Preparation and characterization of first optically active rigid phthalocyanine dimers

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Abstract—The first optically active rigid covalently linked by enantiomerically pure (*R*)- or (*S*)-BINOL metal-free phthalocyanine dimers have been prepared and characterized using electronic absorption, CD, MCD, MS, and NMR techniques as well as semi-empirical molecular orbital calculations.
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High thermal and chemical stability of phthalocyanines (Pcs) along with their unique optical properties promote an extensive use of these molecules as dyes and pigments and more recently as materials for nonlinear optics, optical recording media, light harvesting systems, semiconductors, chemical sensors, photodynamic therapy of cancer, and catalysis.[1] In spite of the large academic interest, the first optically active Pcs[2] were reported only in 1993 and since then, several groups published a limited number of reports on these systems.[3,4] Importantly, to date only monomeric optically active Pcs were reported, while optically active rigid covalently linked Pc dimers remain unknown. Such chiral cavity-containing dimers can be interesting as flexible-size tweezers for molecular recognition of chiral substrates[5] and exceptional platforms for enantioselective catalytic systems.[6] In this Letter we report a preparation and characterization of the chiral Pc enantiomers in which two Pc macrocycles are linked by the *R* or *S* enantiomers of BINOL [(*R*)-(+)- or (*S*)-(−)-1,1′-bi-2-naphthol] (Scheme 1). The preparation of **2R** and **2S** can serve as a proof of the general concept for the preparation of chiral dimeric Pcs, while application of transition-metal complexes of **2S** and **2R** in asymmetric catalysis and molecular recognition will be published as a separate full paper. In synthesis of **2S** and **2R**, the chiral BINOL linkers were chosen because of their well-documented optical stability and strong as well as clearly understandable chiral
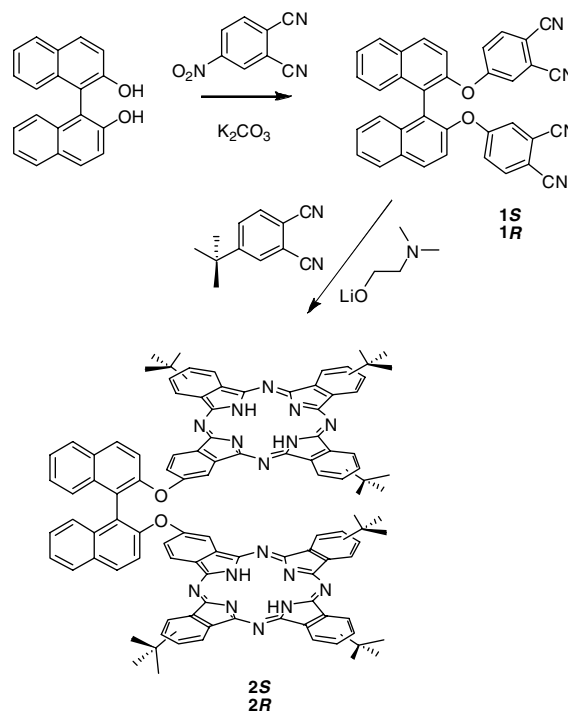
Scheme 1. Synthetic pathway for the preparation of **2S** and **2R**.

field described in the past, which is convenient for circular dichroism (CD) data analysis.[3]

Both **2S** and **2R** were prepared by cross condensation of enantiomerically pure nitriles[7] **1S** or **1R** with 18-fold excess of commercially available 4-*tert*-butyl-phthalonitrile

in the presence of lithium *N,N*-dimethylaminoethanolate in dry refluxing *N,N*-dimethylaminoethanol for 24 h. Target complexes **2S** and **2R** were purified by using several column chromatography separations on silica followed by a set of size-exclusion filtrations and finally chromatography on alumina. Resulting blue microcrystalline compounds were recrystallized from chloroform-methanol and dried in vacuum producing the analytically and enantiomerically pure **2S** and **2R** in ca. 7–10% yield (Supplementary data).[8] Although these yields look low, they are in the typical range for the preparation of low-symmetry[1] as well as chiral[2] Pcs and currently are the subject for optimization in our laboratory. The purity and elemental composition of **2S** and **2R** was confirmed by elemental analysis as well as high-resolution ESI-MS method. Due to the presence of *tert*-butyl groups in **2S** and **2R**, they are soluble in aromatic and aliphatic hydrocarbons, variety of chlorinated solvents, acetone, and THF, while their solubility in short-chain alcohols and the majority of highly polar solvents is low.

Compounds **2S** and **2R** appear in APCI-MS spectra as single [M+1]$^+$ peaks observed at 1648.7 *m/z* and the stability of dimers has been confirmed by additional MS–MS experiments according to which cleavage of dimeric structure occurs only at higher (>60%) collision energies as compared to the dissociation of methyl groups from the *tert*-butyl substituents (Supplementary data).

In analogy with the previously described covalently linked Pc dimers[9] compounds **2S** and **2R** consist of the mixture of positional and *syn* and *anti* isomers (with respect to the position of peripheral *tert*-butyl substituents) as can be seen from NMR spectra of as also confirmed by LC–MS data (Supplementary data). The presence of numerous positional isomers, however, should not affect any potential applications of **2S** and **2R** because of the well-known negligible influence of peripheral *tert*-butyl groups on electronic structure and spectroscopic properties of metal-free and transition-metal Pcs.[1]

Electronic absorption, circular dichroism (CD), and magnetic circular dichroism (MCD) spectra of the optically active dimers **2S** and **2R** in chloroform along with calculated excitation energies and oscillator strengths are presented in Figure 1.

Q-band region of electronic absorption, CD, and MCD spectra of **2S** and **2R** clearly reflects both dimeric nature and low symmetry of these compounds. In analogy with earlier discussed non-chiral Pc dimers,[9–11] the exciton coupling in cofacial *syn* metal-free Pc dimer of effective symmetry D_{2d} should result in a broad blue-shifted (as compared to monomer) Q-band accompanied by a weak tail on its red side. Indeed, the strongest broad absorption peak observed in **2S** and **2R** has maxima at 637 nm and is typical for cofacial Pc dimers. In addition to this band, three shoulders located at ca. 610, 660, and 700 nm were observed in absorption spectra of **2S** and **2R**. The presence of these bands has also been confirmed by MCD spectra according to which Q-band region of **2S** and **2R** consists of four Faraday *B*-terms with two
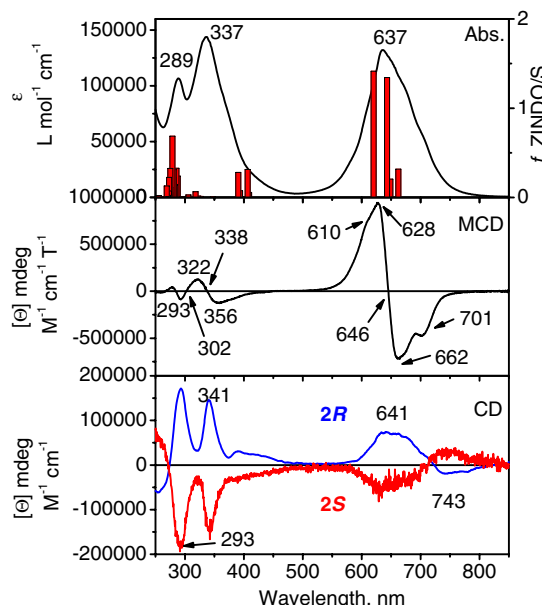

Figure 1. Electronic absorption, MCD, and CD spectra (from top to bottom) of **2S** and **2R** in chloroform. ZINDO/S calculated energies and oscillator strengths are overlaid with the absorption spectrum.

positive and two negative signs located at 610, 628, 662, and 701 nm with energies close to those observed in absorption spectra of **2S** and **2R**. The presence of two prominent shoulders or bands at ca. 660 and 700 nm in absorption and MCD spectra of chiral dimers, respectively, require either the lowering of effective symmetry of **2S** and **2R** from D_{2d} to C_1 (Fig. 2) or presence of significant amount of *anti* isomer, which should have more monomer-like absorption.[9] Indeed, similar MCD spectra have been observed in the case of covalently linked by naphthalene or anthracene cofacial Pc dimers.[9]

Although the quantitative interpretation of exciton coupling in low-symmetry cofacial Pc dimers is a very difficult task,[9,10] four allowed transitions are expected for C_1 symmetry dimers **2S** and **2R** as presented in Figure 2.[11]

In order to confirm band assignments in absorption and MCD spectra of **2S** and **2R**, we conducted semi-empiri-
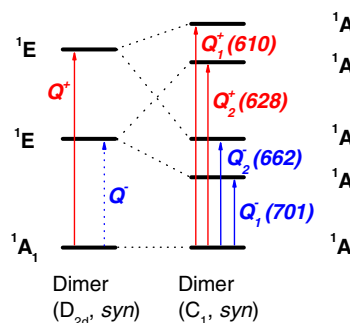

Figure 2. State energy diagram for exciton coupling in Pc dimer with D_{2d} and C_1 symmetries. The solid and broken line arrows mark allowed and forbidden transitions, respectively. Experimentally observed transition energies in **2S** and **2R** are shown in parentheses.

cal calculations at ZINDO/S level.[12] As expected for Pc dimers of C_1 symmetry (Fig. 2) four bands with non-zero oscillator strengths have been predicted for UV–vis spectra of **2S** and **2R** in the Q-band region. All four bands originate from different configuration interactions between closely spaced HOMO–HOMO−1 and LUMO–LUMO+4 molecular orbitals with calculated transition energies and oscillator strengths very close to those observed in experiment (Fig. 1). Moreover, experimentally observed lower intensities for Q_1^- and Q_2^- components (which are forbidden in higher symmetry dimers) as compared to those in Q_1^+ and Q_2^+ components in UV–vis spectra of **2S** and **2R** are in excellent agreement with the semi-empirical calculations.

CD spectra of **2S** and **2R** are the mirror images of each other confirming chirality and enantiomeric purity of new dimers with prominent peaks at ca. 293, 341, 641, and 743 nm. The sign of CD spectrum of **2R** in B-band region is positive, while that in the case of **2S** is negative in agreement to earlier observed (*R*)- and (*S*)-BINOL containing Pcs.[3] The sign of CD spectrum in B-band and Q-band regions of all known monomeric BINOL containing Pcs remains the same, while it changed from positive to negative for **2R** and from negative to positive for **2S** in the Q-band region going from shorter to longer wavelengths reflecting strong excitonic coupling between BINOL linker and two macrocycles.[3,5]

Additional insight into interactions between two Pc macrocycles has been gained by electrochemical methods. The cyclic voltammetry (CV) as well as differential pulse voltammetry (DPV) of both **2S** and **2R** complexes in *o*-dichlorobenzene show two reversible oxidations observed at 0.17 and 0.51 V (Fc/Fc$^+$) and two reversible reduction processes observed at −1.39 and −1.85 V. As expected from the electron-donor nature of aryloxy-BINOL substituent, the first oxidation potential in **2S** and **2R** are lower while the first reduction potentials are higher as compared to those for metal-free tetra-*tert*-butyl phthalocyanine for which they were observed at 0.30 and −1.15 V (Fc/Fc$^+$), respectively. Although all four processes are two electronic in nature, the first oxidation wave both on CV and DPV is significantly broader as compared to the second oxidation as well as both reduction waves indicating the presence of interchromophore interactions, responsible for excitonic coupling observed in electronic absorption, MCD, and CD spectra of **2S** and **2R**.

In summary, as a proof of the concept, we have reported the first example of optically active rigid covalently linked phthalocyanine dimers **2S** and **2R** and characterized those by electronic absorption, CD, MCD, MS, and NMR techniques as well as semi-empirical molecular orbital calculations. The preparation and properties of transition-metal complexes of **2S** and **2R** will be reported in a future paper.

Acknowledgments

Supplementary data

Detailed experimental procedures and characterization data for **1S**, **1R**, **2S**, and **2R**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.016.

References and notes

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8. Spectroscopic data for **1S**, **1R**, **2S**, and **2R**. Compounds **1S** and **1R**: IR (KBr): 2225 cm^{-1} (CN); ^{1}H NMR (δ ppm, 500 MHz, CDCl$_3$): 8.26 (d, *J* = 9 Hz, 2H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.51 (td, *J* = 7.5, 1 Hz, 2H), 7.46 (d, *J* = 9 Hz, 2H), 7.36 (td, *J* = 7.5, 1 Hz, 2H), 7.28 (d, *J* = 9 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 2 Hz, 2H), 7.01 (dd, *J* = 9, 2.5 Hz, 2H); ^{13}C NMR (δ ppm, 125.67 MHz, CDCl$_3$): 160.94, 149.75, 135.13, 133.59, 131.88, 131.66, 128.82, 128.00, 126.74, 125.67, 123.09, 121.78, 121.56, 119.89, 117.35, 115.23, 114.84, 109.09. Compounds **2S** and **2R**: mp > 250 °C; UV–vis in CHCl$_3$, λ_{max} (ε M^{-1} cm^{-1}): 700 sh, 660 sh, 637 nm (132,000), 337 nm (144,000), 289 nm (107,000); ^{1}H NMR (δ ppm, 500 MHz, CDCl$_3$): 7.4–8.99 (m, 36H, Ar-H), 1.6–2.1 (m, 54H, *tert*-Bu), −4.3 (br s, 4H, NH); APCI-MS: 1648.7 [M+1]$^+$ (100%, see figures below); HRMS (ESI-MS): calcd for C$_{108}$H$_{94}$N$_{16}$O$_2$: 1646.7740; found: 1646.7745 (**2R**); 1646.7761 (**2S**); Elemental analysis, calcd for C$_{108}$H$_{96}$N$_{16}$O$_3$ (**2R**·H$_2$O): C, 77.86; H, 5.81; N, 13.45. Found: C, 77.90; H, 5.60; N, 12.73.
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12. The molecular geometry of **2** was optimized at semi-empirical PM3 level using HyperChem 7.51 software. Vertical excitation energies were calculated using configuration interaction approach using all single electron excitations within 7 eV at ZINDO/S level. For expansion coefficients, which describe Q-band region of **2**, see Supplementary data.