approach, Deschenaux et al. were able to obtain an enantiotropic smectic A mesophase by functionalizing [60]fullerene with 12 alkyl chains each terminated by a cyanobiphenyl group.[12] It is therefore amazing to observe liquid crystallinity in [Ln(dbm)$_3$] complexes functionalized by only four alkyl chains.

In conclusion, we obtained lanthanide-containing liquid crystals by forming a bisadduct between tris(β-diketonato)-lanthanide(III) complexes and a salicylaldimine Schiff base. Our method is a new approach to the design of lanthanide-containing metallomesogens. This approach is versatile, because the β-diketone ligand, the addend ligand, and the lanthanide ion can be varied.

Experimental Section

^{1}H NMR spectra were obtained on a Bruker WM-250 spectrometer (250 MHz) using CDCl$_3$ as solvent. IR spectra were recorded on a Bruker FTIR spectrometer IFS66 (KBr pellet technique). Elemental analyses (CHN) were obtained on a CE-Instrument EA-1110 elemental analyzer. Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature controller. DSC traces were recorded with a Mettler–Toledo DSC821e module.

Synthesis of [Ln(dbm)$_3$L$_2$]: [La(dbm)$_3$] was obtained by careful dehydration of the corresponding mono- and dihydrates in vacuo (10^{-3} mbar).[13] A solution of [La(dbm)$_3$] (3 mmol, 2.42 g) in absolute ethanol was added dropwise to a solution of 2-hydroxy-*N*-octadecyl-4-tetradecyloxybenzaldimine (L) (3 mmol, 1.76 g) in absolute ethanol at 50°C. The adduct precipitated immediately. After the mixture had been stirred overnight at room temperature, the precipitate was filtered off, washed with ethanol and dried in vacuo. The compound is obtained as a pale yellow powder. Yield: 2.72 g (91%). IR (KBr): $\tilde{\nu} = 1654$ (C=N, s), 1552 (C=O, s) cm^{-1}. Elemental analysis calcd (%) for $C_{123}H_{175}LaN_2O_{10}$ (1980.6): C 74.57, H 8.91, N 1.42; found: C 74.74, H 8.97, N 1.30.

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Singly and Doubly Oxidized Phthalocyanine (pc) Rings: [Cu(pc)(ReO$_4$)] and [Cu(pc)(ReO$_4$)$_2$]**

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Numerous molecular conductors and semiconductors are known that are based on partially oxidized macrocycles,[1–4] and several singly oxidized metal phthalocyanine complexes have been isolated.[5, 6] Doubly oxidized complexes are more intriguing, with the most widely known example being "Compound I", which results from the double oxidation of ferrihemes.[7] This oxidation occurs by the loss of one electron from the metal ion (giving formally iron(IV)) and one from the ring. There are examples of crystalline doubly oxidized metal phthalocyanine complexes[8–11] where both oxidations are metal centered, but there are only a few reports of doubly ring-oxidized metallophthalocyanine complexes, and these only for solutions.[12–14] As far as we know there have been no reports of isolated compounds in which the phthalocyanine (pc) ring is doubly oxidized.

We describe here the syntheses of the singly and doubly oxidized compounds [Cu(pc)(ReO$_4$)] (**1**) and [Cu(pc)(ReO$_4$)$_2$] (**2**), together with their characterization by means of single-crystal X-ray diffraction (Figure 1) and electron paramagnetic resonance (EPR) methods. The structures of these compounds differ from those of porphyrinic conductors[15] and other singly oxidized derivatives[16] in that they contain isolated, rather than stacked, macrocycles. We show that these both are compounds of Cu^{II}, essentially unperturbed by the oxidation. In **1** the pc ring is singly oxidized to pc$^{\bullet-}$;

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in **2** the pc ring is doubly oxidized to pc^0. Compound **2** is the first compound containing a pc^0 ring to be isolated.

The galvanostatic oxidation of [Cu(pc)] in a 1-chloronaphthalene solution of $[N(C_4H_9)_4][ReO_4]$ yielded crystals of **1** and **2**. The structure of **1** is shown in Figure 1A. There are two independent molecules in the asymmetric unit. They closely resemble one another, each consisting of a Cu(pc) unit with a $Cu{-}OReO_3$ linkage. The angle between the two independent units is 68.56(4)°. The 24-atom cores of both of the symmetry-independent macrocycles are essentially planar, the mean deviations being 0.02(1) Å and 0.03(3) Å. The Cu atoms lie 0.096(1) Å and 0.092(1) Å out of the planes of the 24-atom cores, displaced toward the O atoms. In each macrocycle, one of the fused benzene rings is slightly puckered. The maximum out-of-plane distances are 0.163(7) Å and 0.307(7) Å. The average Cu−N bond length is 1.957(8) Å; the Cu−O distances are normal at 2.440(4) Å and 2.451(5) Å. The van der Waals contacts between neighbors are 3.35–3.37 Å.

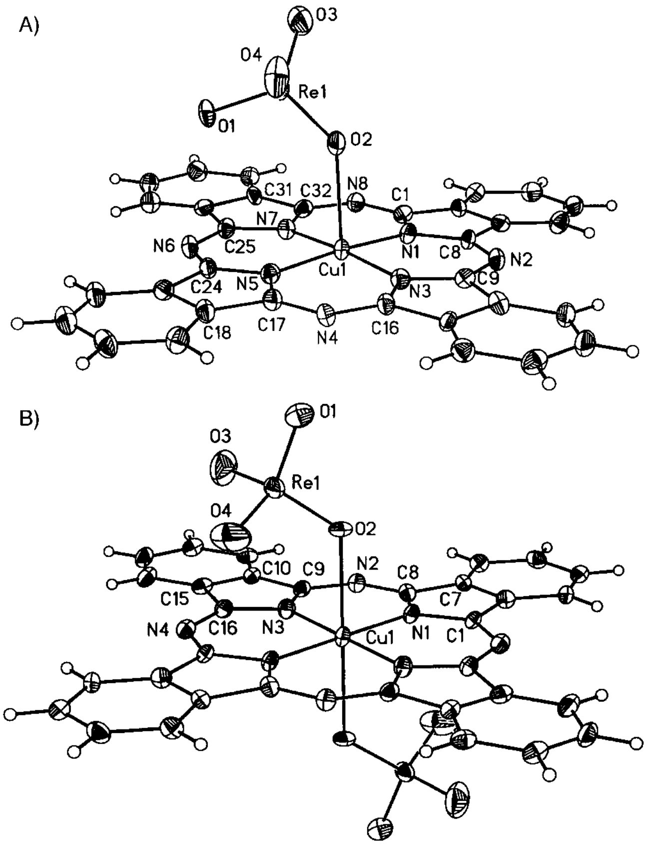

Figure 1. Molecular structures of **1** (A) and **2** (B). The average Cu−O bond length is 2.446(5) Å in **1** and is 2.526(5) Å in **2**. Displacement ellipsoids are set at the 50% probability level.

The structure of **2** is shown in Figure 1B. The molecule, which has a crystallographically imposed center of symmetry, consists of a Cu(pc) unit with two $Cu{-}OReO_3$ linkages. The mean deviation from the 24-atom core is 0.025(16) Å; the maximum deviation is 0.082(8) Å. The average Cu−N distance is 1.97(1) Å; the Cu−O distance is 2.526(5) Å, longer by 0.08 Å than the average value for **1** but still normal. The packing displays a herringbone pattern.

To obtain information about the nature of the oxidation the electronic structure of each compound was investigated by EPR spectroscopy. Crystals of **1** were ground in KBr to produce an isotropic sample for powder EPR analysis. A spectrum taken at 35 GHz (Q-band) and 77 K showed a broad peak, centered at $g = 3.7$. We assign this resonance to the "half-field" transition (or $\Delta m_s = \pm 2$) of an $S = 1$ spin system with zero-field splitting (ZFS) that is large compared with the X-band microwave quantum. This implies that the $[Cu(pc)]^+$ moieties in the crystal exhibit a triplet state formed by the exchange coupling of a d^9 Cu^{II} center and a pc π radical formed by the oxidation of the pc^{2-} ring to pc$^-$. Such an $S = 1$ state has been observed in frozen solutions of Cu^{II} porphyrin radical species by means of EPR spectroscopy,[17] and also by means of magnetic-susceptibility measurements.[16, 18] By analogy,[19] we take the $S = 1$ state of **1** to be the ground state.

The absence of clear fundamental transitions ($\Delta m_s = \pm 1$) in the present spectrum does not permit a precise determination of the triplet-state zero-field splitting parameter (D) but through the use of second-order perturbation theory[20] we estimate $D \approx 0.5\ cm^{-1}$ (14 GHz), substantially larger than the D parameter seen in the corresponding copper–porphyrin systems (0.116 cm^{-1}).[21, 22]

In the two extreme ($S = 1/2$) valence-bond formulations of **2**, the compound would contain either Cu^{III}pc$^-$ with a diamagnetic (d^8) Cu^{III} center and an anion radical pc$^{\bullet -}$, or it would contain Cu^{II}pc^0 with a paramagnetic d^9 Cu^{II} center and a diamagnetic neutral pc^0. To determine the correct description, EPR studies of a single crystal were carried out.

A face-indexed crystal of **2** was fixed to a simple dual-axis goniometer where the primary axis was a Kel-F rod perpendicular to the applied field and the secondary axis was a Kel-F screw. The crystal was aligned with its [101] direction along the secondary axis of rotation so that one set of pc planes was approximately perpendicular to the primary rotation axis. EPR spectra were recorded at 10° intervals of rotation about the primary axis. Figure 2 shows a spectrum for an orientation in which B_0 is perpendicular to the plane of one of the sites, along $g_{\|}$. The values of $g_{\|} = 2.16$ and $A_{\|} = 575$ MHz derived

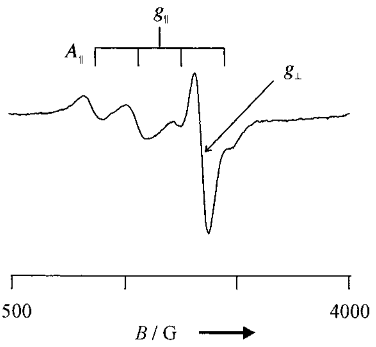

Figure 2. Single-crystal EPR spectrum of compound **2** taken at an orientation that maximizes the observed Cu hyperfine splitting. The measured $A_{\|}$ splitting is 190 G (575 MHz) at $g_{\|} = 2.16$. The observed line widths of the *individual* hyperfine transitions in the $g_{\|}$ region and $g_{\perp}$ peak are both ≈200 MHz, suggesting that the $A_{\perp}$(Cu) is close to zero. The crystal was mounted and manipulated as described in the text. Experimental conditions: Temperature 295 K; microwave frequency, 9.527 GHz; microwave power, 200 mW; modulation amplitude, 10 G; scan time, 4 min.; time constant, 64 ms.

for this site are in good agreement with the values of 2.179 and 605.5 MHz, respectively, for [Cu(pc)].[23]

The spectrum also contains a narrow (40 G peak–peak) feature that occurs at $g = 2.04$ and shows no resolved Cu (or N) hyperfine splittings. Given the structure, this must correspond to the perpendicular resonance for the magnetically inequivalent molecule of **2**. The observed value of $g_{\perp} = 2.04$ is in agreement with that of 2.05 for [Cu(pc)].[23] This line is substantially narrower than that of a Cu(pc) $g_{\perp}$ feature. We attribute the decrease in line width in **2** to inter-ion exchange effects in this magnetically concentrated crystal.[24]

These measurements show that both the g tensor and the ^{63,65}Cu hyperfine interactions are negligibly perturbed when the Cu(pc) unit is doubly oxidized to $[\text{Cu(pc)}]^{2+}$. Thus, the Cu$^{\text{II}}$ ion remains in its d^9 electronic configuration. The similarities in the $g_{\parallel}$ values of $[\text{Cu(pc)}]^{2+}$ and Cu(pc) further show that the energy separation between the ground state $d_{x^2-y^2}$ and the d_{xy} orbitals are essentially the same in these two compounds.

In summary, structural and EPR studies show that [Cu(pc)(ReO_4)] (**1**) contains Cu(pc) units singly oxidized at the ring to produce the spin triplet formed by ferromagnetic coupling between the d^9 Cu$^{\text{II}}$ ion and a π radical delocalized on the ring. Compound **2**, [Cu(pc)$(ReO_4)_2$] which contains $[\text{Cu(pc)}]^{2+}$ moieties, also retains the paramagnetic Cu$^{\text{II}}$ center, and thus contains a diamagnetic, doubly oxidized pc^0 ring.

Experimental Section

Single crystals of both **1** and **2** grew at the anode of an electrolytic cell that consisted of two compartments separated by a glass frit. The [Cu(pc)] starting material was synthesized by metallation of very pure H_2(pc)[2] with $CuCl_2 \cdot x H_2O$ (99.9999%, dehydrated), followed by repeated sublimation. The electrolytic cell was protected from light, kept purged with dry N_2, and maintained at 120(5) °C. Each half-cell contained a solution of 1-chloronaphthalene (20 mL) that was 0.013 M in [N(n-Bu)$_4$][ReO$_4$]; the solution in the anode compartment was saturated with [Cu(pc)] ([Cu(pc)] < 10^{-3} M; $E^1_{\text{ox}} = 0.98$ V versus SCE[25]). A 2.0 μA current was passed through the cell by platinum electrodes for three weeks, during which time the initially blue solution turned green. A few dark-purple crystals of **1** and several dark-red crystals of **2** grew on the anode in about a 1:10 ratio. These crystals were separated manually. The Cu:Re ratio of each crystal was determined by energy dispersive spectroscopy to provide a confirmation of the visual identification. Both compounds are air and light stable.

General crystallographic details: Bruker Smart 1000 CCD diffractometer,[26] Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), ω-scans, $T = 153$ K. For **1**, two hemispheres were collected, one at $2\theta = -28°$, the other at $2\theta = -75°$. The structures were solved by direct methods[27] and refined with the program SHELXTL.[28] Face-indexed absorption corrections were performed in the program XPREP.[28] All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on their respective carbon atoms. Crystal structure analysis of **1**: $C_{32}H_{16}CuN_8O_4Re$, dark purple prism, 0.42 × 0.25 × 0.24 mm, monoclinic, $P2_1/c$, $a = 20.455(4)$ $b = 11.947(2)$, $c = 27.327(6)$ Å, $\beta = 126.86(3)°$, $V = 5343.4(19)$ Å^3, $T = 153$ K, $Z = 8$, $\rho_{\text{calcd}} = 2.054$ g cm^{-3}, $2\theta_{\max} = 56.6°$, 32531 reflections measured, 12544 unique, 10343 observed with $I > 2\sigma(I)$. $\mu = 53.8$ cm^{-1}, min/max transmission = 0.19/0.35. $R_1 = 0.064$, $wR_2 = 0.127$ (all data). Crystal structure analysis of **2**: $C_{32}H_{16}CuN_8O_8Re_2$, Deep red polyhedron, 0.24 × 0.37 × 0.49 mm, monoclinic, $P2_1/c$, $a = 8.9825(18)$, $b = 9.3147(19)$, $c = 17.712(4)$ Å, $\beta = 95.96(3)°$, $V = 1474.0(5)$ Å^3, $T = 153$ K, $Z = 2$, $\rho_{\text{calcd}} = 2.425$ g cm^{-3}, $2\theta_{\max} = 56.54°$, 9208 reflections measured, 3541 unique, 3223 observed with $I > 2\sigma(I)$. $\mu = 89.8$ cm^{-1}, min/max transmission = 0.063/0.18. $R_1 = 0.0550$, $wR_2 = 0.128$ (all data). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149171 (**1**) and CCDC-149172 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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