd ratios (open circles) as a function of the CuPc concentration as weighed out for the synthesis (solution (1)).

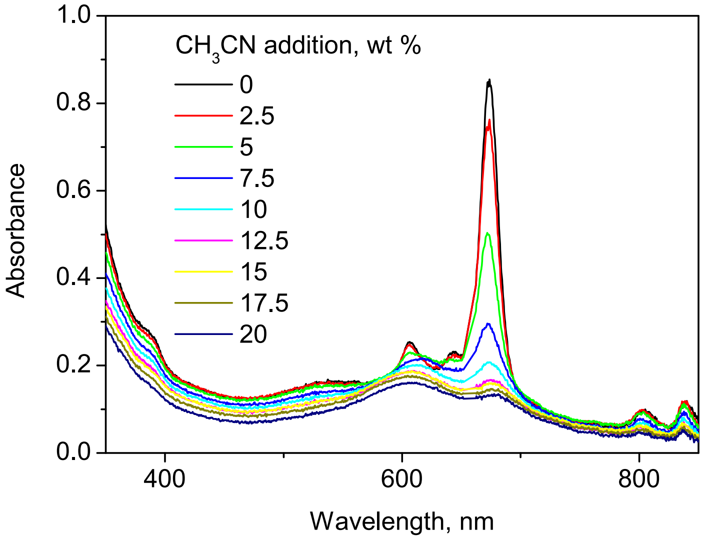

Figure S6. Re-formation of α-CuPc on addition of CH_3CN to an aqueous solution of monomeric CuPc (7.68 x 10^{-6} mol x L^{-1}; 0.89 mpd).

Table S1. Amounts and absorbances used and found in the CuPc-laponite hybrid dispersions

Concentration of CuPc added, mol L^{-1}	nominal[a] mpd	Absorbance α-$CuPc_{616}$	α-CuPc, mol L^{-1} (recalc.)[b]	α- CuPc, mpd (recalc) [b]	Absorbance monomeric $CuPc_{673}$	monomeric CuPc, mol L^{-1} (recalc.)[b]	monomeric CuPc, mpd (recalc.)[b]
6.7×10^{-5}	5	0.090	4.35×10^{-6}	0.504	0.166	1.61×10^{-6}	0.187
1.34×10^{-4}	10	0.159	7.68×10^{-6}	0.891	0.790	7.68×10^{-6}	0.891
2.67×10^{-4}	20	0.338	1.634×10^{-5}	1.894	0.043	4.135×10^{-5}	0.048
5.34×10^{-4}	40	0.506	2.446×10^{-5}	2.834	0.606	5.896×10^{-5}	0.683
8.01×10^{-4}	60	0.203	9.81×10^{-6}	1.137	0.070	6.81×10^{-6}	0.079
1.069×10^{-3}	80	0.222	1.073×10^{-5}	1.243	0.008	7.78×10^{-6}	0.009
2.138×10^{-3}	160	0.309	1.493×10^{-5}	1.730	0.061	5.837×10^{-5}	0.068

[a] theoretical from amount of CuPc applied. [b] recalculations are based on the extinction coefficient of the 10 mpd sample prepared from a 1.34×10^{-4} mol x L^{-1} CuPc containing starting mixture.

Reference for Electronic Supplementary Information

(R1) , Chin Y.; Lim S.H.; Zorlu Y.; Ahsen V.; Kiew L.V.; Chung, L.Y.; Dumoulin, F.; Lee, H.B., Improved Photodynamic Efficacy of Zn(II) Phthalocyanines via Glycerol Substitution. PLoSONE **2014**, *9*, e97894. Open access, doi:10.1371/journal.pone.0097894.