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Synthesis and Copper(I)-Driven Disaggregation of a Zinc-Complexed Phthalocyanine Bearing Four Lateral Coordinating Rings

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A new zinc phthalocyaninate, bearing four flexible phenanthroline-containing 30-membered rings was synthesized by template condensation of a macrocyclic phthalonitrile. The resulting phthalocyanine was an insoluble aggregate. However, in the presence of Cu^{I} ions, the formation of a soluble complex was observed. UV/Vis and DOSY NMR spectroscopic studies showed a monomolecular state for this species in solution. ^{1}H-^{1}H ROESY demonstrated that the macrocyclic substituents adopt a folded conformation, giving the complex a globular shape. The folding originates from stacking interactions between the phthalocyanine core and peripheral copper(I)–phenanthroline complexes.

Introduction

Over the course of the last two decades, comprehensive studies of phthalocyanines bearing lateral macrocyclic substituents have been carried out. By taking advantage of the complexing properties of their peripheral binding sites, it is possible to efficiently control the assembly of these functionalized phthalocyanines.[1–5] For example, interaction of crown–phthalocyanines with alkali metal ions afforded multideck species,[6–11] conducting mesophases,[12,13] and biomimetic models of photosynthesis.[14,15] Interaction between the crown-ether components and secondary ammonium ions afforded pseudo-rotaxanes and rotaxanes.[16–19]

Much less attention was paid to phthalocyanines bearing macrocyclic units capable of peripheral transition metal binding. Interaction of transition metal ions with macrocyclic ligands is one of the most powerful approaches for assembling catenanes and rotaxanes.[20] This approach has been widely used to construct interlocking-ring compounds containing porphyrins,[21,22] but it has never been applied in phthalocyanine chemistry. We would now like to report the efficient synthesis of new phthalocyanine **1**, bearing four lateral 1,10-phenanthroline (phen) containing coordinating rings. Compound **1** was synthesized with the aim of using it as a building block for multicatenanes and rotaxanes, prototypes of new molecular machines and receptors.[23]

Results and Discussion

Synthesis of the Phthalonitrile Precursor

Previously reported (dicyanobenzo)crown ethers containing additional aromatic functional groups, which are precursors to functionalized phthalocyanines, were synthesized by cycloalkylation of aromatic bis(phenols) with open-chain *o*-dibromo derivatives followed by Rosenmund–Braun cyanation.[24–26] This reaction resulted in only moderate yields of macrocyclic phthalonitriles, probably owing to the harsh reaction conditions, which can promote the formation of copper phthalocyaninate, as well as other side reactions. Herein, we report the proposal and successful implementation of a reorganised reaction sequence, introducing cyano groups before formation of the macrocycle (Scheme 1), which avoids the formation of complexes of copper cations with chelating phenanthroline units.

Implementation of this strategy required preparation of a phthalonitrile bearing two diethylene glycol (DEG) chains (**4** in Scheme 1). Previous attempts to prepare **4** either by alkylation of 4,5-dicyanocatechol with chloroethoxyethanol[27] or by Pd/C-catalysed hydrogenolysis of bis{2′-[2′′-(benzyloxy)ethoxy]ethoxy}phthalonitrile[28] were unsuccessful. So, we decided to study the cyanation of the *o*-dibromide, which already contains the required DEG chains. Catechol was first alkylated with 2-(2-chloroethoxy)ethanol yielding diol **2**,[29] which was then bromin-

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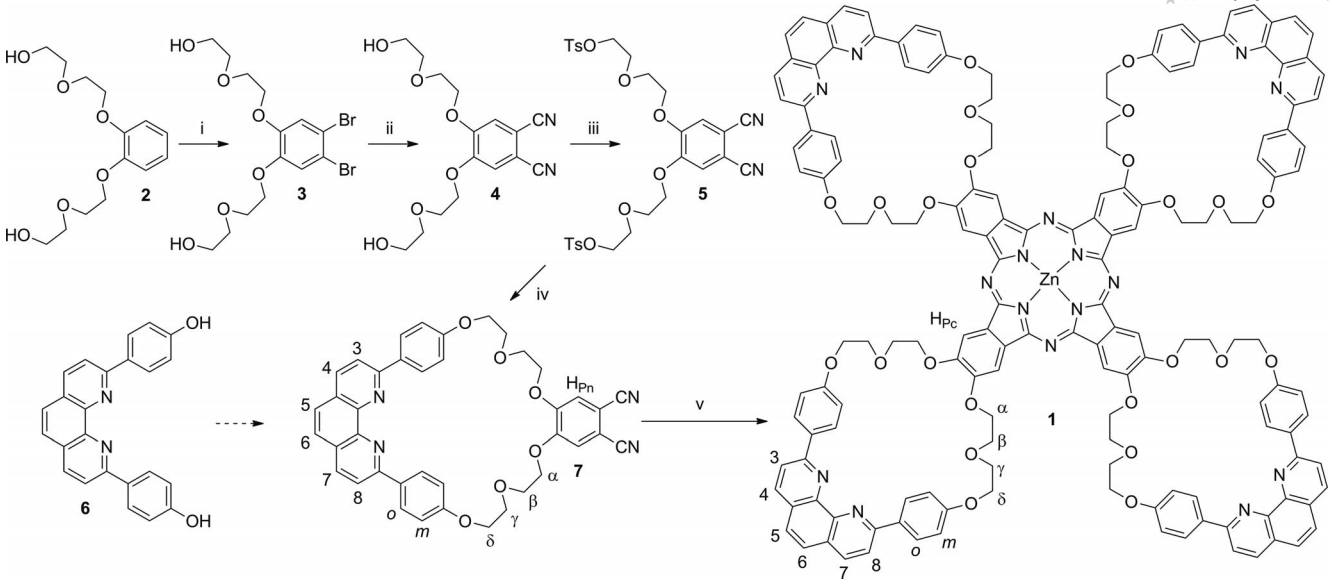

Scheme 1. (i): NBS, DMF, room temp. (yield 75%); (ii): $Zn(CN)_2$, $Pd_2(dba)_3$, dppf, DMAA, 120 °C (yield 85%); (iii): TsCl, K_2CO_3, DMAP, 0→20 °C (yield 63%); (iv): **6**, Cs_2CO_3, DMF, 65 °C (yield 69%); (v): $Zn(OAc)_2$, DBU, *i*AmOH, *o*-DCB, reflux (yield 56%).

ated with *N*-bromosuccinimide (NBS) in *N*,*N*-dimethylformamide (DMF) providing dibromide **3**. However, Rosenmund–Braun cyanation of **3** with CuCN in refluxing DMF failed to convert it into dinitrile **4**. For this reason, we took note of a Pd-catalysed cyanation reaction – an approach widely used to synthesize aromatic mononitriles,[30] but quite rarely used to prepare *o*-dinitriles.[31–33]

Recently, Hanack et al. proposed a general procedure for the preparation of phthalonitriles under mild conditions,[33] which tolerate various functional groups. This method implies cyanation of *o*-dibromides by $Zn(CN)_2$ in the presence of tris(dibenzylideneacetone)dipalladium [$Pd_2(dba)_3$] and 1,1′-bis(diphenylphosphanyl)ferrocene (dppf) in *N*,*N*-dimethylacetamide (DMAA) at 110–120 °C. The addition of polymethylhydrosiloxane (PMHS)[34] made it possible to avoid the use of an inert gas.

Performing this reaction under the proposed conditions[33] in air resulted in a low yield of nitrile **4**. Chromatographic monitoring of the reaction course showed that the conversion of **3** into **4** occurs during the first 15 min, but then the reaction terminates, leaving most of the starting dibromide **3** unreacted. However, when the same reaction was performed under argon, the desired phthalonitrile **4** was obtained in excellent yield (85%).

Tosylation of **4** with TsCl with 4-(dimethylamino)pyridine (DMAP) and excess of K_2CO_3 in acetonitrile afforded open-chain precursor **5**. It was further used for cycloalkylation of 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline (**6**) [35] in the presence of Cs_2CO_3 under high-dilution conditions to afford macrocyclic phthalonitrile **7** in 65% yield.

Therefore, successful completion of steps (iii) and (iv) showed that the phthalonitrile fragment is robust enough to withstand the conditions of both tosylation and cycloalkylation. Thus, this approach looks promising for the preparation of other macrocyclic phthalonitriles bearing labile or coordinating functional groups.

X-ray Crystallography of Macrocyclic Phthalonitrile 7

Slow concentration of a saturated solution of **7** in a mixture of dichloromethane and methanol afforded yellow crystals suitable for X-ray diffraction analysis. Analysis revealed that **7** adopts a chair-like conformation with almost coplanar phenanthroline and phthalonitrile units (angle 2.9°, Figure 1). The 2,9-diarylphenanthroline unit of the macrocycle is almost flat with dihedral angles between aryl and phenanthroline units equal to 6.0 and 4.6°.

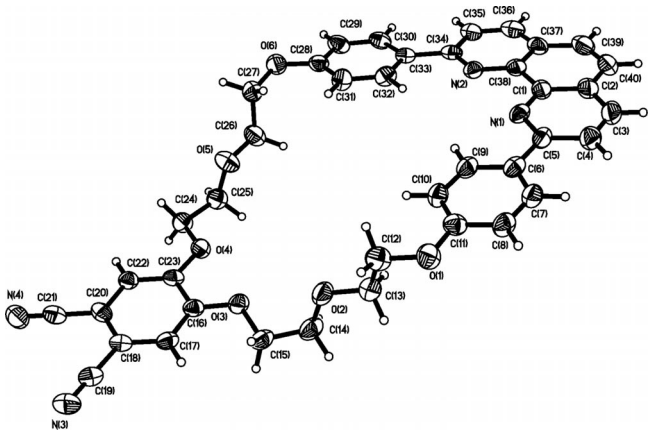

Figure 1. Molecular structure of **7** with thermal ellipsoids drawn at the 50% probability level.

Macrocycle **7** crystallizes with 3 solvate molecules of dichloromethane (Figure 2), in which the hydrogen atoms form weak contacts with the oxygen atoms of the DEG chains as well as the nitrile nitrogen atoms. The molecules in the crystal form head-to-tail dimers with fairly short π–π stacking contacts (C···C 3.519–3.801 Å). In turn, these dimers form layers, inclined at 74.6° with respect to each other (Supporting Information, Figure S8).

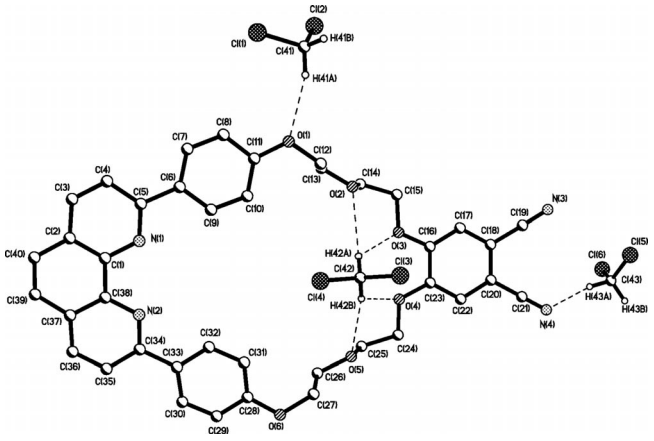

Figure 2. Hydrogen bonds [Å] in the crystal lattice of compound **7**: O(1)···C(41) 3.471, O(2)···C(42) 3.448, O(3)···C(42) 3.258, O(4)···C(42) 3.227, O(5)···C(42) 3.460, N(4)···C(43) 3.247.

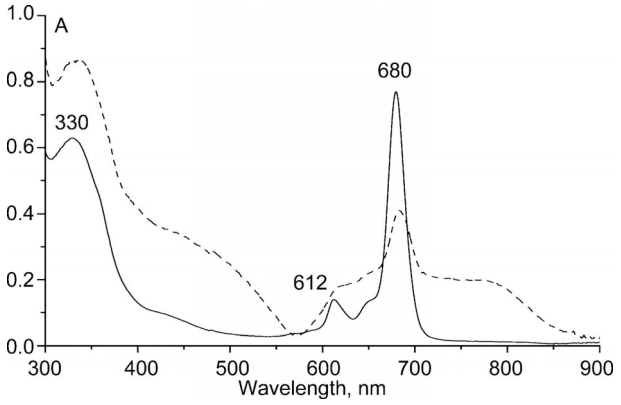

Figure 3. UV/Vis spectra of **1** (suspension) in $CHCl_3/CH_3CN$ (1:1, v/v) before (dashed line) and after treatment with $[Cu(CH_3CN)_4](PF_6)$ (solid line).

Synthesis and Investigation of Phthalocyanine 1

The condensation leading to phthalocyaninate **1** was carried out by treating **7** with zinc acetate and 1,8-diazabicyclo[5.4.0]undecene-7 (DBU) in a refluxing mixture of isoamyl alcohol/1,2-dichlorobenzene (*o*-DCB) (1:1). The resulting compound was found to be almost insoluble in common organic solvents, apparently because of strong aggregation. Therefore, purification and isolation of **1** could not be performed by chromatography. Thus, **1** was purified first by treatment of the reaction mixture with an aqueous ethylenediaminetetraacetic acid (EDTA) solution to remove excess Zn^{II} ions. Then, the soluble organic impurities were extracted with toluene in a Soxhlet apparatus, yielding **1** as a bluish-green insoluble powder.

To overcome the low solubility of **1**, a suspension of **1** in $CHCl_3/CH_3CN$ (1:1) was treated with 4 equiv. of $[Cu(CH_3CN)_4](PF_6)$, which resulted in rapid formation of a transparent green solution. UV/Vis monitoring of this process demonstrated significant changes (Figure 3). The broad structureless band of **1** (mostly in suspension) vanished, and a narrow Q-band at 680 nm with a well-resolved vibration overtone at 612 nm, typical for monophthalocyaninates, was observed, suggesting the monomeric state of the resulting Pc species [**1**·4Cu$^+$]. Notably, addition of Zn^{II} and Ag^I salts did not result in dissolution of **1**.

The NMR spectrum of the soluble compound obtained after addition of copper(I) exhibited the expected number of signals, which were assigned by ^{1}H-^{1}H COSY and ROESY experiments. Increasing the temperature to 55 °C resulted in a small upfield shift and sharpening of the resonance signals attributed to the phen protons, whereas the aromatic protons of the phthalocyanine (Pc) ring (H^{Pc}) did not change position and breadth (Supporting Information, Figure S5). The position of the latter signals is known to be sensitive to aggregation of Pc molecules, which can be hindered by increasing temperature.[36] Therefore, the fact that by raising the temperature the chemical shift and the shape of H^{Pc} were not affected, whereas the H^{phen} resonance signals became sharper, may suggest some dynamic conformational process involving the phen part of the molecule only.

When starting macrocyclic precursor **7** was treated with $[Cu(CH_3CN)_4](PF_6)$ in a mixture of $CDCl_3/CD_3CN$ (1:1, v/v), a small but significant downfield shift of the resonance signals of the phen protons was observed owing to the weak electron-withdrawing effect of the Cu^I centre (Figure 4). However, the ^{1}H NMR spectra of complexes [**7**·Cu$^+$] and [**1**·4Cu$^+$] differed, and it was noticed that the resonance signals of the phen protons in [**1**·4Cu$^+$] were significantly shifted upfield relatively to the spectrum of [**7**·Cu$^+$]. This upfield shift is particularly large for protons 5 and 6 located at the rear of the phen nucleus.

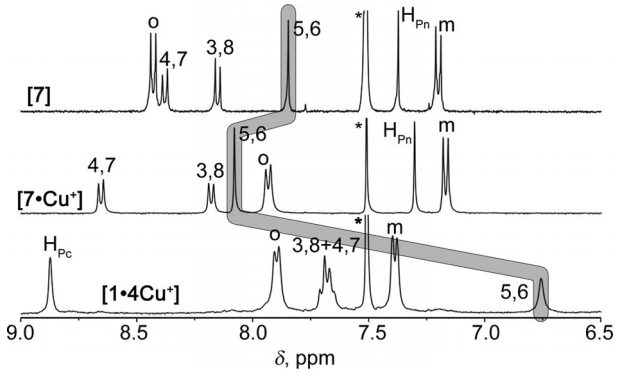

Figure 4. Aromatic region of ^{1}H NMR spectra of **7**, [**7**·Cu$^+$] and [**1**·4Cu$^+$] ($CDCl_3/CD_3CN$ at 25 °C for **7** and [**7**·Cu$^+$] and 55 °C for [**1**·4Cu$^+$]; for the latter compound, it was checked that the chemical shifts of the various protons were only slightly temperature-dependent). Proton numbering is given in Scheme 1.

In the ROESY spectrum of [**1**·4Cu$^+$] cross-peaks between the *o*,*m*-protons of the phenyl groups belonging to the ring and H^{Pc} were observed, suggesting that these two sets of protons are in close proximity in solution (Figure 5).

This can be rationalized by assuming that owing to the flexibility of DEG chains the phen-incorporating rings are folded in such a way that the rear of the phen units lie above

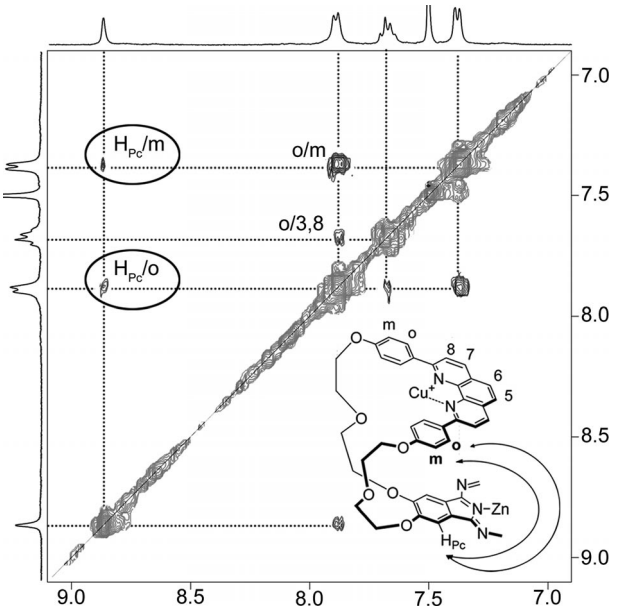

Figure 5. Aromatic region of ^{1}H-^{1}H ROESY spectrum of [**1**·4Cu$^+$] ($CDCl_3$/CD_3CN at 55 °C). The ovals mark the cross-peaks, which suggest a folded conformation of the macrocyclic substituents (inset).

or below the plane of the Pc nucleus. The phen units will thus experience the ring-current effect of the Pc group, and the 4, 5, 6 and 7 protons will undergo a strong upfield shift ($\Delta\delta^{5,6}$ = –1.32 and $\Delta\delta^{4,7}$ = –0.98 ppm, relative to [**7**·Cu$^+$]). This is also the case for protons 3 and 8, but to a lesser extent ($\Delta\delta^{3,8}$ = –0.50 ppm). Another possibility, which could account for the observed upfield shift of the H^{Phen} resonance signals, would be intermolecular stacking between the phen units of a given molecule and the Pc ring of another one.

To distinguish between intra- and intermolecular stacking, ^{1}H-DOSY measurements were performed (Supporting Information, Figure S7). They revealed the presence of a single molecular species with a diffusion coefficient of 3.6×10^{-10} m^2 s^{-1}. Modelling of [**1**·4Cu$^+$] with four folded macrocycles suggested a globular structure with a radius of ca. 12 Å (Figure 6), in good agreement with the hydrodynamic radius estimated from the diffusion coefficient (12.2 Å).

Altogether, the NMR study demonstrates that [**1**·4Cu$^+$] is a monomeric species in solution, with folded macrocyclic units. The folded conformation is likely to be stabilised by the interaction between the electron-deficient [phen·Cu$^+$] units and the electron-donating Pc nucleus.

The presence of CD_3CN in the samples prepared for the NMR spectroscopic measurements could result in axial coordination of one acetonitrile molecule to Zn^{II} in [**1**·4Cu$^+$], which could provide environmental non-equivalence of the two sides of the globular molecule, which in turn could result in the appearance of several sets of resonance signals, leading to complicated NMR spectra. However, in the spectrum of [**1**·4Cu$^+$] each type of protons gave only one resonance signal, suggesting fast exchange of the axial ligands

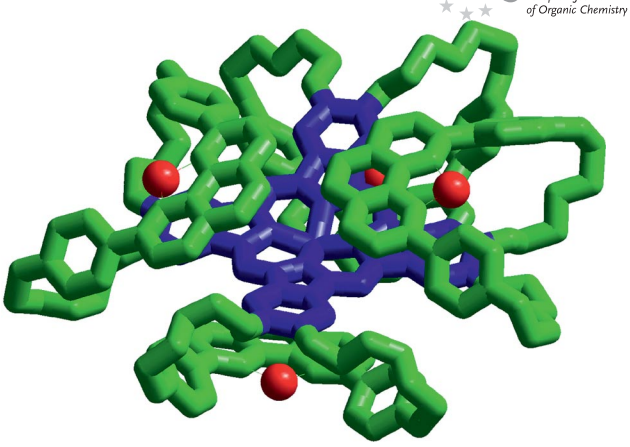

Figure 6. MM+ model of the folded conformation of [**1**·4Cu$^+$]. The phthalocyanine ring is coloured in blue, the lateral macrocycles are coloured in green, the red spheres correspond to copper(I) ions.

in the Zn^{II} coordination sphere, in line with previously reported data.[37] Two acetonitrile molecules are also likely to form coordination bonds with each Cu^I ion introduced into the peripheral macrocycles. Indeed, acetonitrile is a strong π-acceptor and a weak σ-donor, which fulfils the requirements of monovalent copper.

Conclusions

A new phthalocyanine bearing four peripheral coordinating rings has been synthesised in good yield from relatively simple precursors. Owing to the presence of phen groups in the lateral rings, the compound can form stable complexes with transition metals such as copper(I). Coordination of this metal centre to the peripheral rings suppresses completely the aggregation of the phthalocyanines and allows solution studies to be performed. Addition of copper(I) also changes dramatically the conformation of the system, leading to a folded and globular structure. Previously, a similar folding process driven by π–π interactions was evidenced in a gold(III) porphyrinate attached to a phen-containing macrocycle.[38] To the best of our knowledge this type of interaction has never been observed in the case of phthalocyanines bearing peripheral macrocyclic substituents.

It is expected that the system described herein will pave the way to new interlocking-ring compounds incorporating phthalocyanines.

Experimental Section

General: Catechol, 2-(2-chloroethoxy)ethanol, NBS, zinc cyanide, tris(dibenzalacetone)dipalladium(0) [$Pd_2(dba)_3$], dppf, DMAP and DBU were available from commercial suppliers (Aldrich, Merck) and used without further purification. Potassium and caesium carbonates were dried at 120 °C in an oven. The solvents ($CHCl_3$, EtOAc, hexane) were distilled from CaH_2. DMF (Aldrich, ≥ 98.0%) and DMAA (Aldrich, ≥ 99%), were used as received without further purification. 1,2-Bis[2′-(2′′-hydroxyethoxy)ethoxy]-

benzene (**2**)[29] and 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline (**6**)[35] were synthesized as reported previously. NMR spectra were recorded with a Bruker Avance 400 spectrometer (400.14 MHz for ^{1}H and 100.62 MHz for ^{13}C). NMR spectra were referenced against the residual solvent signal.[39] Melting points were measured with a Büchi B-540 melting point analyser. Mass spectra (ES-MS) were recorded with a BrukerMicroTOF spectrometer by the Service de Spectrométrie de Masse (Université de Strasbourg). UV/Vis spectra were measured with a Varian Cary-100 spectrometer in quartz cuvettes with 1 cm optical path. An FT-IR Nexus (Nicolet) spectrophotometer with micro-ATR accessory (Pike) was used to record IR spectra. Elemental analysis was performed with a Carlo–Erba 1106 instrument.

1,2-Dibromo-4,5-bis[2′-(2′′-hydroxyethoxy)ethoxy]benzene (3): Diol **2** (3.66 g, 12.8 mmol) was dissolved in DMF (25 mL), and a solution of NBS (4.98 g, 28.2 mmol) in DMF (25 mL) was added dropwise. After stirring for 2 d, the yellow-orange solution was diluted with water (50 mL), solid Na_2SO_3 was added to cause bleaching of the orange colour, and the mixture was extracted with $CHCl_3$ (3 × 50 mL). The organic extracts were washed with water (3 × 50 mL), dried with Na_2SO_4, and the solvent was removed under reduced pressure. The product was purified by using chromatography on silica [(acetone/hexane, 7:2–2:8 (v/v)], yielding **3** as a viscous yellow oil (4.42 g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.47 (s, 2 H, OH), 3.66, 3.73, 3.88, 4.12 (4 m, 4 × 4 H, α–δ-OCH_2) 7.09 (s, 2 H, 3,6-H_{Ar}) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.75, 69.07, 69.13, 72.93, 115.47, 118.09, 148.49 ppm.

1,2-Dicyano-4,5-bis[2′-(2′′-hydroxyethoxy)ethoxy]benzene (4): Dibromide **3** (1.74 g, 3.92 mmol), $Zn(CN)_2$ (689 mg, 5.88 mmol) and dppf (60.8 mg, 0.11 mmol) were placed in a two-necked flask, DMAA (5 mL) was added, and the mixture was flushed with argon. A degassed suspension of $Pd_2(dba)_3$ (71.8 mg, 78.4 μmol) in DMAA (5 mL) was added by using a syringe through the septum, and the mixture was heated to 120 °C for 2.5 h. After cooling to room temperature, the mixture was diluted with EtOAc (20 mL) and filtered through a layer of silica. The solids were washed with EtOAc, and the combined filtrates were concentrated under reduced pressure to give a brown oil, which was purified by using chromatography on silica (CH_2Cl_2 with 0–3 vol.-% MeOH). The combined fractions, containing **4**, were concentrated. The light-brown sticky solid obtained was transferred into a 25 mL flask, CH_2Cl_2 (10 mL) was added, and the mixture was vigorously stirred for 2 h. Filtration, washing of the solid with cold CH_2Cl_2, and drying afforded dinitrile **4** as a white powder (1.12 g, 85%); m.p. 95–96 °C. ^{1}H NMR (400 MHz, [D_6]acetone): δ = 3.12 (br. s, 2 H, OH), 3.64, 3.91, 4.38 (3m, 16 H, α–δ-OCH_2) 7.61 (s, 2 H, 3,6-H_{Ar}) ppm. ^{13}C NMR (100 MHz, [D_6]acetone): δ = 62.06, 69.81, 70.50, 73.79, 109.25, 116.77, 118.12, 153.44 ppm. FT-IR (neat): $\tilde{\nu}$ = 3285, 3122, 3057, 2942, 2881, 2227 (C≡N), 1590, 1568, 1517, 1448, 1410, 1353, 1291, 1229, 1120, 1089, 1057, 1025, 926, 881, 826 cm^{-1}. HRMS: calcd. for $C_{16}H_{20}N_2NaO_6$ [M + Na]$^+$ 359.121; found 359.123.

1,2-Dicyano-4,5-bis[2′-(2′′-tosyloxyethoxy)ethoxy]benzene (5): Dinitrile **4** (672 mg, 2 mmol) was dissolved in dry acetonitrile (15 mL), dry K_2CO_3 (1.656 g, 12 mmol) was added, and the suspension was cooled to 0 °C. A solution of TsCl (1.146 g, 6 mmol) in CH_3CN (15 mL) was added dropwise. The mixture was warmed to room temperature and vigorously stirred for 40 h. Then, it was filtered, the solids were washed with CH_3CN, the combined filtrates were concentrated resulting in a brown oil that was purified with silica [pentane/$CHCl_3$, 7:3–3:7 (v/v)], yielding target ditosylate **5** as a viscous clear oil (793 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 6 H, CH_3), 3.77, 3.86 (2 m, 2 × 4 H, γ,δ-OCH_2), 4.17 (m, 8 H, α,β-OCH_2), 7.17 (s, 2 H, 3,6-H), 7.32 (d, J = 8.1 Hz, 4 H, *m*-H), 7.77 (d, J = 8.1 Hz, 4 H, *o*-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.78, 69.25, 69.33, 69.44, 69.45, 109.11, 115.82, 117.02, 128.06, 130.01, 133.04, 145.10, 152.40 ppm. FT-IR (neat): $\tilde{\nu}$ = 2229 (C≡N), 1590, 1521, 1449, 1414, 1368, 1349, 1333, 1293, 1232, 1214, 1188, 1172, 1141, 1095, 1023, 1010, 950, 914, 900, 857, 812, 781, 769 cm^{-1}. HRMS: calcd. for $C_{30}H_{32}N_2NaO_{10}S_2$ [M + Na]$^+$ 667.139; found 667.138.

Macrocycle 7: A degassed solution of ditosylate **5** (515 mg, 0.8 mmol) and 2,9-bis(*p*-hydroxyphenyl)-1,10-phenanthroline (**6**) (291 mg, 0.8 mmol) in DMF (175 mL) was added dropwise to a vigorously stirred suspension of Cs_2CO_3 (2.60 g, 8 mmol) in DMF (300 mL) at 70 °C over 8 h. After complete addition, the reaction mixture was stirred for 1 d. The warm reaction mixture was filtered, the solids were washed with DMF, and the filtrate was concentrated. The resulting brown solid was purified by using silica (chloroform) affording target macrocyclic dinitrile **7** as a yellowish solid (369 mg, 69%); m.p. 256–289 °C (decomp.). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (t, J = 5.2 Hz, 4 H, γ-OCH_2), 3.97 (t, J = 5.1 Hz, 4 H, β-OCH_2), 4.24 (t, J = 5.1 Hz, 4 H, α-OCH_2), 4.38 (t, J = 5.2 Hz, 4 H, δ-OCH_2), 7.14 (d, J = 8.6 Hz, 4 H, *m*-H), 7.20 (s, 2 H, 3′,6′-H), 7.76 (s, 2 H, 5,6-H), 8.06 (d, J = 8.4 Hz, 2 H, 3,8-H), 8.27 (d, J = 8.4 Hz, 2 H, 4,7-H), 8.36 (d, J = 8.6 Hz, 4 H, *o*-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.75, 69.24, 69.74, 69.94, 109.08, 115.79, 117.26, 119.37, 125.76, 127.59, 129.29, 133.32, 136.84, 146.18, 152.3, 156.39, 159.86 ppm. FT-IR (neat): $\tilde{\nu}$ = 2974, 2933, 2883, 2226 (C≡N), 1601, 1587, 1573, 1549, 1513, 1487, 1463, 1426, 1409, 1375, 1349, 1286, 1246, 1225, 1174, 1147, 1127, 1082, 1059, 1046, 1025, 1009, 986, 957, 920, 899, 858, 836, 794 cm^{-1}. HRMS: calcd. for $C_{40}H_{32}N_4NaO_6$ [M + Na]$^+$ 687.221; found 687.220.

Zinc(II) Phthalocyaninate 1: Dinitrile **7** (100 mg, 0.15 mmol) and anhydrous $Zn(OAc)_2$ (13.8 mg, 75.3 μmol) were suspended in *i*AmOH (2 mL distilled from Na). Then *o*-DCB (2 mL distilled from CaH_2) was added, followed by DBU (22 μL, 0.15 mmol). The mixture was heated to reflux under a slow stream of argon for 1 d. After cooling to room temperature, the dark-green mixture was diluted with $CHCl_3$ (10 mL), and EDTA (20 mL aq.) was added. The two-phase mixture was vigorously stirred overnight and filtered through a vacuum membrane filter. The precipitate was washed with water and ethanol. Then the membrane with the solid was moistened with toluene, folded, placed into a Soxhlet glass thimble with sintered bottom and extracted with toluene for 1 d. The greenish extract was discarded and the solid phthalocyanine remaining in the thimble was peeled off the membrane under sonication in toluene, the solvent was evaporated, and a bluish-green powder of compound **1** was dried in vacuo (58 mg, 56%); m.p. > 400 °C. FT-IR (neat): $\tilde{\nu}$ = 2919, 2852, 1603, 1586, 1574, 1485, 1398, 1277, 1251, 1173, 1114, 1095, 1053, 924, 892, 833, 791 cm^{-1}. $C_{160}H_{128}N_{16}O_{24}Zn$ (2724.20): calcd. C 70.54, H 4.74, N 8.23; found C 70.64, H 5.00, N 8.24.

Preparation of the NMR Sample of [1·4Cu$^+$]: Solid compound **1** (5.4 mg, 2.0 μmol) and $[Cu(CH_3CN)_4](PF_6)$ (3.0 mg, 8.0 μmol) were dissolved in a mixture of $CDCl_3$ (0.3 mL) and CD_3CN (0.3 mL) under sonication in the presence of several crystals of ascorbic acid. The dark-green solution was filtered through a small piece of cotton into an NMR tube. ^{1}H NMR [400 MHz, $CDCl_3$/CD_3CN (1:1), 55 °C]: δ = 4.18 (br. s, 16 H, γ-OCH_2), 4.29 (br. s, 16 H, β-OCH_2), 4.66 (br. s, 16 H, δ-OCH_2), 4.74 (br. s, 16 H, α-OCH_2), 6.76 (br. s, 8 H, 5,6-H Phen), 7.39 (br. d, 16 H, *m*-H), 7.68 (m, 16 H, 3,8- + 4,7-H Phen), 7.90 (br. d, 16 H, *o*-H), 8.87 (br. s, 8 H, H_{Pc}) ppm. ESI MS: calcd. for $C_{160}H_{128}CuN_{16}O_{24}Zn$ [**1** + Cu]$^+$

2787.75, found 2786.80; calcd. for $C_{160}H_{128}N_{16}O_{24}Zn$ [**1**]$^+$ 2724.20, found 2723.89; calcd. for $C_{160}H_{128}Cu_2N_{16}O_{24}Zn/2$ [**1** + 2Cu]$^{2+}$ 1426.29, found 1425.65.

X-ray Crystallography of 7·3CH_2Cl_2: Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer with a CCD area detector (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å, ω-scans). $C_{43}H_{38}Cl_6N_4O_6$, M = 919.47, monoclinic, space group $P2_1/n$, a = 12.4002(7) Å, b = 22.2817(12) Å, c = 16.1477(8) Å, β = 103.4510(10)°, V = 4339.2(4) Å^3 (120 K), Z = 4, $D_{calcd.}$ = 1.407 g/cm^3, 40058 measured reflections, 9394 [R(int) = 0.0426] independent reflections with $F^2 > 2\sigma(I)$, μ = 0.448 cm^{-1}, R_1 = 0.0681, wR_2 = 0.1781. The semi-empirical method SADABS[40] was applied for the absorption correction. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms in the complexes were placed geometrically and included in the structure-factor calculation in the riding-motion approximation. All the data reduction and further calculations were performed using the SAINT[41] and SHELXTL-97[42] program packages. CCDC-891876 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): ^{1}H, ^{13}C NMR and FT IR spectra of all synthesized compounds, fragment of crystal packing of **7**.

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