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A supramolecular approach for the formation of fullerene–phthalocyanine dyads

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A supramolecular Pc–C_{60} dyad with pseudorotaxane-like geometry has been assembled in solution by the threading of a dibenzylammonium unit attached to a fullerene through the crown ether of an unsymmetrically substituted phthalocyanine, which contains a DB24C8 moiety. Spectroscopic data as well as electrochemical studies suggest a conformation for the complex in which the two bulky subunits are far apart from each other, thus preventing electronic interactions between both electroactive subunits.

Introduction

[60]Fullerenes are one of the acceptor units most frequently used in the construction of photovoltaic devices on account of their unique electrochemical properties—namely their ability to reversibly accept up to six electrons.[1] On the other hand, phthalocyanines[2] (Pcs) are the best known azaporphyrin analogues. They are very versatile and stable aromatic chromophores with unusual physico-chemical properties that can play a crucial role in different fields of materials science. Therefore, much attention has been devoted to the study of Pcs as organic building blocks applicable as active components in gas sensors, electrochromic devices, field effect transistors and photovoltaic cells. These two redox-active moieties have been covalently linked following different synthetic strategies to form phthalocyanine–fullerene hybrids.[3] In the case of the dyad reported by us in which the Pc and C_{60} subunits are connected through a pyrrolidine spacer, the presence of inter- and intramolecular electronic interactions in the ground state has been ascertained for the first time by electrochemical studies.[3d]

Supramolecular chemistry represents an elegant alternative approach for the construction of functional systems by means of noncovalent bonding interactions.[4] Recently, supramolecular C_{60}[5] and Pc[6] dimers have been self-assembled *via* hydrogen bonding between complementary recognition motifs. Some of them[5a,6] are based on the recognition motif developed by one of us, involving medium-sized crown ether macrocycles, such us dibenzo-24-crown-8 (DB24C8), and secondary dialkylammonium cations, *e.g.*, dibenzylammonium (DBA^+) as its PF_6^- salt.[7] These two components assemble in solution and in the solid state to form stable complexes with a pseudorotaxane superstructure. Although some complexes between C_{60} and planar aromatic macrocycles such as porphyrins[8] or porphyrazines[9] have been reported, there are no supramolecular hydrogen bonded Pc–C_{60} dyads described in the literature to our knowledge.

Here, we report the first example of a Pc–C_{60} pseudorotaxane-like complex formed in solution [**1**·**2**-H][PF_6] (Fig. 1). This inclusion complex consists of two components: an unsymmetrically substituted phthalocyanine **1** containing a DB24C8 unit attached to the Pc core, and a C_{60} derivative **2**-H·PF_6,[5a] in which a secondary dibenzylammonium moiety has been linked to the C_{60} by a modified Bingel reaction.[10] These two components, which both contain different electroactive subunits, can be assembled in a $CHCl_3$ solution by threading the dibenzylammonium chain of **2**-H·PF_6 through the DB24C8 ring of component **1**, thus forming the typical stable pseudorotaxane-like complex.[7] By arranging the two electroactive subunits in such a geometry we expected them to be close enough to exhibit electronic coupling between the Pc and C_{60} components. For this reason, we have carried out electrochemical studies, but these did not reveal a measurable interaction as reflected in the redox properties upon complexation.

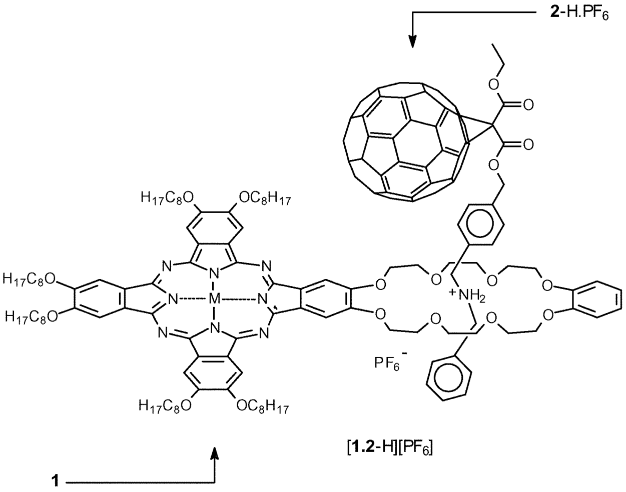

Fig. 1 Structure of proposed [2]pseudorotaxane [**1**·**2**-H][PF_6].

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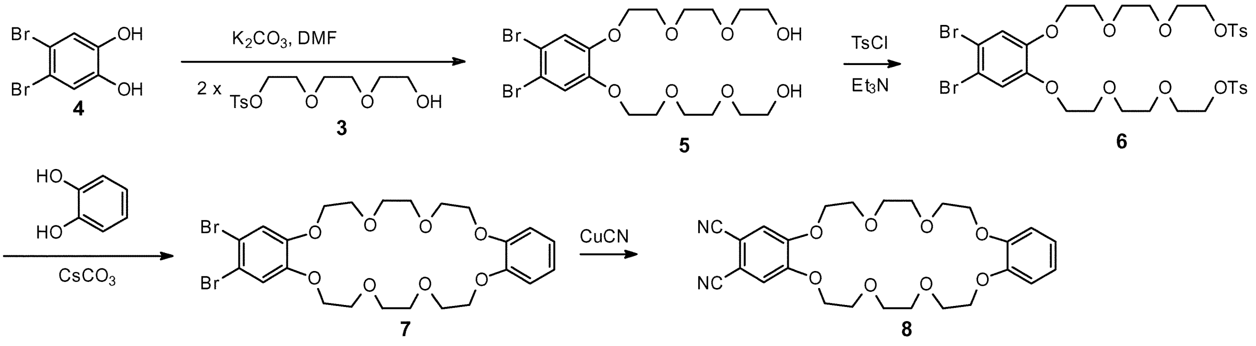


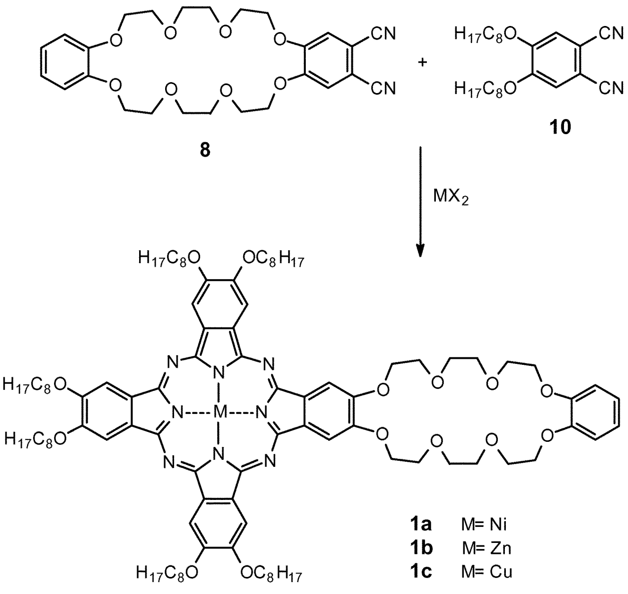
Scheme 1 Synthesis of the dicyano-24C8 derivative **8**.

Results and discussion

Synthesis

The dicyano-24C8 derivative **8** was prepared following a standard stepwise procedure,[11] the key step of which is the formation (Scheme 1) of a crown ether, as a result of a macrocyclization reaction of catechol with the diol **5** *via* its bis(toluene-*p*-sulfonate) derivative **6**. Under semi-high-dilution conditions (Cs_2CO_3–MeCN, in the presence of CsOTs and LiBr), the dibromo-DB24C8 derivative **7** was obtained in 80% yield. Further conversion into the dinitrile derivative by means of the Rosenmund–von Braun reaction gave rise to the Pc precursor **8** in 55% yield. This last step was highly dependent on the experimental conditions, affording different yields of compound **8** for each batch, and, in some cases, variable amounts of a by-product which has been identified as the mononitrile derivative **9**.

The convergent synthesis of phthalocyanines **1a–c** is outlined in Scheme 2 and synthetic details are given in the Experimental section. The three compounds were obtained in 16–30% yield by the crossover condensation of the dicyano-24C8 **8** and 4,5-bis(octyloxy)phthalonitrile (**10**)[12] in the presence of the corresponding metal salt. These reactions afforded mixtures of all the possible phthalocyanines. In each case, they were separated and purified by flash chromatography. Compounds **1a–c** were characterized by mass spectrometry and by NMR and UV–vis spectroscopy. Thus, Pcs **1a**, **1b**, and **1c** showed their corresponding molecular ions at *m*/*z* = 1708.8, 1715.1 and 1713.9, respectively. Their UV–vis spectra exhibited absorptions in the range λ_{max} = 671–678 nm that are assigned to their Q-bands. The ^1H NMR spectra of compounds **1a** and **1b** show well-resolved sets of resonances which, in agreement with their UV–vis spectra, suggest that these DB24C8–phthalocyanines do not form strong aggregates in solution. The aromatic phthalocyanine protons appear at δ = 8.3–8.2 and 9.0–8.9 for **1a** and **1b**, respectively.



Scheme 2 Synthesis of phthalocyanines **1a–c**.

Complexation studies

^1H NMR spectroscopy has proven to be the best technique for the characterization in solution of [2]pseudorotaxane complexes formed between DB24C8 type macrocycles and dibenzylammonium hexafluorophosphate derivatives.[7] The main reason is the unusually slow host–guest exchange on the ^1H NMR time-scale at room temperature, a phenomenon which gives rise to three sets of resonances assigned to i) the two free components and ii) the 1 : 1 complex. This situation allows the determination of the stoichiometry and the association constant (K_a) of the complex by integration of the signals of the three species at equilibrium. Moreover, the ^1H NMR spectra of these types of complexes display some diagnostic signals that help in their characterization, for instance, for the CH_2N^+ protons of the complexed ammonium salt and for the 1,2-dioxybenzene protons on the DB24C8 macrocycle. Since the pseudorotaxane-like superstructures of some of these complexes, especially the one formed between DB24C8 and DBA·PF_6, have been determined by X-ray crystallography and NOE studies,[7] the superstructures of complexes based on this particular recognition motif can be shown to be similar by simply analyzing their ^1H NMR spectra.

The ^1H NMR spectrum (500 MHz, 298 K) of a 1 : 1 mixture of **1a** and **2**-H·PF_6 (c = 2.4 mM) in $CDCl_3$ (Fig. 2) displays some of the above-mentioned, characteristic resonances, indicating that complexation is taking place by threading of the fullerene-containing diammonium salt through the DB24C8 subunit of compound **1a**. In particular, the characteristic high field shift and splitting of the resonances assigned to the 1,2-dioxybenzene unit are observed. As in the case of the phthalocyanine dimer already reported by us,[6] the signals of the Pc core become nonequivalent and strongly upfield-shifted upon complexation. Fortunately, diagnostic

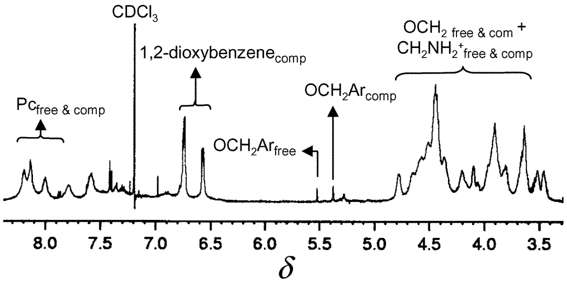


Fig. 2 Partial ^1H NMR spectrum (500 MHz, 298 K, $CDCl_3$) of a 1 : 1 mixture of **1a** and **2**-H·PF_6.

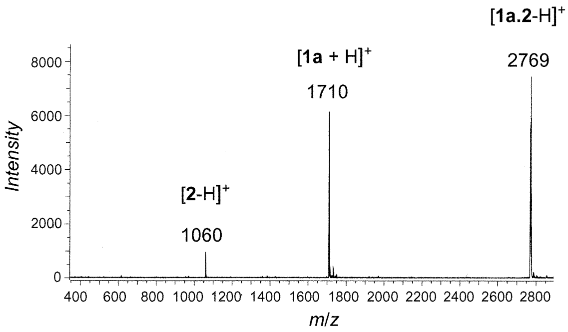


Fig. 3 MALDI-TOF mass spectrum (matrix: dithranol) of a mixture of **1a** and **2**-H·PF_6.

signals for both free and complexed $ArCH_2O$ subunits on the fullerene component **2**-H·PF_6 were identified. The comparison of the intensities of these two singlets allowed us to determine the association constant (K_a = 15300 M^{-1}), which is similar in magnitude to that reported for related complexes in the same solvent.[5a,7]

The formation of the 1 : 1 complex [**1a**·**2**-H][PF_6] was also evidenced by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry using dithranol (anthracene-1,8,9-triol) as the matrix. The spectrum recorded from a 1 : 1 mixture of the fullerene-containing diammonium salt **2**-H·PF_6 and the crowned phthalocyanine **1a** displays an intense peak at *m*/*z* = 2769 (Fig. 3) which corresponds to the supramolecular ion [**1a**·**2**-H]$^+$ after loss of the PF_6^- counterion.

The UV–vis spectrum of a dilute solution ($c = 3.2 \times 10^{-6}$ M) of **1a** in CH_2Cl_2 did not change significantly upon addition of an equimolar amount of the fullerene derivative **2**-H·PF_6, thus indicating negligible electronic interactions between the chromophores in the ground state. This observation is consistent with the electrochemical results discussed in the following section.

Similar results to those described above were obtained for the complexation of **1b** and **2**-H·PF_6 to yield [**1b**·**2**-H][PF_6]. Complex [**1c**·**2**-H][PF_6] could not be studied by ^{1}H NMR due to the presence of the paramagnetic central ion.

Electrochemical studies

The redox properties of both the individual components **1b** and **2**-H·PF_6 and the [2]pseudorotaxane [**1b**·**2**-H][PF_6] were studied by cyclic voltammetry (CV) at room temperature in CH_2Cl_2 (+ 0.1 M NBu_4PF_6). Potentials were measured (Table 1) against the ferrocene/ferricinium (Fc/Fc$^+$) couple as internal reference. Since **1a** and **1b** have similar complexing abilities with **2**-H·PF_6, compound **1b** was selected for these studies because of its better electron-donor character. As previously reported,[5a] two quasi-reversible reduction waves at $E_{1/2}$ = −1.08 and −1.45 V were observed (Fig. 4) for the fullerene-containing diammonium salt **2**-H·PF_6. Upon addition of the crown ether phthalocyanine **1b**, these waves did not change significantly, revealing that complexation does not influence the reduction properties of the fullerene component and suggesting that the electroactive units are not close enough to allow measurable electronic interactions between them.

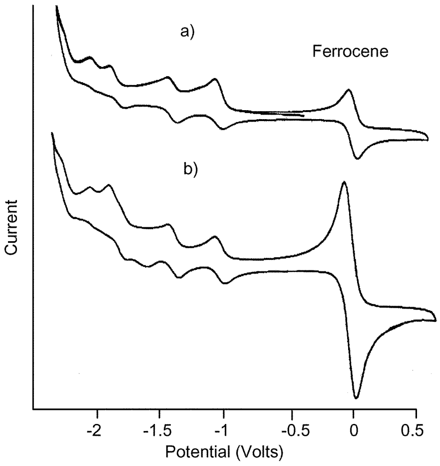


Fig. 4 Cyclic voltammograms (sweep rate 100 mV s^{-1}) for a) **2**-H·PF_6 and b) a 1 : 1 mixture of **1b** and **2**-H·PF_6 (6.4×10^{-4} M), in CH_2Cl_2 (+ 0.1 M $TBAPF_6$) at room temperature.

Molecular modeling studies have confirmed that the fullerene-containing diammonium salt can adopt several conformations in the complex in which the carbon sphere is too far from the phthalocyanine ring. Probably, and in agreement with the ^{1}H NMR spectrum of the complex, the C_{60} subunit prefers to be far from the phthalocyanine ring of **1b** for steric reasons.

Conclusions

A supramolecular approach has been applied successfully for the first time to the preparation of fullerene–phthalocyanine dyads. A supramolecular complex has been formed by attaching covalently both electroactive subunits to a dibenzylammonium hexafluorophosphate salt and a DB24C8 macrocycle, respectively, to allow molecular recognition by hydrogen bonding between these two recognition motifs, namely, DB24C8 and (DBA)$^+$. Electrochemical and UV–vis studies failed to reveal measurable electronic interactions between the Pc and the C_{60} subunits in the ground state. The preparation of related noncovalent Pc–C_{60} dyads as targets for electron and energy transfer processes is under investigation.

Experimental

Chemicals were purchased from Aldrich Chemical Co. and used as received without further purification. Compounds **3** and **4** were prepared according to refs. 13 and 11, respectively. UV–vis spectra were recorded with a Hewlett-Packard 8453 instrument. IR spectra were recorded on a Bruker Vector 22 spectrophotometer. FAB-MS and HRMS spectra were determined on a VG AutoSpec instrument. MALDI-TOF MS were recorded with a Bruker Reflex III spectrometer. NMR spectra were recorded with Bruker WM-200-SY, Bruker AC-300 and Bruker DRX-500 instruments. Column chromatography was carried out on silica gel Merck-60 (230–400 mesh, 60 Å), neutral alumina 90 active and TLC on aluminium sheets precoated with silica gel 60 F_{254} (E. Merck).

Table 1 Electrochemical data[a] of compounds **1b** and **2**-H·PF_6 and the supramolecular complex [**1b**·**2**-H][PF_6]

Compound	E_{ox}	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4
1b	+0.03 (185)	−1.56 (190)	−1.87 (160)		
2-H·PF_6	—	−1.08 (88)	−1.45 (110)	−1.97 (irrev.)	−2.13 (irrev.)
[**1b**·**2**-H][PF_6]	—	−1.05 (110)	−1.42 (118)	−1.96 (irrev.)	−2.11 (irrev.)

[a] $E_{1/2}$ potential given in V *vs.* Fc/Fc$^+$ observed by cyclic voltammetry on glassy carbon in CH_2Cl_2 solutions containing 0.1 M NB_4PF_6; ΔE values in mV are in parentheses at v = 0.1 V s^{-1}.

1,2-Bis{2′-[2″-(2‴-hydroxyethoxy)ethoxy]ethoxy}-4,5-dibromobenzene (5)

A mixture of **3**[13] (13.98 g, 45.94 mmol), 4,5-dibromocatechol (**4**)[11] (3.06 g, 11.4 mmol) and potassium carbonate (21.14 g, 153 mmol) in dimethylformamide (80 ml) was stirred under argon at 100 °C for 2.5 days. The mixture was allowed to cool down to room temperature and afterwards it was poured into water. The organic layer was extracted with dichloromethane, washed four times with water, and dried over $MgSO_4$. Chromatography on silica gel of the obtained oil using an 8 : 1 mixture of dichloromethane and methanol as eluent provided **5** as an oil. Yield 6.08 g (100%). Selected spectroscopic data: ^{1}H NMR δ ($CDCl_3$): 7.13 (s, 2H, arom.), 4.20–3.60 (4 × m, 24H, OCH_2). LSIMS-MS (*m*-NBA) *m*/*z*: 531 $(M+H)^+$. Found: C, 40.2; H, 5.0. Calc. for $C_{18}H_{28}Br_2O_8$: C, 40.6; H, 5.3%.

1,2-Bis{2′-[2″-(2‴-tosyloxyethoxy)ethoxy]ethoxy}-4,5-dibromobenzene (6)

A mixture of the dibromide **5** (6.08 g, 11.4 mmol), tosyl chloride (8.41 g, 44.1 mmol) and triethylamine (2.31 g, 22.8 mmol) in dichloromethane (85 ml) was stirred at room temperature for 24 h until the reaction was complete. The solution was poured into dilute hydrochloric acid and the organic layer was extracted, washed four times with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel using a 1 : 1 mixture of ethyl acetate and hexanes, and then ethyl acetate, as eluents. Compound **6** was collected from the second fraction as an oil. Yield 5.85 g (61%). Selected spectroscopic data: ^{1}H NMR δ ($CDCl_3$): 7.78 (d, J = 8.3 Hz, 4H, arom., tosyl ring), 7.32 (d, J = 8.3 Hz, 4H, arom., tosyl ring), 7.12 (s, 2H, arom.), 4.18–4.05 (m, 8H, OCH_2), 3.85–3.66 (2 × m, 16H, OCH_2), 2.43 (s, 6H, CH_3). LSIMS-MS (*m*-NBA) *m*/*z*: 839 $(M+H)^+$. Found: C, 45.2; H, 5.1. Calc. for $C_{32}H_{40}Br_2O_{12}S_2$: C, 45.5; H, 4.8%.

2,3-Dibromo-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (7)

To a mixture of Cs_2CO_3 (4.53 g, 13.90 mmol) in dry acetonitrile (460 ml) a solution of catechol (383 mg, 3.48 mmol) in dry acetonitrile (230 ml) was added dropwise at 75 °C under argon. The reaction mixture was heated under reflux for 2 h and then a solution of the bis(toluene-*p*-sulfonate) **6** (2.92 g, 3.48 mmol) in acetonitrile (231 ml) was added dropwise. After addition of CsOTs (1 g, 3.3 mmol) and LiBr (605 mg, 6.97 mmol), the mixture was stirred at reflux temperature for 2.5 days to drive the reaction to completion. The solvent was evaporated under reduced pressure and the residue was suspended in dichloromethane, washed with water and dried over magnesium sulfate. Filtration and evaporation of the solution gave a white solid which was chromatographed on silica gel using ethyl acetate as eluent. Yield 1.69 g (80%). Selected spectroscopic data: ^{1}H NMR δ ($CDCl_3$): 7.06 (s, 2H, arom.), 6.88 (br s, 4H, arom.), 4.21–4.05 (m, 8H, OCH_2), 3.99–3.85 (m, 8H, OCH_2), 3.81 (s, 8H, OCH_2). LSIMS-MS (*m*-NBA) *m*/*z*: 606 $(M + H)^+$, 629 $(M + Na)^+$. Found: C, 47.1; H, 5.2. Calc. for $C_{24}H_{30}Br_2O_8$: C, 47.5; H, 5.0%.

2,3-Dicyano-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (8)

A mixture of **7** (1.69 g, 2.78 mmol) and CuCN (996 mg, 11.12 mmol) was heated under reflux in dimethylformamide (42 ml) under argon for 24 h. After this time the reaction was complete and the solution was allowed to cool down to room temperature and subsequently poured into 33% aqueous ammonia (30 ml). Air was bubbled through the blue solution for 2 h, and afterwards the mixture was extracted with dichloromethane, washed with water and dried over $MgSO_4$. After filtration and evaporation, the residue was chromatographed on deactivated (5% H_2O) neutral aluminium oxide using ethyl acetate as eluent. Yield 762 mg (55%). Selected spectroscopic data: ^{1}H NMR δ ($CDCl_3$): 7.11 (s, 2H, arom.), 6.89, 6.88 (AA′BB′ system, 4H, arom.), 4.22–4.11 (m, 8H, OCH_2), 3.96–3.87 (m, 8H, OCH_2), 3.82 (s, 8H, OCH_2). ^{13}C NMR δ ($CDCl_3$): 152.3, 148.8, 121.5, 116.4, 115.7, 114.0, 108.9, 71.6, 71.3, 70.0, 69.3. IR (KBr) ν: 3127, 3062 (CH), 2930, 2892, 2874, 2838 (CH), 2231 (CN), 1591, 1520, 1507, 1451, 1356, 1291, 1253, 1228, 1216, 1134, 1100, 1058, 1035, 969 cm^{-1}. LSIMS-MS (*m*-NBA) *m*/*z*: 498 (M^+), 499 $(M+H)^+$, 521 $(M+Na)^+$. Found: C, 62.3; H, 6.5; N, 5.4. Calc. for $C_{26}H_{30}N_2O_8$: C, 62.6; H, 6.1; N, 5.6%.

2-Cyano-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo-[*b*,*n*][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (9)

Compound **9** was obtained in variable yields during the synthesis of the dicyano derivative **8**, and isolated from the first eluted fractions of the column chromatography. ^{1}H NMR δ ($CDCl_3$): 7.40 (dd, J = 4, 8.3 Hz, 1H, H^3), 7.10 (d, J = 8.3 Hz, 1H, H^4), 6.95–6.80 (m, 5H, H^1 + H catechol), 4.20–4.00 (2m, 8H, OCH_2), 3.80–3.70 (m, 8H, OCH_2), 3.65 (s, 8H, OCH_2). LSIMS-MS (*m*-NBA) *m*/*z*: 473 (M^+), 474 $(M + H)^+$, 496 $(M + Na)^+$.

[9,10,16,17,23,24-Hexakis(octyloxy)-$2^2,2^3,2^5,2^6,2^8,2^9,2^{18},2^{19},2^{21},2^{22},2^{24},2^{25}$-dodecahydrobenzo[*n*][1,4,7,10,13,16,19,22]-octaoxacyclotetracosino[2,3-*b*]phthalocyaninato]nickel(II) (1a)

A mixture of the phthalonitrile derivative **8** (30 mg, 0.06 mmol), 4,5-bis(octyloxy)phthalonitrile **10** (69 mg, 0.18 mmol) and $Ni(OAc)_2 \cdot 4H_2O$ (18 mg, 0.07 mmol) in *N*,*N*-dimethylaminoethanol (0.5 ml) was stirred at 140 °C for 24 h. After addition of methanol, the dark solid was filtered and washed with the same solvent. Chromatography of the crude on silica gel using $CHCl_3$ and then a 50 : 1 mixture of $CHCl_3$ and MeOH afforded the nickel phthalocyaninate **1a** which was collected as a green solid from the second fraction. Yield 16 mg (16%). ^{1}H NMR δ ($CDCl_3$): 8.27–8.25 (2 × br s, 8H, Pc ring), 6.84, 6.83 (AA′BB′ system, 4H, arom), 4.71–3.95 (6 × m, 36H, OCH_2), 2.25–2.15, 1.89–1.75, 1.65–1.25, 1.09–0.99 (5 × m, 90H, aliphatic); UV–vis ($CHCl_3$) (log ε/dm^3 mol^{-1} cm^{-1}) λ_{max} 289 (4.89), 310 (4.78), 411 (4.36), 605 (4.39), 643 (sh, 4.45), 671 nm (5.21); MALDI-TOF-MS (dithranol) *m*/*z* 1709 (M^+).

[9,10,16,17,23,24-Hexakis(octyloxy)-$2^2,2^3,2^5,2^6,2^8,2^9,2^{18},2^{19},2^{21},2^{22},2^{24},2^{25}$-dodecahydrobenzo[*n*][1,4,7,10,13,16,19,22]-octaoxacyclotetracosino[2,3-*b*]phthalocyaninato]zinc(II) (1b)

A mixture of **8** (30 mg, 0.06 mmol), 4,5-bis(octyloxy)phthalonitrile **10** (69 mg, 0.18 mmol) and $Zn(OAc)_2 \cdot 2H_2O$ (16 mg, 0.07 mmol) in *N*,*N*-dimethylaminoethanol (0.5 ml) was stirred at 140 °C under Ar for 24 h. After addition of methanol the green solid was filtered and washed with the same solvent. Chromatography of the crude material on silica gel using $CHCl_3$ and then a 100 : 1 mixture of $CHCl_3$ and MeOH afforded the zinc phthalocyaninate **1b** which was collected as a green solid from the second fraction. Yield 31 mg (30%). ^{1}H NMR δ ($CDCl_3$): 8.94, 8.90 (2 × br s, 8H, Pc ring), 6.72, 6.40 (AA′BB′ system, 4H, arom.), 4.70–4.55, 4.28–2.50, (6 × m, 36H, OCH_2), 2.25–2.02, 1.86–0.60 (5 × m, 90H, aliphatic); UV–vis ($CHCl_3$) (log ε/dm^3 mol^{-1} cm^{-1}) λ_{max} 355 (4.56), 612 (4.11), 656 (sh, 4.15), 678 nm (4.91); MALDI-TOF-MS (dithranol) *m*/*z*: 1715 (M^+).

[9,10,16,17,23,24-Hexakis(octyloxy)-2^2,2^3,2^5,2^6,2^8,2^9,2^{18},2^{19},2^{21},2^{22},2^{24},2^{25}-dodecahydrobenzo[*n*][1,4,7,10,13,16,19,22]-octaoxacyclotetracosino[2,3-*b*]phthalocyaninato]copper(II) (1c)

A mixture of **8** (31 mg, 0.062 mmol, 4,5-bis(octyloxy)phthalonitrile **10** (120 mg, 0.31 mmol) and $Cu(OAc)_2 \cdot H_2O$ (27 mg, 0.134 mmol) in pentanol (10 ml) was refluxed under Ar in the presence of DBU (7 drops) for 48 h. The reaction mixture was allowed to cool down to room temperature and subsequently methanol (20 ml) was added. The resulting precipitate was filtered, washed with methanol and dried. The green solid was chromatographed on silica gel using chloroform as eluent. Yield 23 mg (22%). UV–vis ($CHCl_3$) (log ε/dm^3 mol^{-1} cm^{-1}) λ_{max} 292 (4.87), 339 (4.85), 401 (4.68), 627 (4.66), 678 nm (4.79); MALDI-TOF-MS (dithranol) *m*/*z*: 1714 (M^+).

Electrochemical studies

All electrochemical experiments were performed on a BAS 100W electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN) at room temperature with a three-electrode configuration in CH_2Cl_2 containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte, which was recrystallized twice from ethanol and dried under vacuum. A glassy carbon (GC, 3 mm) was used as the working electrode and the counter electrode was a platinum wire (1 mm). A non-aqueous Ag/Ag$^+$ electrode served as reference and ferrocene served as internal reference. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. The scan rate was generally 100 mV s^{-1} unless otherwise specified.

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