

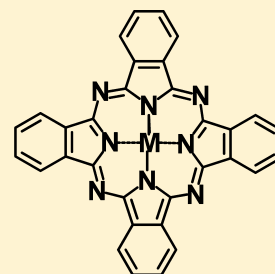
# Solubility Properties of Unsubstituted Metal Phthalocyanines in Different Types of Solvents

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**S** Supporting Information

**ABSTRACT:** We investigated quantitatively the solubility properties of a number of unsubstituted metal phthalocyanines with various metal atoms such as Co, Cu, Fe, Mg, Mn, Ni, Sn, and Zn. We studied three categories of solvents: conventional solvents, ionic liquids, and acids. The conventional liquids comprised 20 typical representatives from acetone to toluene. We tested two ionic liquids and five acids. For each solution we measured the molar absorption coefficient and the saturation concentration (or estimated these values if the solubility was too low). The absorption coefficients and saturation concentrations were derived from UV–vis absorption measurements of the Q-band. The solution spectra are presented and discussed as well as the chemical properties (stability) of the solutions.



## INTRODUCTION

Metal phthalocyanines (M-PC), as in Figure 1, have attracted considerable attention because of their unique optical and

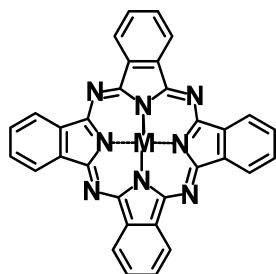


Figure 1. Metal phthalocyanine.

electronic properties<sup>1</sup> together with their high chemical and thermal stability.<sup>2</sup> They are organic semiconductor molecules<sup>3</sup> with numerous applications such as organic solar cells,<sup>4–8</sup> chemical sensors,<sup>9–12</sup> and electronic devices like field effect transistors<sup>13–15</sup> and optical data storage.<sup>16–18</sup> Recently high efficient organic solar cells containing phthalocyanine molecules were produced.<sup>19</sup> Spectroscopic studies are available on phthalocyanine in vapor,<sup>20</sup> in solids,<sup>21</sup> and in solution.<sup>22</sup> There are also many theoretical studies on their spectroscopic properties.<sup>1,23–29</sup>

Unsubstituted metal phthalocyanines are barely soluble in common solvents,<sup>30,31</sup> and little quantitative information is available on their solubility. Therefore many research activities focused on synthesizing soluble phthalocyanines by adding functional groups to the molecule.<sup>32,33</sup> Unfortunately most of the substituted phthalocyanines are not as stable as the unsubstituted compounds, and their electronic properties are also different from those of the unsubstituted phthalocyanines.<sup>1,34,35</sup>

Room temperature wet-technologies like printing and spin coating have numerous advantages in the preparation of organic films with less rigorous preparation conditions. More parameters are available to control the nucleation and growth of the film, like solvent, temperature, and the concentration of the solution. But the general poor solubility of unsubstituted metal phthalocyanines limits their use in low cost wet technologies.<sup>36</sup> In the following article we present a systematic study on the solubility of unsubstituted metal phthalocyanine in a series of various solvents including different types of solvents such as neutral conventional solvents, acids, and ionic liquids. The aim of the study is a systematic quantitative assessment of the solubility of various unsubstituted metal phthalocyanines, their saturation solubilities, and their interactions with the solvents. The solubility was quantified and evaluated by UV–vis spectroscopy.

We found only a few molar absorption coefficients of dissolved phthalocyanines published. Kumar et al.<sup>21,22,37,38</sup> and Stillman and Hollebon<sup>39</sup> measured ZnPC, CuPC, FePC, and MnPC with dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as liquid solvents. In other cases the PCs were “dissolved” in glassy and polymer matrixes. The molar absorption coefficients measured by Kumar et al. in different media are different for each metal phthalocyanine. Also, the molar absorption coefficients measured by Stillman et al. in DMF and Kumer et al. in DMSO do not agree (our results do not show such large deviations).

## UV–VIS SPECTRA OF METAL PHTHALOCYANINES

Experimental and theoretical studies show that the UV–vis spectrum of metal phthalocyanines mainly originates from  $\pi \rightarrow \pi^*$

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transitions of the strong Q-band ((600 to 750) nm) and the broad B-band ((300 to 450) nm) with weaker transitions near those bands.<sup>1,23–25,39</sup> Gouterman et al. showed that to a first approximation the strong Q-band ((600 to 750) nm) originates from  $\pi \rightarrow \pi^*$  transitions from  $a_{1u}$  to  $e_g^*$  orbitals. The broad B-band is caused by transitions between  $a_{2u}$  and  $b_{1u}$  to  $e_g^*$  orbitals, as in Figure 2.<sup>20,23,25,40</sup>

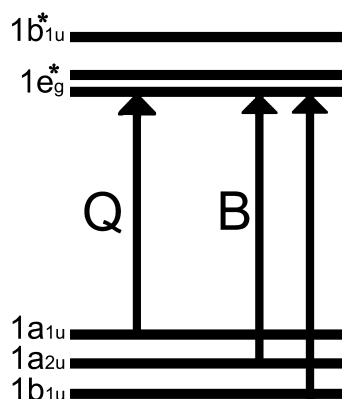


Figure 2.  $\pi \rightarrow \pi^*$  transition, according to the calculations of Stillman et al.<sup>29</sup>

Dissolved phthalocyanines often show solvatochromic effects, such as changes in the position, intensity, or half-width of the absorption bands.<sup>31,39,41–45</sup> New absorption bands appear due to a charge transfer, and the absorption bands can be red or blue-shifted.<sup>39,46,47</sup> The dimerization of phthalocyanine molecules at high solution concentrations can cause a (reversible) band shift.<sup>48</sup> The deformation of the phthalocyanine molecules due to interactions with the solvent molecules may change the symmetry of the molecules, influencing the absorption spectra. The splitting of absorption bands can be observed in the case of  $D_{2h}$  to  $C_{2v}$  transitions.<sup>49</sup>

However, although the absolute position of the absorption bands and their shape can be solvent-dependent, their relative positions remain roughly constant,<sup>50</sup> and usually the oscillation strength does not vary drastically. The strength of the oscillation is related to the molar absorption coefficient<sup>51</sup> of the absorption bands. Thus the absorption coefficients can be used to determine the concentration of the material. According to Stillman et al. the high-energy B-band represents mostly the charge transfer transition.<sup>1,28,29,47,52</sup> The less solvatochromic Q-band is in most cases well-separated from its neighbor bands, and there is no vibronic mixing between the Q-band and the higher lying states.<sup>39</sup>

Therefore, we used for our solubility studies the absorption intensity of the Q-band as a measure for the solute concentrations. We neglected the influence of the vibronic transitions near the Q-band, since in most cases they were much smaller than the Q-bands. In cases in which more than one intensive Q-band exists (Q-band splitting), we took only the molar absorption coefficient of the stronger transition as a measure for the solubility. In general, to a rough approximation the molar absorption coefficient of the Q-band is in the range of  $10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ .<sup>53</sup> Dimerization may change the molar absorption coefficient of the Q-band slightly, for example, from  $2.5\cdot 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  (monomer) to  $2.2\cdot 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  (dimer) as shown by Hush and Woosley.<sup>54</sup> Our measurement shows that depending on the central metal atom the molar absorption coefficient may change by up to 1 order of magnitude, whereas solvent effects cause only smaller variations.

## EXPERIMENTAL SECTION

**Materials and Methods.** CuPC (> 99 %) and ZnPC (> 99 %) were kindly supplied by Minakem Leuna. The other phthalocyanines, MgPC (~ 90 %), MnPC (~ 90 %), CoPC (> 97 %), FePC (~ 90 %), NiPC (~ 85 %), and SnPC (~ 97 %), were purchased from Sigma Aldrich. All of the solvents and their abbreviations (as used in the following) that were tested are listed in Table 1 with their purities as obtained from the suppliers. All of the chemicals were used without further treatment. It can be assumed that minor impurities should have a minor effect on the absorption spectra of phthalocyanine.<sup>53</sup> The absorption spectroscopy measurements were performed with an Agilent 8453 spectrophotometer. The light paths of the cuvettes were chosen as (1, 0.1, or 0.01) cm, respectively, to optimize the absorption range for the measurement.

We used two measurement protocols:

- (1) The molar absorption coefficients were derived from the relation between the absorption intensity and the amount-of-substance concentration of metal phthalocyanine (Figure 3).
- (2) The saturation concentrations were derived from the absorption intensities of saturated solutions using the molar absorption coefficients determined by our own measurements according to protocol 1. If the solubility was too low to reliably measure a precise molar absorption coefficient in the applied solvent, we used a mean value of the measured molar absorption coefficients of a similar kind of solvent and with similar spectra.

**Molar Absorption Coefficient Measurements.** For the molar absorption coefficient measurements we used only the following selection of solvents: acids, SA and TFA; ionic liquids, STOR; conventional solvents, DMAC, DMF, DMPU, DMSO, and NMP.

For the other solvents from Table 1 the solubility was typically too low to obtain quantitative concentration data, or their solvatochromic/chemical effects were too strong. They were not used for the molar absorption coefficient studies.

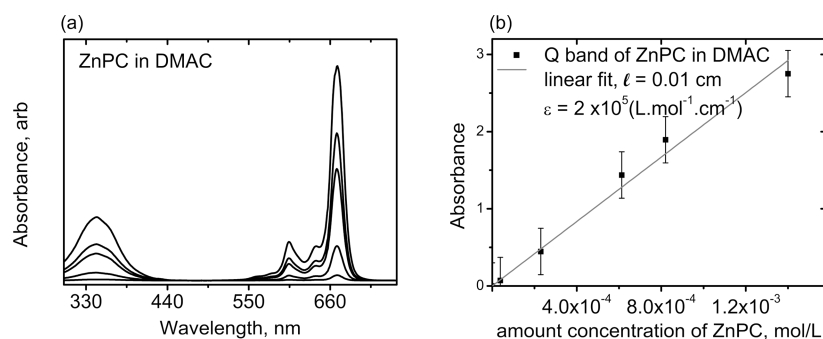
We prepared a stock solution of each phthalocyanine. From this we derived 3 to 4 diluted solutions. Acid solutions were prepared by shaking (20 min with 500 mot/min). Metal phthalocyanine molecules can be dissolved in many acids and usually interact with acids. This interaction can lead to protonation of metal phthalocyanine. This will be discussed later in each case. The solutions with conventional liquids and with ionic liquids were prepared by sonication (10 min) at room temperature.

The main uncertainty in the concentration data (estimated: 10 %) originates from the weighing errors of the low sample weights because of the typically rather low solubilities.

**Saturation Concentration Measurements.** An amount of metal phthalocyanine exceeding the maximum solubility (i.e., leading to the precipitation of undissolved PCs) was introduced into the various solvents to obtain saturated solutions.

After typically (20 to 30) min the saturated solutions were separated from the undissolved phthalocyanine by centrifugation at room temperature for 10 min at 25.000 g. FA solutions were centrifuged at 0 °C to reduce the catalytic decomposition of acid<sup>55,56</sup> (see also below). The spectroscopic measurements with the clear supernatants were performed immediately after the centrifugation.

The dispersion of the solid PC particles in the rather viscous ionic liquids takes longer than only a few minutes. Typically



**Figure 3.** (a) Absorption spectrum of ZnPC in DMAC for different concentrations. (b) Absorption intensity of the Q-band versus the amount-of-substance concentration of ZnPC. The slope of the line yields the molar absorption coefficient of ZnPC in DMAC at the Q-band.

**Table 1. Solvents Used in This Study**

	solvents	abbreviation	purity (%)	density	supplier
			kg·m <sup>-3</sup>		
Acids					
1.	acetic acid	AA	99.8	1048	Fisher Scientific
2.	formic acid	FA	99.5	1220	Fisher Scientific
3.	phosphoric acid	PA	99	1680	Fisher Scientific
4.	sulfuric acid	SA	99.99	1840	Sigma-Aldrich
5.	trifluoroacetic acid	TFA	99	1535	Acros Organics
Ionic Liquids					
6.	1-ethyl-3-methylimidazolium acetate	STOR	90	1027	BASF
7.	1-ethyl-3-methylimidazolium ethyl sulfate	EMIM	99	1024	Iolitec
Conventional Solvents					
8.	acetone		99.5	790	J.T.Baker
9.	acetonitrile	ACN	99.95	786	Merk
10.	anisole		99	995	SAFC
11.	benzene		99.5	880	Roth
12.	chlorobenzene	CBZ	99.8	1106	Sigma-Aldrich
13.	chloroform	TCM	99.5	1490	Chemsolute
14.	decanol		98	825	Alfa Aesar
15.	dichloromethane	DCM	99.8	1330	VWR
16.	dioxane		99	1034	Acros Organics
17.	dimethylacetamide	DMAC	99.97	940	Fisher Scientific
18.	dimethylformamide	DMF	99	994	AppliChem
19.	1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidin-7-one	DMPU	98	1060	Alfa Aesar
20.	dimethyl sulfoxide	DMSO	99.9	1100	Merck
21.	ethanol	EtOH	99.8	790	VWR
22.	ethyl acetate	EtOAc	99.5	900	chemsolute
23.	isopropanol	IPA	99.7	785	chemsolute
24.	methanol	MeOH	99.8	790	J.T.Baker
25.	N-methyl-2-pyrrolidone	NMP	99.8	1026	Roth
26.	tetrahydrofuran	THF	99.9	890	Sigma-Aldrich
27.	toluene		99	866	Acros Organics

after 24 h the solution reached its maximum concentration. The ionic liquid solutions were shaken per hand occasionally and finally centrifuged one day after preparation.

## RESULTS AND DISCUSSION

**Spectroscopic Measurements and Analysis.** The molar absorption coefficients and saturation concentrations were determined spectroscopically via the Lambert–Beer law assuming a linear relationship between the absorbance,  $A_\lambda$ , the molar absorption coefficient,  $\epsilon_\lambda$ , of the absorbing species at wavelength  $\lambda$ , the amount-of-substance concentration,  $c$ , and the light path,  $l$ :

$$A_\lambda = \epsilon_\lambda \cdot l \cdot c \quad (1)$$

### Determination of the Molar Absorption Coefficients.

The molar absorption coefficients were determined from the slope of the absorption intensity of the Q-band versus the amount-of-substance concentration (as an example, see Figure 3). For this protocol the maximum solubility had to be sufficiently high, and the solution had to be sufficiently stable. Then the coefficients could be derived with sufficient certainty (typically  $\pm 10\%$ ). However, sufficiently high solubility was not given for many of the conventional solvents and some of the ionic solvents. Some of the acidic solutions were not sufficiently stable. In these cases we do not present a molar absorption coefficient (Table 2).

Table 2. Molar Absorption Coefficient of Metal Phthalocyanines Derived from the Intensities of the Q-Band<sup>a</sup>

solvents	CoPC	CuPC	FePC	MgPC	MnPC	NiPC	SnPC	ZnPC
Acids								
SA	1.5	1.6	0.34	1.2	0.5	1.7	0.6	2.4
TFA	1.3	1.3	0.18	1.1	<i>b</i>	4.2	1	1.4
Ionic Liquids								
STOR	<i>c</i>	<i>c</i>	0.47	3.7	<i>c</i>	<i>c</i>	<i>c</i>	3.1
Conventional Solvents								
DMAC	0.8	<i>c</i>	0.12	2.4	0.18	<i>c</i>	<i>c</i>	2
DMF	1.1	<i>c</i>	0.26	2.1	0.28	<i>c</i>	<i>c</i>	2.7
DMPU	1.8	<i>c</i>	0.5	2.7	0.18	<i>c</i>	<i>c</i>	2
DMSO	<i>c</i>	<i>c</i>	0.1	1.7	0.38	<i>c</i>	<i>c</i>	2.1
NMP	1.3	<i>c</i>	0.1	1.8	0.11	<i>c</i>	<i>c</i>	1.6
From Literature								
DMF <sup>22</sup>		0.16	0.23		2.3			4.00
DMSO <sup>39</sup>	1.2		7.6			1.5		2.9
glass <sup>21,37</sup>	1.20	5.60	1.60		3.50	4.00		1.60
doped glass <sup>76</sup>	3.8	4.00	2.50		1.50	1.60		1.70
polymer <sup>77</sup>		3.00						2.00

<sup>a</sup>The unit is ( $10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). The uncertainty in the coefficient is estimated to be  $\pm 10\%$  of the reported values. <sup>b</sup>Due to strong spectral changes, the results are not reliable. <sup>c</sup>Due to the low solubility (concentration  $<10^{-4} \text{ mol}\cdot\text{kg}^{-1}$ ), the results are not reliable.

For the spectroscopic determination of the saturation concentration we need a molar absorption coefficient. In those cases where we could not reliably derive its value from the concentration-dependent absorptivity due to low solubility, we derived a mean molar absorption coefficient. This mean coefficient is the averaged value of the molar coefficients of solutions of the same PC dissolved in other solvents (but of the same kind) with sufficiently high concentrations and with very similar spectra.

Only in the case of SnPC and NiPC we had to use mean molar absorption coefficients for conventional solvents that were derived from acidic solutions because there were no conventional solvents of sufficient solubility.

**Determination of the Concentration of the Saturated Solutions.** With the help of the molar absorption coefficients, the maximum (saturation) concentrations,  $c_{\text{max}}$ , were determined from the measured saturation intensities,  $A_{(\text{max})\lambda}$ , of the Q-bands, using eq 1.

If we could not determine a molar absorption coefficient for the individual PC solution we used a mean molar absorption coefficient that was derived as described above (further details on the mean coefficient can also be found in the discussion of the results on the individual saturation solution properties below). The detailed results on the maximum concentration of metal phthalocyanines,  $c_{\text{max}}$ , in different solvents are listed in Table 3. Before we discuss the results for the individual PC solutions in detail, here are first a few, more general remarks:

- Metal phthalocyanines dissolve quite well in SA, and the saturation concentration in SA is reported to be  $1 \text{ mol}\cdot\text{kg}^{-1}$ . We prepared and measured the spectra of metal phthalocyanine in SA, but we did not determine the saturation concentration. It is known that at high concentration the metal atom can be removed from the phthalocyanine molecules. This decomposition of metal phthalocyanine is time-, concentration-, and temperature-dependent.<sup>57–60</sup> SA solutions are not stable. Accordingly, here we do not present the spectra of phthalocyanines in SA.
- TFA and FA almost always alter the spectra of the phthalocyanines compared to those obtained by the conventional solvents. Ellis et al. suggest that TFA

protonates all four nitrogen atoms in the porphyrin section<sup>61</sup> and transforms it into a diacid. Studies of Ledson et al. show that in phthalocyanine just the outer bridge nitrogen atoms are protonated.<sup>50</sup> Ledson et al. discuss that the outer nitrogen may play a role and the molecule can be slightly deformed.<sup>50</sup> Through the protonation of the phthalocyanines new energy bands become active, and the absorption band shifts. Obviously the acidity of solvents affects the spectra, as can be seen also from the spectral modifications in the case of EMIM, the more acidic ionic solvent, compared to STOR; see the following measurements for ZnPC and MgPC.

- FA can be decomposed catalytically by phthalocyanines ( $\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}_2$ ). Hanke and Tanaka et al. studied the activation energy for the catalytical decomposition of FA in the presence of metal phthalocyanine and at different temperatures.<sup>55,62</sup> To minimize this reaction we used cold FA for our studies. Even cooling the solution was often not sufficient to avoid decomposition. In several cases no saturation concentration could be determined with FA as the solvent. The measured spectra are shown in the Supporting Information.
- We estimate that the main uncertainty in the maximum concentration results originates mainly from erroneous mean molar absorption coefficients. In addition we might not have reached the maximum equilibrium concentration due to the solubility kinetics or decomposition, and so forth. The uncertainty sources are mostly limited to the local condition of the measurement process. Based on this we conservatively assumed an uncertainty for our saturation concentrations of up to  $\pm 50\%$  of the presented values.

**Detailed Results on the Saturation Concentrations.** CoPC. CoPC dissolves with measurable amounts in many of the conventional solvents, in the acids, and also to some degree in the ionic liquids (see Figure 4). The typical Q-bands are relatively unaltered in the conventional solvents and in the ionic liquids. In the acids typical shifts and broadenings are observed. The spectrum of CoPC in TFA has the typical protonation band of CoPC near the Q-band.<sup>41</sup> The unpaired

Table 3. Maximum Concentration,  $c_{\max}^a$ 

solvent	CoPC	CuPC	FePC	MgPC	MnPC	NiPC	SnPC	ZnPC
Acids								
FA	$5.75 \cdot 10^{-6}$	<i>c</i>	$3.1 \cdot 10^{-5}$	$1.63 \cdot 10^{-3}$	<i>b</i>	$6.36 \cdot 10^{-4}$	$2.96 \cdot 10^{-5}$	$3.02 \cdot 10^{-1}$
PA	<i>b</i>	<i>c</i>	$1.73 \cdot 10^{-5}$	<i>b</i>	<i>b</i>	<i>c</i>	<i>c</i>	<i>c</i>
TFA	$8.63 \cdot 10^{-4}$	$2 \cdot 10^{-3}$	$2.94 \cdot 10^{-3}$	$5.52 \cdot 10^{-4}$	<i>b</i>	$3.2 \cdot 10^{-4}$	$7.43 \cdot 10^{-4}$	$2.19 \cdot 10^{-3}$
Ionic Liquids								
STOR	$1.91 \cdot 10^{-6}$	$4.71 \cdot 10^{-7}$	$3.61 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$	<i>c</i>	$1.25 \cdot 10^{-4}$	$2.02 \cdot 10^{-6}$	$9.19 \cdot 10^{-4}$
EMIM	$8.53 \cdot 10^{-7}$	<i>c</i>	$4.32 \cdot 10^{-4}$	$1.75 \cdot 10^{-4}$	$6.64 \cdot 10^{-3}$	<i>c</i>	<i>c</i>	$3.1 \cdot 10^{-5}$
Conventional Solvents								
acetone	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	$1.01 \cdot 10^{-4}$	<i>c</i>	<i>c</i>	<i>c</i>
ACN	$5.22 \cdot 10^{-7}$	<i>c</i>	$5.09 \cdot 10^{-6}$	$2.76 \cdot 10^{-4}$	$6.81 \cdot 10^{-6}$	<i>c</i>	<i>c</i>	$3.65 \cdot 10^{-6}$
anisole	$1.75 \cdot 10^{-6}$	$4.57 \cdot 10^{-7}$	$1.01 \cdot 10^{-5}$	$1.05 \cdot 10^{-4}$	$7.32 \cdot 10^{-4}$	$1.23 \cdot 10^{-6}$	$8.36 \cdot 10^{-6}$	$2.8 \cdot 10^{-6}$
benzene	<i>c</i>	$2.61 \cdot 10^{-7}$	<i>b</i>	$3.91 \cdot 10^{-6}$	$6.85 \cdot 10^{-5}$	<i>c</i>	$4.86 \cdot 10^{-7}$	<i>c</i>
CBZ	$1.14 \cdot 10^{-7}$	$3.74 \cdot 10^{-7}$	$1.56 \cdot 10^{-5}$		$6.39 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$1.41 \cdot 10^{-5}$	<i>c</i>
TCM	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>	$2.26 \cdot 10^{-5}$	<i>c</i>
decanol	<i>c</i>	<i>c</i>	$2.68 \cdot 10^{-5}$	$1.9 \cdot 10^{-4}$	$1.32 \cdot 10^{-4}$	<i>c</i>	<i>c</i>	$5.33 \cdot 10^{-5}$
DCM	<i>c</i>	<i>c</i>	$5.95 \cdot 10^{-6}$	$1.32 \cdot 10^{-5}$	$6.28 \cdot 10^{-3}$	$4.31 \cdot 10^{-4}$	$2.57 \cdot 10^{-5}$	<i>c</i>
dioxane	$3.92 \cdot 10^{-5}$	$4.42 \cdot 10^{-7}$	$4.76 \cdot 10^{-6}$	$5.63 \cdot 10^{-4}$	$2.47 \cdot 10^{-3}$	<i>c</i>	$2.05 \cdot 10^{-6}$	$1.27 \cdot 10^{-4}$
DMAC	$4.03 \cdot 10^{-5}$	<i>c</i>	$3.21 \cdot 10^{-4}$	$3.12 \cdot 10^{-4}$	$7.47 \cdot 10^{-3}$	<i>c</i>	$7.53 \cdot 10^{-6}$	$9.96 \cdot 10^{-4}$
DMF	$2.06 \cdot 10^{-4}$	<i>c</i>	$2.71 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$8.24 \cdot 10^{-3}$	<i>c</i>	$8.73 \cdot 10^{-6}$	<i>c</i>
DMPU	$6.47 \cdot 10^{-4}$	$3.75 \cdot 10^{-6}$	$6.05 \cdot 10^{-4}$	$7.35 \cdot 10^{-4}$	$5.99 \cdot 10^{-3}$	$7.26 \cdot 10^{-4}$	$1.27 \cdot 10^{-6}$	$5.59 \cdot 10^{-3}$
DMSO	$3.32 \cdot 10^{-5}$	<i>c</i>	$1.94 \cdot 10^{-4}$	$2.63 \cdot 10^{-4}$	$1.97 \cdot 10^{-3}$	<i>c</i>	$5.6 \cdot 10^{-6}$	$5.58 \cdot 10^{-4}$
EtOH	$3.46 \cdot 10^{-7}$	<i>c</i>	$1.01 \cdot 10^{-5}$	$4.29 \cdot 10^{-5}$	$1.92 \cdot 10^{-3}$	<i>c</i>	<i>c</i>	$2.38 \cdot 10^{-6}$
EtOAc	<i>c</i>	<i>c</i>	<i>c</i>	$2.38 \cdot 10^{-5}$	$2.99 \cdot 10^{-5}$	<i>c</i>	<i>c</i>	<i>c</i>
IPA	<i>c</i>	<i>c</i>	<i>c</i>	$7.67 \cdot 10^{-6}$	$1.43 \cdot 10^{-4}$	<i>c</i>	<i>c</i>	$1.53 \cdot 10^{-6}$
MeOH	$1.33 \cdot 10^{-7}$	<i>c</i>	$1.05 \cdot 10^{-5}$	$7.48 \cdot 10^{-7}$	$1.84 \cdot 10^{-3}$	<i>c</i>	$2.38 \cdot 10^{-7}$	$1.23 \cdot 10^{-6}$
NMP	<i>b</i>	$5.36 \cdot 10^{-7}$	$2.85 \cdot 10^{-4}$	$5.48 \cdot 10^{-3}$	$3.45 \cdot 10^{-4}$	<i>c</i>	$5.15 \cdot 10^{-7}$	$6.92 \cdot 10^{-3}$
THF	$9.87 \cdot 10^{-5}$	$9.1 \cdot 10^{-6}$	$1.25 \cdot 10^{-5}$	$6.48 \cdot 10^{-3}$	$6.62 \cdot 10^{-3}$	$1.43 \cdot 10^{-6}$	$2.9 \cdot 10^{-6}$	$7.97 \cdot 10^{-4}$
toluene	$8.3 \cdot 10^{-8}$	$3.25 \cdot 10^{-7}$	$7.15 \cdot 10^{-7}$	$2.75 \cdot 10^{-6}$	$6.03 \cdot 10^{-5}$	$5.63 \cdot 10^{-7}$	$1 \cdot 10^{-6}$	<i>c</i>

<sup>a</sup>The unit is molality ( $\text{mol} \cdot \text{kg}^{-1}$ ). The uncertainty in the amount of MPC maximum concentration is estimated to be  $\pm 50\%$  of the reported values. <sup>b</sup>Due to strong spectral changes, the results are not reliable. <sup>c</sup>Due to the low solubility (concentration  $< 10^{-8} \text{ mol} \cdot \text{kg}^{-1}$ ) and low absorption ( $< 0.05$ ), the results are not reliable.

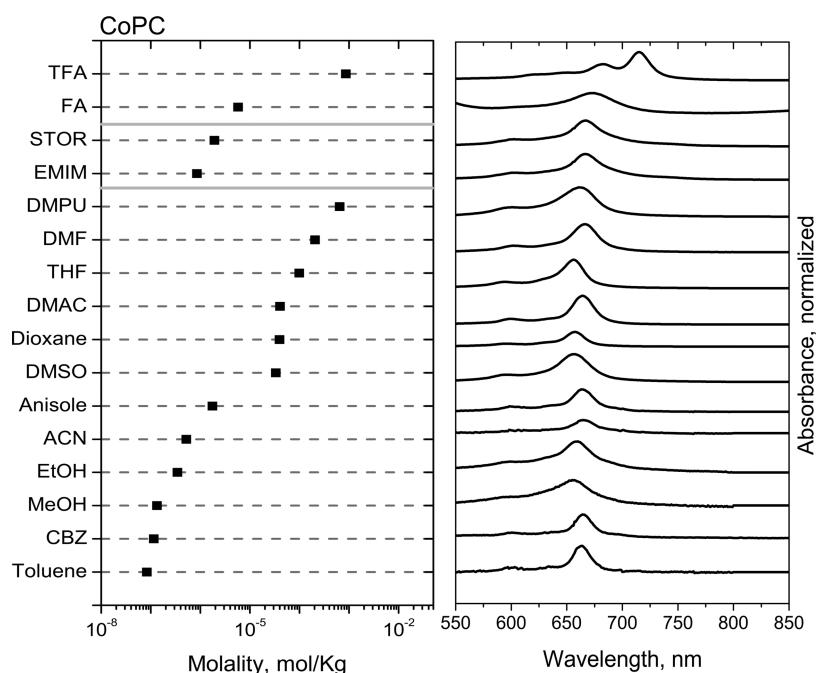
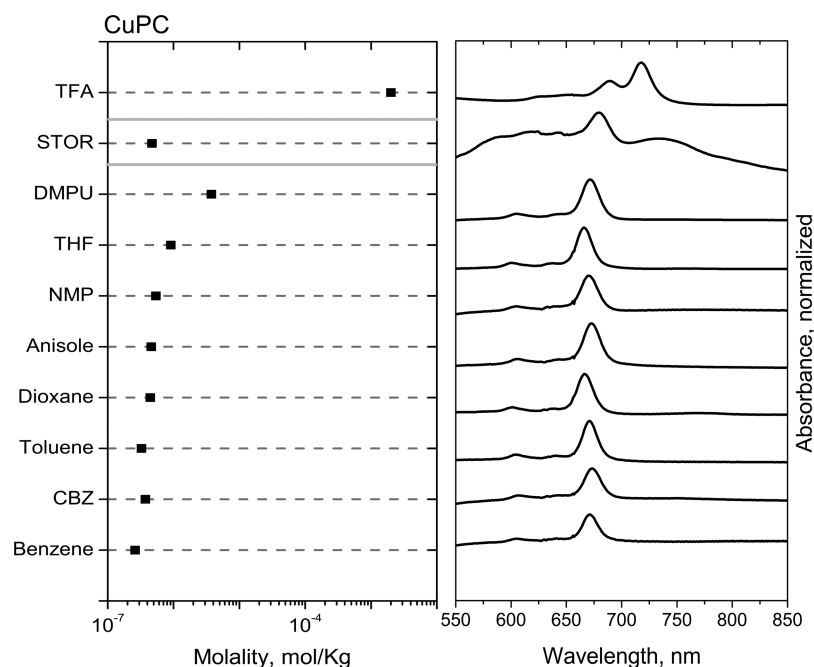


Figure 4. Maximum concentration of CoPC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

electron of the Cobalt in phthalocyanine can interact with solvents and also oxygen.<sup>63,64</sup> This results in shifts of the absorption bands.

The molar absorption could not be measured accurately in the ionic liquids and also in many conventional solvents due to low solubility. The estimation of the concentration in these



**Figure 5.** Maximum concentration of CuPC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

cases is based on a mean value of the measured molar absorption coefficients ( $(1.3 \pm 0.7) \cdot 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) in those solvents with higher solubility and similar spectra.

CoPC solutions are not long-term (days) stable. Solution preparations and measurements should be done within less than a few hours.

**CuPC.** CuPC is hardly soluble in any of the tested solvents (Figure 5). The spectra of CuPC dissolved in conventional solvents show the typical, “normal” Q-band. CuPC only dissolves in one of the ionic liquids, STOR, albeit with a very low concentration and with a somewhat distorted spectrum. CuPC dissolves with high concentrations only in TFA where it becomes protonated and new bands appear in the absorption spectrum.<sup>65,66</sup>

Due to the low solubility (less than  $10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ ), the molar absorption coefficients of CuPC in conventional solvents and the ionic liquid could not be measured individually. For estimating the concentrations we used the molar absorption coefficient ( $(1.4 \pm 0.7) \cdot 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) derived from TFA solutions. CuPC is quite stable (weeks) in the solutions.

**FePC.** FePC dissolves at reasonable concentrations in many of the solvents. However, many spectra, including even those from some conventional solvents show shifts, broadening, and splittings (Figure 6). The low saturation concentrations ( $<10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ ) are derived with a mean molar absorption coefficient ( $(2.7 \pm 1.4) \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ).

FePC solutions are not very stable (less than 4 h). Unlike in the case of most other PCs, the metal center of FePC can be oxidized easily in interaction with the solvents.<sup>41</sup> A broadening/change of the absorption band due to oxidation can be seen for most solutions.<sup>30,41,67–69</sup> According to Minor et al. with increasing the oxidation of the central metal the Q-band changes, and different species of FePC can be produced in the solution.<sup>40</sup> The instability of FePC can be seen easily by visual observation as pronounced color changes within several hours in conventional solvents. With TFA it occurs within less than one hour. This effect is time- and temperature-dependent.

There is also a dimerization effect of FePC at high concentrations in solvents like NMP, DMF, and DMSO. It results in a shift and broadening of the absorption band. In NMP and DMF the interaction of the nearly parallel phthalocyanine rings in the dimers causes the splitting of the monomer transition and the generation of new transitions.<sup>48</sup>

**MgPC.** MgPC is the most soluble phthalocyanine which we studied (Figure 7). Most of the conventional solutions have a regular Q-band at 670 nm. With the ionic liquid EMIM the absorption bands are red-shifted and split. These shifts and spectra modifications are even more pronounced for the acidic solutions due to the protonation of MgPC and symmetry changes of the molecule.<sup>39,46,67,70</sup>

MgPC dissolves in FA in rather high concentrations (more than  $10^{-3} \text{ mol} \cdot \text{kg}^{-1}$ ), producing a dark blue liquid. The broadened absorption band is a sign of activation of several transitions near Q-band. FA decomposes in the presence of MgPC.<sup>55,71</sup> Therefore the maximum concentration value presented is not very accurate.

For the low solubility samples we used a mean molar absorption coefficient ( $(2.1 \pm 1.6) \cdot 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) based on an average of the conventional solution data with sufficiently high solubility.

The solutions of MgPC are stable for a week (except for the FA solution).

**MnPC.** MnPC shows comparatively high solubilities in many conventional solvents and one of the ionic liquids (EMIM) (Figure 8). The Q-bands are usually regular, except for NMP and DMPU solutions.

MnPC is (as FePC and CoPC) well-known for its charge transfer between the metal and the phthalocyanine ring.<sup>72</sup> In interaction with the solvent the central metal can oxidize from Mn(II) to Mn(III).<sup>73,74</sup> The different coordinations of the solvent molecules on phthalocyanine causes changes in the spectra.<sup>73</sup> We could not produce stable solutions in acids and measure their spectra. For poor solvents, the maximum concentration is estimated with a mean molar absorption coefficient of  $(2.7 \pm 1.4) \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ .

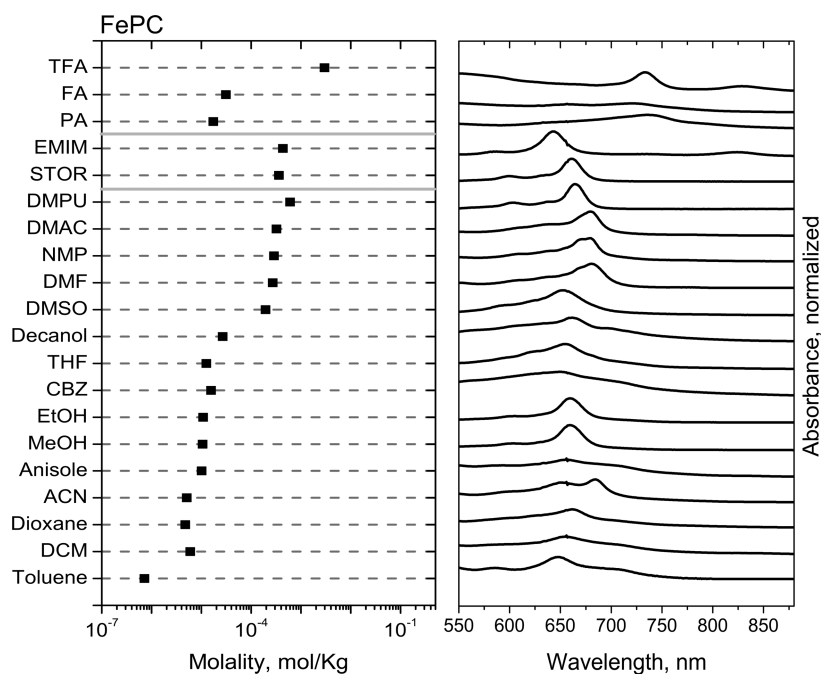


Figure 6. Maximum concentration of FePC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

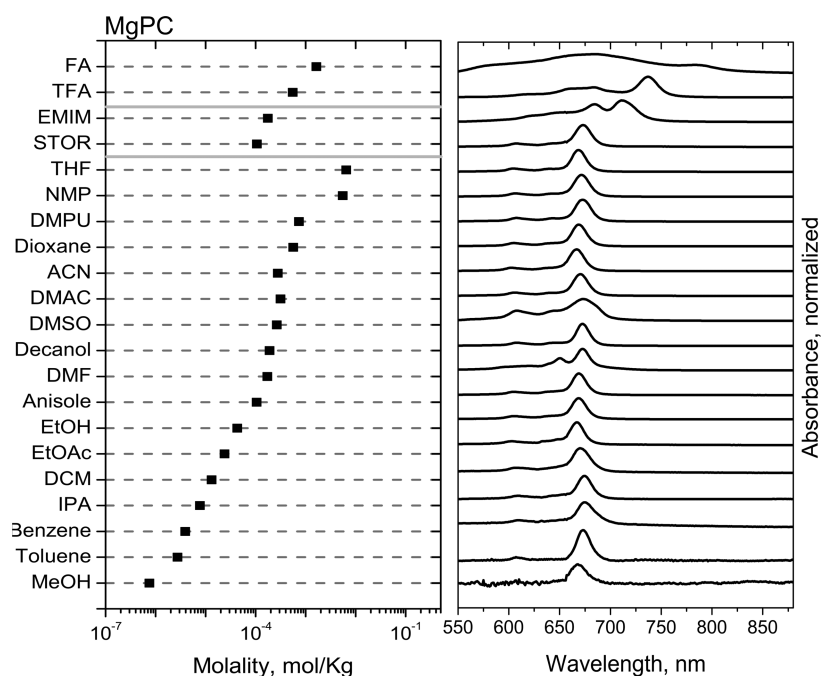


Figure 7. Maximum concentration of MgPC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

MnPC solutions are not very stable and have to be prepared and measured within less than 4 h.

**NiPC.** NiPC has a solubility below a reasonable spectroscopic quantification limit in most of our solvents. As Figure 9 shows, the Q-band is typically split into two bands. Supposedly this originates from a lowered symmetry of the molecule resulting in nondegenerate electronic states.<sup>49</sup> For estimating the concentration, we assumed that the most intensive absorption band has the “normal” oscillation strength of the symmetrical phthalocyanines with degenerated LUMO ( $e_g$ ) and thus single Q-bands.<sup>53</sup> We used a mean value of molar absorption coefficient of  $(3 \pm 1.5) \cdot 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ , derived from the

spectra of solutions of TFA and SA (Supporting Information) which had a sufficiently high solubility to quantify a molar absorption coefficient. NiPC solutions are stable for more than one day.

**SnPC.** SnPC has also rather low solubilities in our selection of solvents (Figure 10). The Q-bands in all conventional solvents are quite regular. In acids the spectra are shifted in comparison with conventional solvents. Edwards and Gouterma reported that strong acidic solvent like TFA cause a dimerization or exciton coupling between SnPC rings.<sup>53</sup>

Due to the low solubility in conventional solvents, the molar absorption coefficient could not be measured individually for

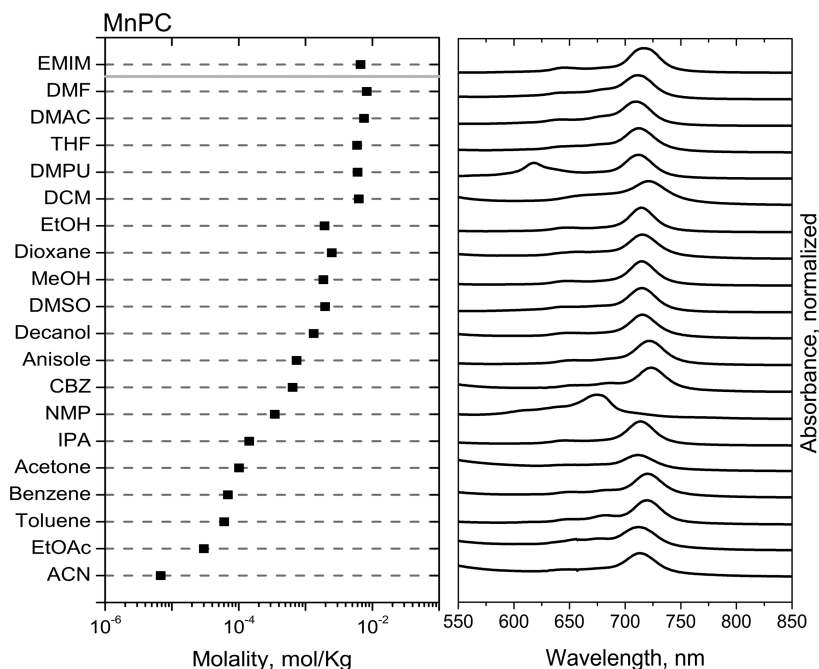


Figure 8. Maximum concentration of MnPC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

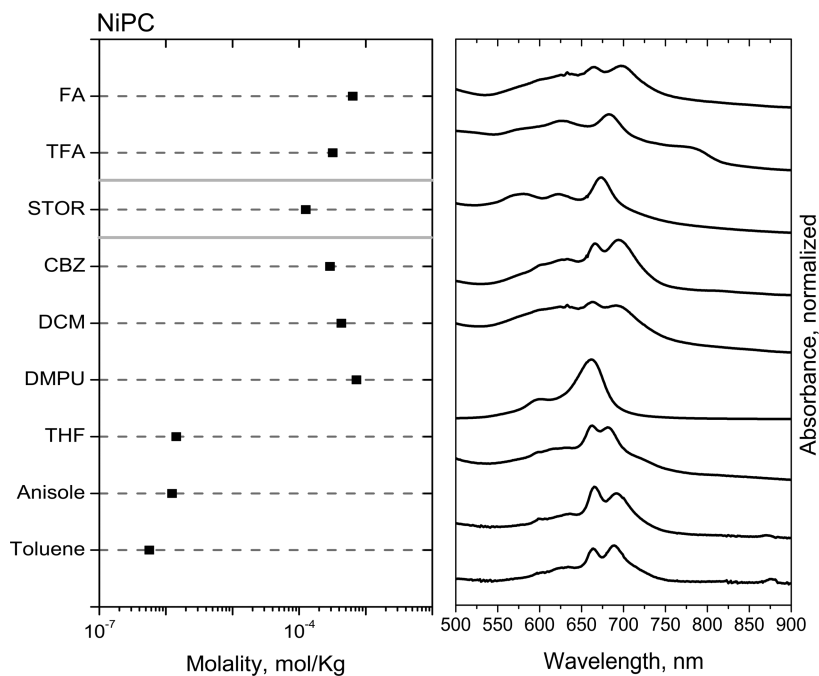


Figure 9. Maximum concentration of NiPC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

most of the solvents. For the conventional solvents we could just estimate the molar absorption coefficient in DCM (roughly  $4 \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). To estimate the saturation solubility for the various solvents we used a mean absorption coefficient ( $(7 \pm 4) \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ) derived from DCM, SA, and TFA solutions.

SnPC solutions are stable for more than one day.

**ZnPC.** ZnPC is comparatively soluble in many solvents (many types of solvents, Figure 11). In conventional solvents typical, regular Q-bands appear. In acidic solutions the Q-band shifts and broadens, and new absorption bands appear.

The band broadening is similar to MgPC and other phthalocyanines in acidic solutions. Hanke et al. show that the activation energy for the decomposition of FA in the presence of ZnPC is slightly higher than for FePC, CuPC, NiPC, and CoPC, respectively.<sup>62,75</sup> On the solubility Nyokong et al. suggest that in a first charge transfer interaction with the solution the electron is centered on the phthalocyanine ring rather than on the zinc atom.<sup>31,41</sup>

For the poor solvents the saturation concentration was estimated with a mean molar absorption coefficient of  $(2.2 \pm 1.1) \cdot 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ .

ZnPC solutions (including FA) are quite stable (weeks).



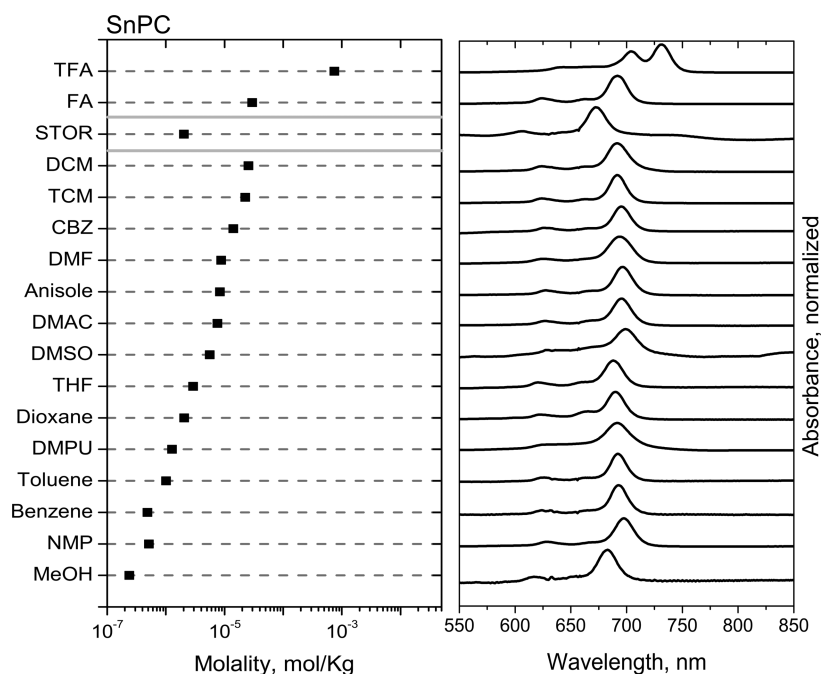


Figure 10. Maximum concentration of SnPC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

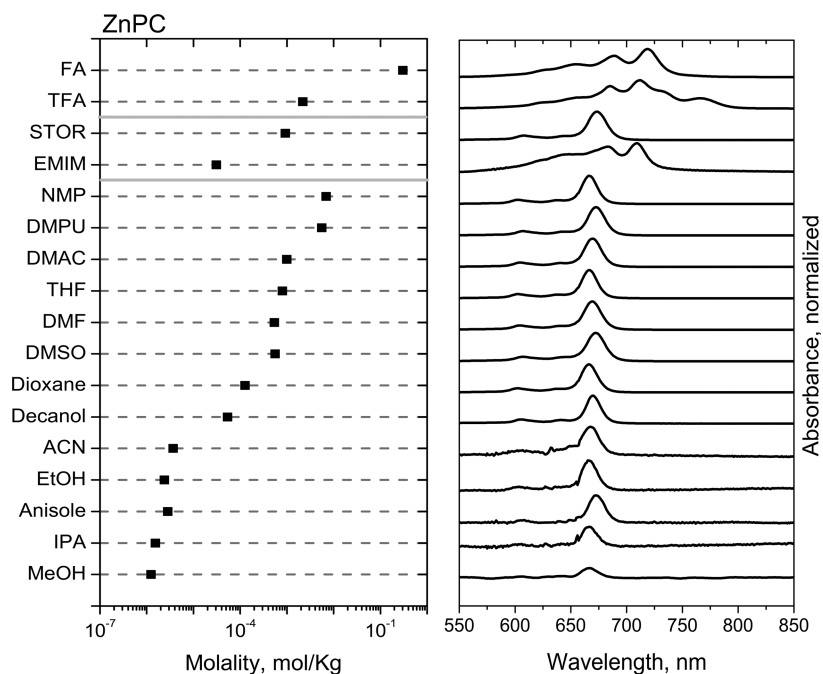


Figure 11. Maximum concentration of ZnPC in different solutions (left) and their corresponding normalized Q-band absorption spectra (right).

## CONCLUSION

We studied quantitatively the solubility and spectral solution properties of the unsubstituted metal phthalocyanines CoPC, CuPC, FePC, MgPC, MnPC, NiPC, SnPC, and ZnPC in different conventional solvents, ionic liquids, and acids. For each metal phthalocyanine solution the molar absorption coefficient was measured (above  $10^{-4}$  mol·kg<sup>-1</sup>) or at least estimated (for the low solubility cases), based on the absorption intensity of the Q-band. We also determined the saturation concentration for quite a number of solvents, including “conventional” solvents (e.g., toluene, DMSO, etc.), ionic liquids, and acids (in particular TFA). The spectra of the solutions are presented. Solvent-induced

spectral alterations are discussed, in particular in view of the chemical stability of the solutions. We find that MgPC and ZnPC have the highest solubility and their solutions are stable in ambient atmosphere for weeks. FePC, MnPC, and CoPC can be dissolved with considerable concentrations, but their solutions are less stable and alter within hours up to one day. This can be seen from the broadening and shift of the Q bands. CuPC, NiPC, and SnPC are little soluble in most of the tested solvents and the molar absorption coefficients and saturation concentrations could only be estimated (except for TFA, where the solubility is rather high). CuPC, NiPC, and NiPC solutions are rather stable (more than one day) in ambient conditions.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

UV–vis spectra of metal phthalocyanine dissolved in FA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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