Near-Infrared Absorbing Ligand-Oxidized Dinuclear Phthalocyanines

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Abstract: Ligand-oxidized annulated dinuclear phthalocyanine zinc(II) and lithium(I) complexes absorbing in the NIR region ($\lambda = 1000$–2200 nm) with high extinction coefficients are described. Analogous mononuclear Pc complexes were used for comparison. The oxidized Pcs were characterized in solution by electronic absorption, EPR and NMR spectra. The NIR transitions were explained by using MO diagrams calculated semiempirically. The reversible oxidation behavior of the phthalocyanine complexes was also estimated by cyclic voltammetry. These new extremely long wavelength absorbing phthalocyanines are interesting as materials with new electronic properties.

Keywords: cyclic voltammetry · EPR spcetroscopy · oxidation · phthalocyanines

Introduction

The redox properties of phthalocyanine (Pc) complexes are a subject of considerable interest[1,2] due to their importance for redox catalysis/electrocatalysis,[3] enzymatic redox catalysis modelling[4] and electrochromism.[5] The chemical, electrochemical and photochemical oxidation of phthalocyanines producing radical cations was well studied.[2] As chemical oxidants, halogens, nitric acid, metals in high oxidation states were employed. If the central metal atom is not redox-active, the electron is removed from the Pc ring. This results in significant changes of the UV/Vis absorption spectra.[2] These spectra were analyzed by using spectral deconvolution technique and MO calculations. Since these species are paramagnetic, they were also studied by electron paramagnetic resonance (EPR) spectroscopy.

The formal charge on the ligand in normal Pc complexes is -2, accordingly, they are named Pc(-2).[2] Thus, neutral Pc(-2)M^{II} complexes upon one-electron ring oxidation give [Pc(-1)M^{II}]$^{+\cdot}$ radical cations. Interesting examples of ring-oxidized Pcs are neutral Pc(-1)Li^{I} and Pc(-1)Lu^{III}Pc(-2).[6] Especially Pc(-1) complexes were extensively studied since some of them are molecular metals (partially oxidized salts) and intrinsic semiconductors (neutral complexes).[6,7] Pc$_2$Lu and aggregates of PcLi—not the monomers—in solution have NIR absorption bands at ≈ 1300 and ≈ 950 nm, respectively. These bands are of general charge resonance nature and are typical for radical dimers and mixed valence systems.[8,9] Conducting mixed-valence Pcs absorb the IR light polarized along the highly conducting stacking axis which is typical for 1D conductors.[7] In all these examples phthalocyanine π-systems are stacked "face-to-face" (without covalent connection). Another type of strong interaction between Pc π systems is realized in ligand-bridged, conjugated Pc dimers,[10] which can be considered as models of conjugated Pc polymers expected to be intrinsic conductors.[10a] Such dinuclear Pcs first prepared by Simon et al.[10b] have attracted considerable attention in the recent years.[10] Their ring-oxidized forms should have interesting electronic properties which can be studied by UV/Vis/NIR spectroscopy.

In this work, we describe the preparation of substituted ring-oxidized annulated dinuclear Pc zinc(II) and lithium(I) complexes having intense absorptions in the NIR with high extinction coefficients by chemical oxidation of the corresponding phthalocyanine complexes. Analogous mononuclear Pcs were used for comparison. The oxidized Pcs were characterized in solution by electronic absorption, EPR and NMR spectra; the NIR transitions were explained using orbital diagrams. The reversible oxidation/reduction behavior

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of the phthalocyanine complexes is also examined by cyclic voltammetry.

Results and Discussion

For the mononuclear and annulated dinuclear phthalocyanines Zn^{II} and Li^{I} were selected as non-redox-active central metal ion. In order to study properties of monomolecular dissolved phthalocyanines in organic solvents, bulky 2,6-dimethylphenoxy groups were chosen as substituents at the Pcs to prevent possible aggregation[10h] because oxidized Pc(−1) complexes show tendency towards aggregation.[2, 6a,c−e]

The first compound studied for ligand oxidation was the stepwise oxidation of the dinuclear Zn_2**2** with bromine in chlorobenzene solution compared with the mononuclear **Zn1**. The mononuclear **Zn1** and dinuclear Zn_2**2** zinc phthalocyanine complexes were synthesized by usual metalation

M**1** (M= Zn, Li)

R =

M_2**2** (M= Zn, Li)
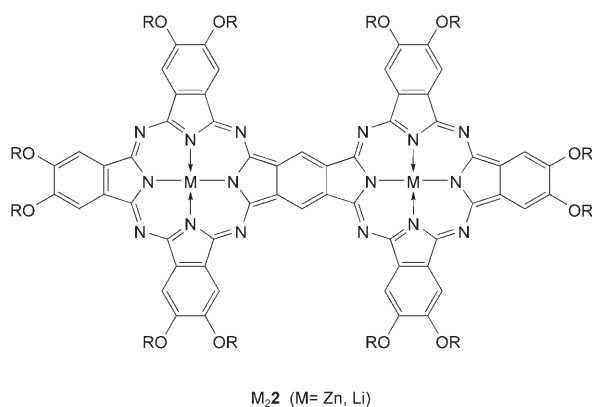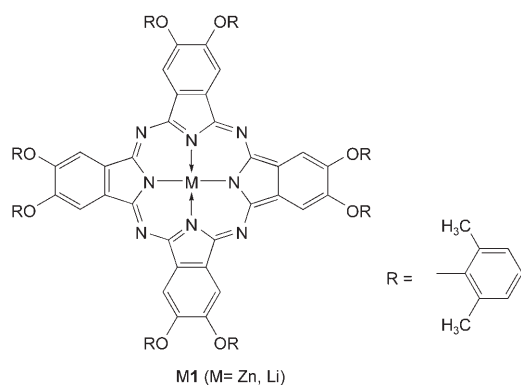
of the corresponding metal-free phthalocyanines.[10h] The UV/Vis spectral changes for **Zn1** by addition of bromine are shown in Figure 1. The addition of one equivalent of Br_2 gives spectrum typical for non-aggregated ring-oxidized species of Pc(−1) type.[2,6] Some excess of Br_2 is needed to complete the oxidation (disappearance of the Q band at $\lambda = 674$ nm) and the formation of [**Zn1**]$^{+\cdot}$. The mononuclear
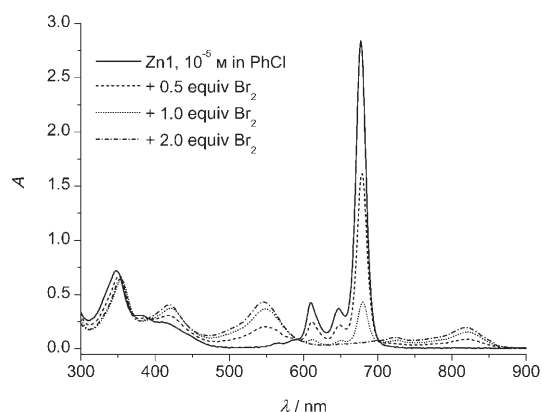

Figure 1. Spectral changes during oxidation of **Zn1** with Br_2.

[**Zn1**]$^{+\cdot}$ is characterized by a weak Q band at $\lambda = 818$ nm ($\varepsilon \approx 2.0 \times 10^4 \, M^{-1} \, cm^{-1}$) and a series of stronger bands at 546 ($\varepsilon \approx 4.3 \times 10^4 \, M^{-1} \, cm^{-1}$), 420 ($\varepsilon \approx 4.1 \times 10^4 \, M^{-1} \, cm^{-1}$), 353 nm ($\varepsilon \approx 6.4 \times 10^4 \, M^{-1} \, cm^{-1}$). No NIR absorptions at $\lambda > 850$ nm were observed. The oxidation of dinuclear Zn_2**2** with bromine in chlorobenzene results in more complex spectral changes (Figure 2). Addition of the first 0.5 equivalent of Br_2 leads to a decrease of the intensity of the Q band at $\lambda = 848$ nm of Zn_2**2**, and a new band at $\lambda = 1057$ nm appears, which increases upon addition of further 0.5 equiv Br_2. Then the absorption at $\lambda = 1057$ nm ($\varepsilon \approx 1.0 \times 10^5 \, M^{-1} \, cm^{-1}$) decreases to zero upon addition of a further equivalents of Br_2. A new intense absorption band appears at $\lambda = 1195$ nm. As in the case of **Zn1**, some excess of Br_2 is needed to reach the maximal intensity at $\lambda = 1203$ nm ($\varepsilon \approx 1.3 \times 10^5 \, M^{-1} \, cm^{-1}$) which remains constant by further addition of bromine. This behavior clearly demonstrates a two-step oxidation process. The band at $\lambda = 1057$ nm can be assigned to the radical-cation [Zn_2**2**]$^{+\cdot}$ of Pc(−1)−Pc(−2) type and the band at $\lambda = 1203$ nm to the dication [Zn_2**2**]$^{2+}$ of Pc(−1)−Pc(−1) type. All spectral changes are essentially immediate. The oxidation process can be reversed by reduction with hydroquinone in pyridine in the presence of a small amount of ferro-
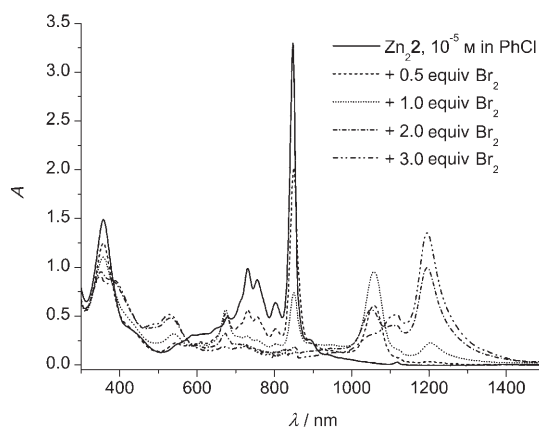

Figure 2. Spectral changes during oxidation of Zn_2**2** with Br_2.

cene.[11a] The initial Q band is immediately recovered with >90% efficiency.[11b]

NIR absorption spectra at $\lambda > 1400$ nm for $[Zn_2\mathbf{2}]^{+\cdot}$ and $[Zn_2\mathbf{2}]^{2+}$ prepared by oxidation of $Zn_2\mathbf{2}$ with <1 equiv or an excess of Br_2, respectively, were also measured in 1 cm KBr cuvette on a FT-IR spectrometer using concentrations of $\approx 10^{-4}$ M of the Pcs in chlorobenzene. For $[Zn_2\mathbf{2}]^{+\cdot}$ a broad band at $\lambda = 2220$ nm (4550 cm^{-1}; $\varepsilon \approx 1.6 \times 10^4$ M^{-1}cm^{-1}) is observed. $Zn_2\mathbf{2}$ does not absorb in this region, and $[Zn_2\mathbf{2}]^{2+}$ shows only the tail of the band at 1203 nm (see Figures S1 and S2, Supporting Information). Similar NIR absorption bands ($\lambda \approx 1050$ and ≈ 2200 nm for $[Zn_2\mathbf{2}]^{+\cdot}$, and $\lambda \approx 1200$ nm for $[Zn_2\mathbf{2}]^{2+}$) are observed in other solvents such as benzene, toluene, chloroform or carbon tetrachloride after addition of either a small amount (< 1 equiv) or an excess of bromine, respectively.

The second compound investigated for ligand oxidation was a substituted binuclear phthalocyanine lithium complex. It is known that Pc(−1)Li complexes were obtained by chemical or electrochemical oxidation of PcLi$_2$.[6] In this work the oxidized dinuclear substituted dilithium complex Li$_2\mathbf{2}$ of the Pc(−1)−Pc(−1) type was prepared, as shown in Equation (1), from the metal-free dinuclear Pc (H$_4\mathbf{2}$),[10h] by metalation with lithium methoxide followed by chemical oxidation with 5,6-dichloro-2,3-dicyano-p-benzoquinone (DDQ). Analogously the mononuclear lithium Pc(−1) complex Li$\mathbf{1}$ was obtained in the same way for comparison [Eq. (2)]. Both Li complexes are stable compounds and well-soluble in aromatic or halogenated hydrocarbon solvents.

$$H_4\mathbf{2} \xrightarrow{\text{LiOMe}} Li_4\mathbf{2} \xrightarrow{\text{DDQ}} Li_2\mathbf{2} \qquad (1)$$

$$H_2\mathbf{1} \xrightarrow{\text{LiOMe}} Li_2\mathbf{1} \xrightarrow{\text{DDQ}} Li\mathbf{1} \qquad (2)$$

The UV/Vis/NIR spectra of the ligand oxidized complexes Li$\mathbf{1}$ and Li$_2\mathbf{2}$ in chlorobenzene are shown in Figure 3. The spectrum of Li$\mathbf{1}$ contains similar bands as reported for non-aggregated LiPc(−1) (weak Q band at $\lambda = 800$ nm with $\varepsilon = 1.3 \times 10^4$ M^{-1}cm^{-1} and intense B bands at $\lambda = 517$ nm ($\varepsilon = 5.2 \times 10^4$ M^{-1}cm^{-1}), 400 ($\varepsilon = 3.5 \times 10^4$ M^{-1}cm^{-1}), 345 nm ($\varepsilon = 7.8 \times 10^4$ M^{-1}cm^{-1}).[2a,6e] The spectrum of Li$_2\mathbf{2}$ shows an intense NIR band at $\lambda = 1151$ nm ($\varepsilon = 9.5 \times 10^5$ M^{-1}cm^{-1} and is quite similar to the spectrum of $[Zn_2\mathbf{2}]^{2+}$ obtained after oxidation of $Zn_2\mathbf{2}$ with an excess of Br_2 (Figure 2). The spectra of Li$\mathbf{1}$ and Li$_2\mathbf{2}$ contain patterns of corresponding metal-free phthalocyanines at $\lambda = 703$ and 852 nm, respectively, as unavoidable impurities (The same was pointed out for unsubstituted LiPc(−1)[6b]). In the IR spectra (taken in KBr) of Li$\mathbf{1}$ and Li$_2\mathbf{2}$ no bands of H$_2\mathbf{1}$ and H$_4\mathbf{2}$ at 3296 cm^{-1} (N-H) are observed which means that these impurities are rather small (but with high UV/Vis extinction coefficients). Both Li$\mathbf{1}$ and Li$_2\mathbf{2}$ show corresponding molecular ion peaks in their mass spectra (electrospray ionization, negative ion mode). In the case of Li$_2\mathbf{2}$ singly and doubly charged ions are seen. No peaks of corresponding metal-free phthalocyanines are observed due to low contents and higher method

sensitivity to Li$\mathbf{1}$ and Li$_2\mathbf{2}$, which easily give ions upon reduction. Both Li$\mathbf{1}$ and Li$_2\mathbf{2}$ undergo immediate reductive demetalation upon addition of a drop of hydroquinone in methanol to their chlorobenzene solutions and formation of H$_2\mathbf{1}$ and H$_4\mathbf{2}$, respectively. The yield calculated for the reduction of Li$_2\mathbf{2}$ from H$_4\mathbf{2}$ Q-band intensity (not influenced by hydroquinone/methanol) was >90%.

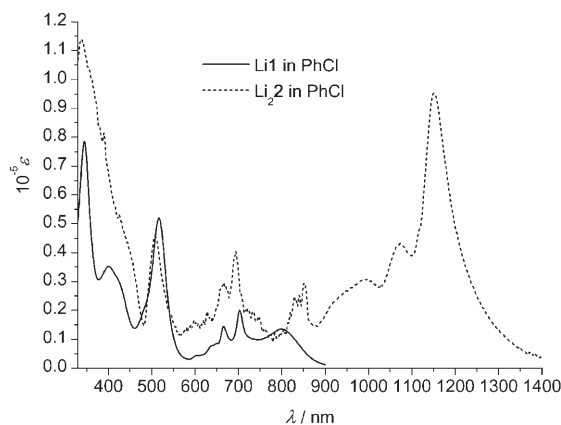Figure 3. UV/Vis/NIR spectra of Li$\mathbf{1}$ and Li$_2\mathbf{2}$ in chlorobenzene.

NIR absorption bands in the spectra of Li$_2\mathbf{2}$, $[Zn_2\mathbf{2}]^{+\cdot}$ and $[Zn_2\mathbf{2}]^{2+}$ not present in mononuclear Pc(−1) complexes are observed for the first time for linked and annulated Pcs. For a planar Pc dimer with other substituents spectroelectrochemically studied no NIR absorptions were described.[10c] However, NIR absorptions are also present in the spectra of structurally different sandwich-type lanthanide bisphthalocyanines such as Pc$_2$Lu (or Pc(−1)LuPc(−2), with absorptions at λ(lgε) = 1370 (4.1), 1250 (4.0), 900 (3.8), 655 (5.2), 460 nm (4.6) for hexadecaalkoxy-substituted derivatives;[6b] absorptions of same-substituted $[Pc(-1)LuPc(-1)]^+BF_4^-$ at λ(lgε) = 940 (4.3), 695 (4.6), 630 (4.2), 495 nm (4.7))[6a,b,d,f,g] and aggregated (not monomolecular) Pc(−1)Li ($\lambda \approx 940$ nm, $\varepsilon \approx 10^4$).[6a,c,e]

The absorptions of the oxidized annulated binuclear Pcs investigated in this work can be explained by a molecular orbital model considering low-energy transitions between split levels (intermacrocyclic charge transfer/charge resonance).[8,9] In the porphyrin family, for a *meso–meso* butadiyne-bridged Zn triarylporphyrin dimer different oxidation states were implied by voltammetry and examined in situ from the UV to the mid-IR region. The radical anion and -cation of the porphyrin dimer show NIR-IR absorptions at $\lambda \approx 1000$ nm ($\varepsilon \approx 8 \times 10^4$ M^{-1}cm^{-1}) and ≈ 2500 nm ($\varepsilon \approx 4 \times 10^4$ M^{-1}cm^{-1}); the dianion absorbs at $\lambda \approx 1150$ nm ($\varepsilon \approx 5 \times 10^4$ M^{-1}cm^{-1}).[12a] The absorptions were explained by a simple orbital model and later calculated using time-dependent density functional theory (TDDFT).[12b] These spectra are very similar to the absorptions observed in this work for $[Zn_2\mathbf{2}]^{+\cdot}$ ($\lambda = 1057$ nm, $\varepsilon \approx 1.0 \times 10^5$ M^{-1}cm^{-1}; 2220 nm, $\varepsilon \approx 1.6 \times 10^4$ M^{-1}cm^{-1}) and $[Zn_2\mathbf{2}]^{2+}$ ($\lambda = 1203$ nm, $\varepsilon \approx 1.3 \times 10^5$ M^{-1}cm^{-1}), respectively. The explanation is analogous to

those used for LuPc$_2$[6f] and porphyrin dimer above-mentioned.[12] A partial orbital diagram (ZINDO/s RHF method for the unsubstituted analogue of Zn$_2$**2**) is shown in Figure 4. The absorption at $\lambda = 848$ nm in the spectrum of
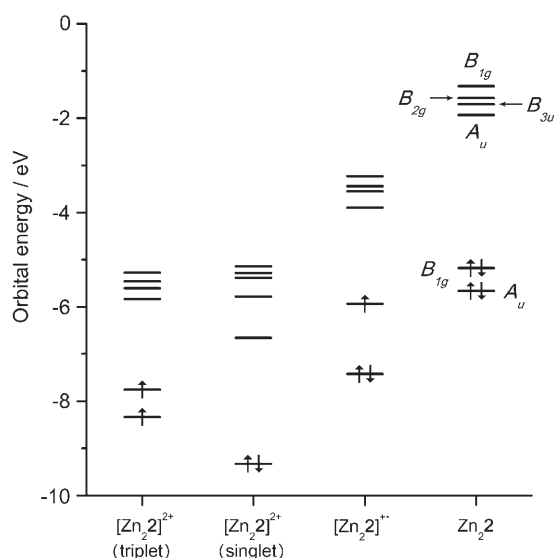

Figure 4. Partial orbital diagrams for unsubstituted analogues of Zn$_2$**2** and its cations.

Zn$_2$**2** is the transition from HOMO (B$_{1g}$) to LUMO (A$_u$).[10c] If one or two electrons are removed, the levels are shifted as shown in Figure 4. For [Zn$_2$**2**]$^{+\cdot}$, two longest-wavelength transitions are possible: intervalence from A$_u$ to semi-occupied B$_{1g}$ which can be assigned to the band at $\lambda = 2220$ nm, and from B$_{1g}$ to A$_u$ LUMO (analogous transition at $\lambda \approx 900$ nm for LuPc$_2$ is named "red vibronic")[6f] which explains the band at $\lambda = 1157$ nm. For [Zn$_2$**2**]$^{2+}$ in the case of singlet ground state, the long-wavelength transition is possible from A$_u$ HOMO to B$_{1g}$ LUMO, for triplet ground state: from B$_{1g}$ SOMO to A$_u$ LUMO. Both possibilities can explain the band at $\lambda = 1203$ nm (see discussion of EPR spectra below).

EPR and NMR spectra: Three of the Pc(−1) derivatives described here must be paramagnetic: [Zn**1**]$^{+\cdot}$, [Zn$_2$**2**]$^{+\cdot}$ and Li**1**. [Zn$_2$**2**]$^{2+}$ and Li$_2$**2** can be considered as a kind of Pc(−1) radical dimers. From other point of view, a classical double bond structure can be drawn for them. But it is not clear a priori whether they have singlet or triplet ground state. All these species were studied by EPR in toluene solutions. Zn**1** and Zn**2** were oxidized with Br$_2$ to generate

Table 1. EPR data for paramagnetic Pc(−1) complexes.

Compound	g	Peak-to-peak width/G
Li**1**	2.0022	6.7
[Zn**1**]$^{+\cdot}$	2.0024	6.3[a]
[Zn$_2$**2**]$^{+\cdot}$	2.0024	5.4

[a] Determined from lower-resolution spectrum.
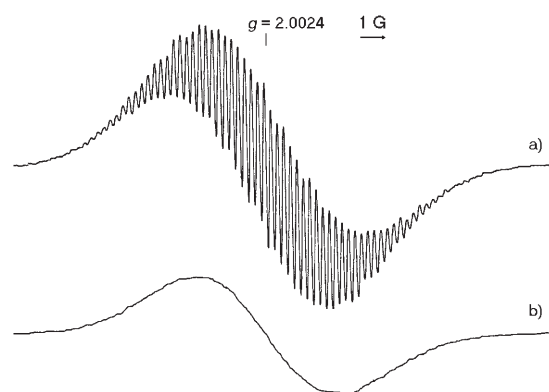
Figure 5. EPR spectra of a) [Zn**1**]$^{+\cdot}$ and b) [Zn$_2$**2**]$^{+\cdot}$ in toluene.

[Zn$_2$**2**]$^{+\cdot}$ (<1 equiv Br$_2$, control by UV/Vis/NIR), [Zn$_2$**2**]$^{2+}$ and [Zn**1**]$^{+\cdot}$ (excess of Br$_2$). [Zn**1**]$^{+\cdot}$, [Zn$_2$**2**]$^{+\cdot}$ and Li**1** show EPR signals very similar to described for other Pc(−1) species[2e,f,6c] (Table 1). The spectra for [Zn**1**]$^{+\cdot}$ and [Zn$_2$**2**]$^{+\cdot}$ are shown in Figure 5. In the case of [Zn**1**]$^{+\cdot}$ the ultrafine structure of the signal is partially resolved, which was not observed before for Pc(−1) complexes.[2e,f,6c,d] For [Zn$_2$**2**]$^{2+}$ and Li$_2$**2** no signals of triplet species ($\Delta M_s = 1$ and 2) were seen in the temperature range from 130 K to room temperature. The dinuclear Li$_2$**2** shows only a very weak signal similar to the signal of mononuclear Li**1** which may belong to H$_2$Pc(−2)−LiPc(−1) as impurity. From these data, taking into account also electronic spectra, singlet ground states can be postulated for [Zn$_2$**2**]$^{2+}$ and Li$_2$**2**. However, triplet states could be undetected since they usually have very broad spectra. Therefore the dinuclear Pc(−1)−Pc(−1) complexes were further studied by NMR in CCl$_4$. The spectra of Li$_2$**2** and [Zn$_2$**2**]$^{2+}$ are very similar (Table 2) containing three

Table 2. NMR data for diamagnetic dinuclear Pc complexes.

Compound (solvent)	CH$_3$	Ar-H of R	Ar-H of Pc
Li$_2$**2** (CCl$_4$)	2.27, 2.39, 2.51	7.20–7.30	no signals
[Zn$_2$**2**]$^{2+}$ (CCl$_4$)	2.18, 2.30, 2.41	7.11–7.29	no signals
H$_4$**2** (CDCl$_3$)[10h]	2.38, 2.48, 2.62	7.32–7.44	8.15, 8.29, 9.06, 11.14
Zn$_2$**2** (C$_6$D$_6$, 60 °C)	2.29, 2.37, 2.66	7.25–7.49	8.67–8.72, 9.69, 11.67

peaks at ≈ 2.3 ppm (methyl protons) and a broad signal at ≈ 7.2 ppm (aromatic protons of the substituents R) slightly (0.1–0.2 ppm) upfield-shifted compared to H$_4$**2** in CDCl$_3$[10h] and Zn$_2$**2** in C$_6$D$_6$. Surprisingly, no signals of Pc aromatic protons are observed. This is in contrast to H$_4$**2**[10h] and Zn$_2$**2** which show signals of fourteen aromatic Pc protons between 8.1–8.9, 9.1–9.7 and 11.1–11.7 ppm. Based on these results [Zn$_2$**2**]$^{2+}$ and Li$_2$**2** can be considered as antiferromagnetically coupled radical dimers having low-lying triplet excited states[13] rather than classical organic closed-shell systems. This has to be confirmed in further investigations by temperature dependent NMR spectra and measurements of the magnetic susceptibility.

Cyclic voltammetry: CV measurements was used to study the redox behavior of Zn**1** and Zn$_2$**2** in 1,2-dichlorobenzene (DCB) solution containing 0.1 M tetrabutylammonium per-
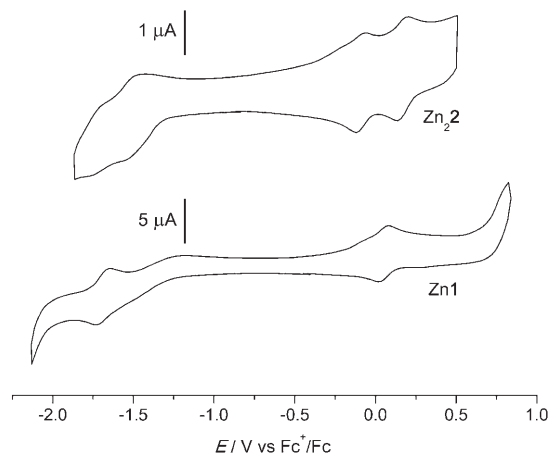

Figure 6. Cyclic voltammograms of Zn**1** and Zn$_2$**2** in DCB.

chlorate as electrolyte. Cyclic voltammograms are shown on the Figure 6 and potential values are listed in Table 3. The

Table 3. Redox potentials of Zn**1** and Zn$_2$**2** in DCB.

Compound	E/V vs Fc$^+$/Fc
Zn**1**	0.05, −1.69
Zn$_2$**2**	0.17, −0.09, −1.49, −1.73

results are quite similar to reported values[10c] for analogous mono- and dinuclear ZnPcs (with other substituents). The first oxidation and reduction waves of the mononuclear Zn**1** are split on going to the binuclear Zn$_2$**2** showing stepwise oxidation/reduction of two interacting Pc rings. The splitting ($\Delta E \approx 0.25$ V) is almost symmetrical for oxidation, whereas the middle between first and second reduction waves of Zn$_2$**2** is slightly shifted positively compared to the first reduction wave of Zn**1**.

Conclusion

Ring-oxidized annulated dinuclear phthalocyanine zinc(II) and lithium(I) complexes absorbing in the NIR with very high extinction were prepared and investigated. Analogous mononuclear Pcs were used for comparison. The chemical oxidation of the dinuclear Zn$_2$**2** with bromine clearly demonstrates a two-step oxidation process. In solution the band at $\lambda = 1057$ nm can be assigned to the radical-cation [Zn$_2$**2**]$^{+\cdot}$ of Pc(−1)−Pc(−2) type and the band at $\lambda = 1203$ nm to the dication [Zn$_2$**2**]$^{2+}$ of Pc(−1)−Pc(−1) type. For [Zn$_2$**2**]$^{+\cdot}$ a broad band at $\lambda = 2220$ nm (4550 cm^{-1}) is observed. The spectrum of the oxidized phthalocyanine lithium complex Li$_2$**2** shows also an intense NIR band at $\lambda = 1151$ nm. The

oxidation of mononuclear complexes exhibits only absorptions at $\lambda < 850$ nm. The absorptions of the oxidized annulated binuclear Pcs investigated in this work can be explained by a partial orbital diagram (ZINDO/s RHF method) considering low-energy transitions between split levels (intermacrocyclic charge transfer/charge resonance).

The ring-oxidized complexes [Zn**1**]$^{+\cdot}$, [Zn$_2$**2**]$^{+\cdot}$ and Li**1** show EPR signals very similar to those described for other Pc(−1) species with g-factor values close to that of a free electron. Because Li$_2$**2** and [Zn$_2$**2**]$^{2+}$ show no signals of Pc aromatic protons they should be considered as antiferromagnetically coupled radical dimers having low-lying triplet excited states rather than classical organic closed-shell systems. Work is in progress to confirm this proposal. The first oxidation and reduction waves in cyclic voltammograms of mononuclear Zn**1** are split on going to binuclear Zn$_2$**2** showing stepwise oxidation/reduction of two interacting Pc rings.

These extremely long wavelength absorbing phthalocyanines are interesting as materials with new electronic properties and therefore will be further investigated in the solid state.

Experimental Section

Measurements: Electronic absorption spectra were recorded on a Perkin–Elmer Lambda 2 and Lambda 9 spectrophotometers, IR-spectra on a Perkin–Elmer Spectrum 1000 and a FSM 1201 FT-IR spectrometers, NMR spectra on a Bruker Avance DPX 200 (200 MHz) and MS-ESI on a Bruker Esquire LC mass-spectrometer.

EPR spectra were recorded on a Bruker ER 200 D-SRC spectrometer (working frequency ≈ 9.5 GHz) with ER041 microwave bridge, ER 4105 DR double resonator and ER 4111 VT variable temperature unit. Diphenylpicrylhydrazyl (DPPH) was used as an external reference ($g = 2.0037$). The compounds were dissolved in toluene ($\approx 10^{-4}$ M). Then Zn**1** and Zn$_2$**2** were oxidized with bromine vapor introduced by a capillary pipette (protection from light!). An excess of Br$_2$ was used to get [Zn**1**]$^{+\cdot}$ and [Zn$_2$**2**]$^{2+}$, and a small amount (≈ 0.5 equiv) to get [Zn$_2$**2**]$^{+\cdot}$ in approx. equimolar mixture with Zn$_2$**2** (NIR spectra were recorded for control). The solutions were deaerated by three freeze–pump–thaw cycles and then ampoules were sealed in vacuo.

For cyclic voltammetry a Wenking VSG 83 triangle generator combined with Keithley DMM 2000 digital millimetre was used. Straight platinum wire (0.5 mm diameter) was employed as a working electrode. Twisted platinum wire and Ag wire were used as an auxiliary and a pseudo-reference electrode, respectively. Tetrabutylammonium perchlorate (0.1 M in o-dichlorobenzene) was used as an electrolyte and ferrocene as an internal standard. All measurements were carried out under nitrogen; the solutions were deaerated by continuous nitrogen bubbling prior to each measurement. The concentrations of the compounds studied were $\approx 10^{-4}$ M; the scan rate was 50 mV s^{-1}.

Theoretical calculations: Molecular orbital calculations were performed using ZINDO/s RHF method within HyperChem R. 5.02[14] software for unsubstituted analogue of Zn$_2$**2** and its cations. The σ–σ and π–π overlap weighing factors were 1.267 and 0.585, respectively. The initial geometry of Zn$_2$**2** was constructed from D_{4h}-symmetrized X-ray structure of the unsubstituted PcZn[15] and used for cations as well.

Materials: The synthesis of H$_2$**1** and H$_4$**2** was previously described.[10h] Zinc acetate dihydrate (Fluka), 5,6-dichloro-2,3-dicyano-p-benzoquinone (Sigma-Aldrich), lithium wire (Fluka), bromine (Fluka), hydroquinone (Fluka) purchased in the highest available grade were used without further purification. The solvents (analytical reagent grade) were dried, distilled and stored under nitrogen. For chromatographic separations, silica

gel 60 (40–63 μm) was used. For electrochemical measurements, tetrabutylammonium perchlorate (Fluka, electrochemical grade) was used as purchased, 1,2-dichlorobenzene (Fluka, puriss., ≥99%) was distilled under reduced pressure, and ferrocene (Aldrich) was recrystallized from hexane.

Syntheses

Zinc 2,3,9,10,16,17,23,24-octakis(2,6-dimethylphenoxy)phthalocyanine (Zn1): A solution of zinc diacetate dihydrate (44 mg, 0.2 mmol) in DMF was added to a suspension of H$_2$**1**[10h] (30 mg, 20 μmol) in toluene (2 mL) and the resulting mixture was heated under reflux for 15 h. The reaction mixture was cooled to room temperature and diluted with methanol (12 mL). The precipitate was separated by centrifugation, washed with methanol, vacuum-dried, then dissolved in toluene and purified by chromatography on silica gel eluting with toluene containing 3 vol.% of diethyl ether. The green fraction was collected, the solvent evaporated, the residue recrystallized from toluene and then vacuum-dried at 60°C to give green crystals (24 mg, 77%). ^{1}H NMR (200 MHz, CDCl$_3$, 25°C, TMS): δ = 8.19 (s, 8H), 7.30–7.41 (br, 24H), 2.43 ppm (s, 48H); IR (KBr): $\tilde{\nu}$ = 3022, 2952, 2922, 2854, 1608, 1588, 1590, 1478, 1452, 1398, 1346, 1272, 1222, 1188, 1138, 1090, 1028, 920, 894, 862, 840, 814, 764, 748, 726, 696, 588, 516 cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 674 (338000), 644 (42000), 608 (47000), 355 nm (106000 M^{-1} cm^{-1}); MS (ESI, positive mode): m/z: 1537 [M^++H], 1559 [M^++Na]; MS (ESI, negative mode): m/z: 1571 [M^-+Cl].

Compound Zn$_2$**2**: The same procedure was used to metalate H$_4$**2**[10h] (24 mg, 10 μmol). After chromatography with 8 vol.% Et$_2$O/toluene, reprecipitation from toluene with hexane and drying Zn$_2$**2** was obtained as a black powder (18 mg, 71%). ^{1}H NMR (200 MHz, C$_6$D$_6$, 60°C, TMS): δ = 11.67 (s, 2H), 9,69 (s, 4H), 8.67–8.72 (br, 8H), 7.25–7.49 (br, 36H), 2.66 (s, 24H), 2.37 (s, 24H), 2.29 ppm (s, 24H); IR (KBr): $\tilde{\nu}$ = 3064, 3040, 3022, 2952, 2920, 2852, 1610, 1588, 1474, 1454, 1398, 1374, 1346, 1276, 1222, 1186, 1134, 1094, 1068, 1044, 1022, 894, 808, 766, 746, 722, 584, 508 cm^{-1}; UV/Vis (THF): λ_{max} (ε) = 840 (470000), 794 (62000), 748 (93000), 722 (108000), 587 (sh, 24000), 363 nm (187000 M^{-1} cm^{-1}); MS (ESI, positive mode): m/z: 1258 [M^{2+}+2H].

Oxidation of Zn1 and Zn$_2$2 with bromine: 10^{-4} N solution of bromine in chlorobenzene was prepared directly before use. Only glass equipments were used for bromine solutions (no plastic caps). Bromine (8 mg, 50 μmol) was dissolved in chlorobenzene (10 mL). An aliquot (1 mL) of the solution was diluted to 10 mL. The dilution procedure was repeated. 10^{-5} M solutions of phthalocyanines were prepared by dissolving phthalocyanine (0.2 μmol) in chlorobenzene (20 mL). Concentrations were normalized by varying the solvent volumes depending on the exact weights of bromine and phthalocyanines. 10^{-4} N solution of bromine was added in 0.1 mL aliquots to 2 mL of phthalocyanine solution in a 1 cm (3 mL) quartz UV/Vis cuvette. The solution was mixed by shaking, and the UV/Vis/NIR spectrum was recorded at each step. The optical densities were normalized dividing by the dilution coefficient. For NMR measurement, Zn$_2$**2** in CCl$_4$ ($\approx$10^{-4} M) was oxidized with an excess of Br$_2$ vapor introduced by a capillary pipette into the NMR tube (part of the solution was used to check the NIR spectrum).

Compound Li1: Lithium (5 mg) was dissolved in methanol (2 mL). H$_2$**1** (30 mg, 20 μmol) was added to this solution, and the resulting mixture was heated under reflux for 20 min. After cooling the mixture was separated by centrifugation, the precipitate washed with methanol (1 mL), vacuum-dried and extracted with acetone (6 mL). The solution was evaporated under reduced pressure, the precipitate was vacuum-dried. A solution of 2,3-dichloro-5,6-dicyano-p-benzoquinone (14 mg, 60 μmol) in toluene (3 mL) was added to this precipitate. The resulting mixture was sonicated for 1 min and then stirred at room temperature for 30 min. The precipitate was separated by centrifugation, washed with toluene (1 mL) and then extracted with carbon tetrachloride. The solution was evaporated under reduced pressure, the residue reprecipitated from dichloromethane with hexane and then vacuum-dried at 50°C to give a brown powder (14.7 mg, 50%). IR (KBr): $\tilde{\nu}$ = 3066, 3042, 3025, 2952, 2922, 2856, 1601, 1587, 1456, 1440, 1388, 1321, 1272, 1258, 1221, 1187, 1090, 1026, 885, 861, 814, 763 cm^{-1}; UV/Vis/NIR (chlorobenzene): λ_{max} (ε): 800

(13000), 517 (52000), 400 (35000), 345 nm (78000 M^{-1} cm^{-1}); MS (ESI, negative mode): m/z: 1480 [M^-].

Compound Li$_2$2: Lithium (5 mg) was dissolved in methanol (2 mL). H$_4$**2** (24 mg, 10 μmol) was added. The mixture was refluxed for 20 min and then cooled to room temperature. The precipitate was separated by centrifugation, washed with methanol (1 mL), vacuum-dried and extracted with acetone (5 mL). The solution was evaporated under reduced pressure, and the residue was vacuum-dried. A solution of 2,3-dichloro-5,6-dicyano-p-benzoquinone (14 mg, 60 μmol) in toluene (3 mL) was added. The mixture was sonicated for 1 min and then stirred for 30 min at room temperature. Toluene (12 mL) and then hexane (15 mL) were slowly added to the mixture with stirring. The resulting suspension was separated by centrifugation, the solution evaporated under reduced pressure, the residue reprecipitated from dichloromethane with hexane and dried at 50°C to give a black powder (14.6 mg, 60%). ^{1}H NMR (200 MHz, CCl$_4$, 25°C, TMS): δ = 7.20–7.30 (br, 36H), 2.51 (s, 24H), 2.39 (s, 24H), 2.27 ppm (s, 24H); IR (KBr): $\tilde{\nu}$ = 3065, 3042, 3024, 2952, 2922, 2854, 1608, 1588, 1462, 1440, 1394, 1346, 1322, 1273, 1254, 1219, 1184, 1091, 1068, 1032, 884, 862, 762, 707 cm^{-1}; UV/Vis/NIR (chlorobenzene): λ_{max} (ε): 1151 (95000), 1074 (43000), 996 (31000), 694 (40000), 507 (46000), 338 nm (114000 M^{-1} cm^{-1}); MS (ESI, negative mode): m/z: 1201 [M^{2-}], 2402 [M^-].

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