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Three-Step Synthesis and Absorption and Emission Properties of Peripherally Peralkynylated Tetrapyrazinoporphyrazines

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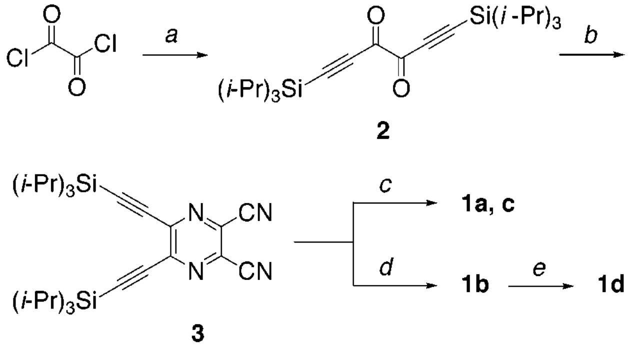
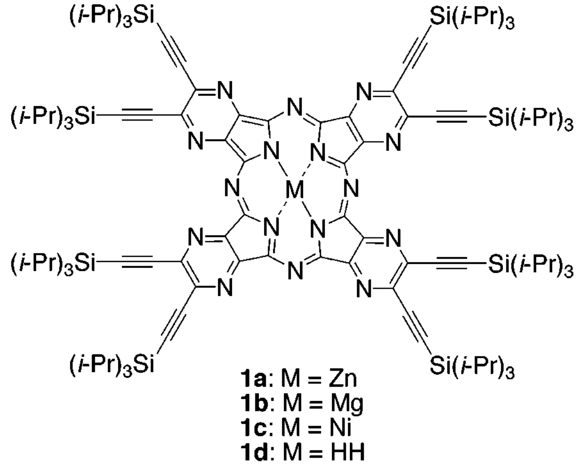
Peripheral alkynyl substitution of strongly absorbent chromophores, among them porphyrins[1] and the phthalocyanines,[2] is becoming an increasingly popular strategy for the design of functional dyes and molecular devices. The interest in structural modifications of this kind arises mainly from two factors. First, the acetylenic units enlarge the π-systems of the chromophores and induce bathochromic shifts in the electron absorption and emission spectra. Second, terminal alkynyl groups can be invoked to serve as covalent linkers for the assembly of delocalized multichromophor chains or two-dimensional polymer networks. Although peralkynylation of a given chromophor is often hampered by the tedious preparation of suitable precursors,[2a] a lower degree of alkynyl substitution frequently results in the formation of a mixture of regioisomers. We have therefore explored the possibility of employing small acetylenic building blocks for the rapid assembly of alkynylated chromophores. We report herein a short synthesis of 2,3,9,10,16,17,23,24-octalkynyl tetrapyrazinoporphyrazines[3] (TPyPors) **1** from oxalyl chloride, along with some of the optical properties associated with the 72 π-electrons of **1**.

Scheme 1[a]



[a] Reagents and conditions: (*a*) $(i\text{-Pr})_3$Si-C≡C-H, BuLi, CuBr, LiBr, THF, 0 °C, 85%; (*b*) diaminomaleic dinitrile, AcOH, 5 min., r.t., 81%; (*c*) Zn(OAc)$_2$ (for **1a**) or NiCl$_2$ (for **1c**), urea, quinoline, 140 °C, 5 min, 35%; (*d*) Mg(OBu)$_2$, BuOH, 15 min., reflux, 33%; (*e*) *p*-TsOH, THF, r.t., 5 min, 70%.



1a: M = Zn
1b: M = Mg
1c: M = Ni
1d: M = HH

Key intermediate for the preparation of peripherally peralkynylated TPyPors **1** is the terminally triisopropylsilyl-protected hexa-1,5-diyne-3,4-dione **2**, which we have recently made available by a copper-mediated alkynylation of oxalyl chloride[4] (Scheme 1). Reaction of **2** with diaminomaleic dinitrile in acetic acid furnished the 2,3-dialkynyl-5,6-dicyanopyrazine **3**[4] in 81% yield. The cyclotetramerization of **3** either using Mg(OBu)$_2$ in refluxing butanol or heating a quinoline solution of **3**, Zn(OAc)$_2$, and urea to 140 °C for 5 min furnished the corresponding metal-coordinated TPyPors **1a** and **1b** in ca. 30% yield. Using appropriate metal salts, other metalla-TPyPors (e.g., **1c** from **3** and NiCl$_2$) can be readily obtained by the urea/quinoline route. We were unable to prepare the metal-free TPyPor **1d** from the reaction of LiOPent in pentanol,[5] presumably as a result of protodesilylation of the alkynes and subsequent decomposition of the material under these more basic conditions.[6] However, the magnesium derivative **1b** can be easily demetalated by

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(4) Faust, R.; Weber, C.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron* **1997**, *53*, 14655−14670.

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(6) Controlled protodesilylation of **1a** and isolation of the corresponding octaethynyl TPyPor is possible using tetrabutylammonium fluoride in THF at −78 °C. Faust, R.; Weber, C., unpublished results.

(7) The high binding affinity of **1d** towards metal ions prevents its purification by standard column chromatography techniques on SiO$_2$ because of recomplexation with residual metal ions. Instead, **1d** was purified by repeatedly washing the crude reaction product with bidistilled water.

(8) Kobayashi, N. In *Phthalocyanines − Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim, 1993; Vol. 2, pp 97−161.

10.1021/jo9821527 CCC: $18.00

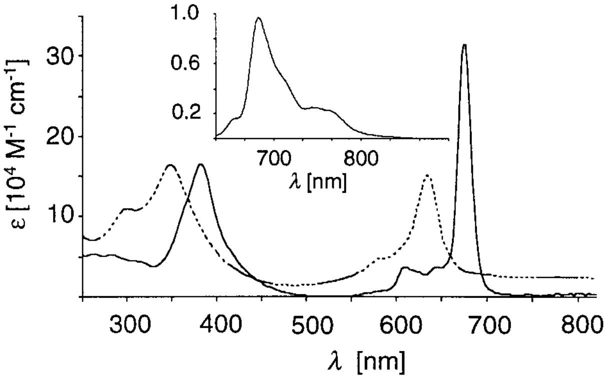
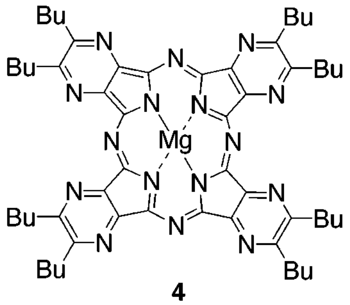


Figure 1. Electronic absorption spectra of **1b** (solid line) and **4** (dashed line) in CH_2Cl_2 at 298 K. The inset shows the fluorescence spectrum of **1b** (arbitrary units, $c = 3 \times 10^{-10}$ mol L^{-1} in $CHCl_3$) upon irradiation at 381 nm at 298 K.

stirring it together with excess *p*-toluenesulfonic acid in THF at room temperature for 5 min to provide **1d** in 70% yield.

The TPyPors **1a**−**c** are conveniently purified by column chromatography on silica gel, eluting with hexane/ethyl acetate mixtures or with THF.[7] Analytically pure samples can be obtained by further purifying **1a**−**c** by gel permeation chromatography (GPC) techniques (BioBeads S-X1, THF). The good solubility of **1a**−**d** in common aprotic organic solvents allows their complete analytical and spectroscopic characterization, in particular by routine ^{13}C NMR spectroscopy. TPyPors **1** are dark green, air-stable solids that despite the presence of eight alkynyl groups remain unchanged when heated to up to 400 °C.

The electron absorption spectra of the peralkynylated TPyPors **1a**−**c** are dominated by the two transitions typical for this class of compounds[8] and do not differ significantly from one another (Figure 1). In CH_2Cl_2, the higher energy *B*-band of **1b** has its maximum at 382 nm ($\lambda = 165\,000$ M^{-1} cm^{-1}), whereas the *Q*-band at the far red end of the visible spectrum appears as an intense, sharp maximum at 674 nm ($\lambda = 315\,000$ M^{-1} cm^{-1}). In comparison with the spectral data of nonalkynylated magnesium 2,3,9,10,16,17,23,24-octa-butyl-TPyPor **4**[9] [*B*-band, 348 nm ($\lambda = 164\,000$ M^{-1} cm^{-1}); *Q*-band, 634 nm ($\lambda = 151\,000$ M^{-1} cm^{-1})], both main absorptions of **1b** are bathochromically shifted by ca. 40 nm and, because of the rigidity of the alkynyl groups, have a significantly increased intensity (Figure 1). In fact, the optical properties of **1** are superior in this respect to those of common (nonacetylenic) metalla-phthalocyanines {cf. [Mg-phthalocyanine(imidazole)$_2$][10] in CH_2Cl_2: *B*-band, 345 nm ($\lambda =$ ca. 60 000 M^{-1} cm^{-1}); *Q*-band, 672 nm ($\lambda =$ ca. 190 000 M^{-1} cm^{-1})} but are hypso- and hypochromically shifted compared to those of peralkynylated phthalocyanines [e.g., Zn-2,3,9,10,16,17,23,24-octa(1-octynyl)phthalocyanine in THF: *B*-band, 370 nm ($\lambda = 162\,000$ M^{-1} cm^{-1}); *Q*-band, 708 nm ($\lambda = 370\,000$ M^{-1} cm^{-1})].[2a] Because of the lower symmetry of the metal-free derivative **1d**, its *Q*-band is split into two absorptions at 654 ($\lambda = 126\,000$ M^{-1} cm^{-1}) and 682 nm ($\lambda = 177\,000$ M^{-1} cm^{-1}) in CH_2Cl_2, and its *B*-band is observed at 368 nm ($\lambda = 141\,000$ M^{-1} cm^{-1}).



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The magnesium TPyPor derivative **1b** was also examined for its fluorescence behavior.[11] Thus, irradiating chloroform solutions of **1b** ($c = 3 \times 10^{-10}$ mol L^{-1}) at either 380 or 670 nm gives rise to an emission at 687 nm with a shoulder at 740 nm (inset Figure 1). The fluorescence quantum yield Φ_F was determined to be 67.9% in $CHCl_3$ solution at room temperature, a value characteristic for large, rigid polycyclic aromatic hydrocarbons such as pyrene[12] but significantly higher than that of (nonacetylenic) phthalocyanine metal complexes (cf. the fluorescence quantum yield of Zn-tetra-^{t}Bu-phthalocyanine in benzene:[13] $\Phi_F = 37\%$). Interestingly, the relative intensities of these emissions are reversed in hexane solution ($c = 2.5 \times 10^{-9}$ mol L^{-1}, rt) where a low intensity emission at 677 nm and an intense fluorescence at 774 nm are observed upon irradiation at 381 nm. We attribute this phenomenon to reabsorption of the emitted light in more concentrated solution or to excimer emissions[12] of TPyPor aggregates formed in hexane solution. The aggregation behavior of octaalkynyl TPyPor derivatives is also evident from their corresponding UV−vis absorption spectra in nonpolar solvents at these concentrations.

The short, three-step synthesis (overall yield 20% from oxalyl chloride), the good solubility, and the superior optical properties of octaalkynyl TPyPors **1** make them an attractive alternative to conventional phthalocyanines. We are currently exploring methodologies to prepare unsymmetrical, dialkynylated TPyPors for the assembly of chromophore units around a dehydroannulene core.

Experimental Section

General Methods. All reactions were performed in an argon atmosphere. Melting points are uncorrected. The degree of carbon substitution was determined by *J*-modulated spin−echo NMR experiments and is given in parentheses after the corresponding *δ* values. Solvents were purified and dried according to standard procedures.[14] Tetrahydrofuran was distilled from sodium/benzophenone immediately prior to use. Silica gel (60−200 mesh) for column chromatography was kindly provided by Merck KGaA, Darmstadt. The fluorescence quantum yield of **1b** was determined in deaerated $CHCl_3$ solutions at room temperature relative to isoviolanthrone dyes as previously reported.[15]

General Procedure for the Synthesis of [2,3,9,10,16,17,23,24-Octakis(triisopropylsilylethynyl)tetrapyrazinopor-

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(9) Compound **4** was prepared analogously to **1b** from deca-5,6-dione and had analytical data identical to those previously reported: Moerkved, E. H.; Wang, C. *J. Prakt. Chem.* **1997**, *339*, 473−476.

(10) *Phthalocyanines − Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: Weinheim 1989; Vol. 1, p 140.

(11) We are grateful to Dr. U. Panne, TU München, and to Drs. G. Seybold and G. Wagenblast, BASF AG, Ludwigshafen, for recording the fluorescence spectra.

(12) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991; p 111.

(13) Lawrence, D. S.; Whitten, D. G. *Photochem. Photobiol.* **1996**, *64*, 923−935.

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(15) Wagenblast, G.; Seybold, G. *Dyes Pigm.* **1989**, *11*, 303−317.

phyrazinato]zinc(II) 1a or -nickel(II) 1c. To a solution of **3**[4] (491 mg, 1.0 mmol) in quinoline (3 mL) were added 1.0 mmol of the corresponding metal salt (185 mg of zinc(II) acetate or 130 mg of nickel(II) chloride, respectively) and an excess of urea (1.50 g, 25.0 mmol). The reaction mixture was quickly heated to 140 °C and was stirred at this temperature for 5 min. After the mixture had cooled to rt, the solvent was evaporated and the crude product was flash chromatographed (SiO_2; hexane/ethyl acetate 3:1), affording compounds **1a** or **1c** as deep green solids. Analytically pure compounds **1a** and **1c** were obtained by GPC with THF as eluent.

1a. Yield: 178 mg (0.09 mmol, 35%). Mp: > 400 °C. IR (KBr): $\tilde{\nu}$ 2942 (s) (CH), 2865 (s) (CH), 2075 (w) ($C{\equiv}C$), 1462 (m) (CH), 1314 (s) (CN). UV (CH_2Cl_2): λ_{max} (ϵ) 392 nm (170 900), 612 nm (35 600), 622 nm (32 000), 648 (37 600), 676 (317 700). ^1H NMR (250.13 MHz, THF/D_2O): δ 1.5−1.3 (m, 168H, CH, CH_3). ^{13}C NMR (62.89 MHz, THF/D_2O): δ 151.3 (C), 148.9 (C), 141.9 (C), 105.7 (C), 101.5 (C), 19.4 (CH_3), 12.5 (CH). MALDI-TOF-MS: m/z 2029.9 (100) [MH^+]. Elemental analysis ($C_{112}H_{168}N_{16}Si_8Zn\cdot 2H_2O$): calcd C 65.15, H 8.40, N 10.85; found C 65.38, H 8.47, N 10.71.

1c. Yield: 141 mg (0.07 mmol, 28%). Mp: >400 °C. IR (KBr): $\tilde{\nu}$ 2943 (s) (CH), 2865 (s) (CH), 2157 (w) ($C{\equiv}C$), 1465 (m) (CH), 1320 (s) (CN). UV (CH_2Cl_2): λ_{max} (ϵ) 338 nm (116 800), 370 nm (142 000), 402 nm (80 900), 594 nm (38 700), 606 nm (31 800), 634 (43 000), 656 (310 300). ^1H NMR (250.13 MHz, THF/D_2O): δ 1.4−1.3 (m, 168H, CH, CH_3). ^{13}C NMR (62.89 MHz, THF/D_2O): δ 146.6 (C), 143.5 (C), 142.3 (C), 104.7 (C), 101.6 (C), 18.6 (CH_3), 11.7 (CH). MALDI-TOF-MS: m/z 2023.0 (100) [MH^+]. Elemental analysis ($C_{112}H_{168}N_{16}Si_8Ni\cdot 2H_2O$): calcd C 65.36, H 8.42, N 10.89; found C 65.75, H 8.69, N 10.85.

Synthesis of [2,3,9,10,16,17,23,24-Octakis(triisopropylsilylethynyl)tetrapyrazino-porphyrazinato]magnesium(II) 1b. To a solution of **3**[4] (491 mg, 1.0 mmol) in butanol (1 mL) was added 1.0 mL of a 1.0 M solution of magnesium butanolate in butanol. The reaction mixture was heated to reflux and stirred for 5 min. After the mixture had cooled to rt, the solvent was evaporated and the crude product was chromatographed (SiO_2, hexane/ethyl acetate 3:1; GPC, THF) as described above affording compound **1b** as a deep green, analytically pure solid. Yield: 164 mg (0.083 mmol, 33%). Mp: >400 °C. IR (KBr): $\tilde{\nu}$ 2943 (s) (CH), 2866 (s) (CH), 2154 (w) ($C{\equiv}C$), 1464 (m) (CH), 1313 (s) (CN). UV (CH_2Cl_2): λ_{max} (ϵ) 382 nm (176 900), 608 nm (40 300), 644 (38 900), 674 (314 600). ^1H NMR (250.13 MHz, THF/D_2O): δ 1.5−1.3 (m, 168H, CH, CH_3). ^{13}C NMR (62.89 MHz, THF/D_2O): δ 149.8 (C), 148.7 (C), 140.9 (C), 105.0 (C), 100.4 (C), 18.6 (CH_3), 11.7 (CH). MALDI-TOF-MS: m/z 1989.3 (100) [MH^+]. Elemental analysis ($C_{112}H_{168}N_{16}Si_8Mg\cdot 2H_2O$): calcd C 66.47, H 8.57, N 11.07; found C 66.51, H 8.53, N 10.75.

Synthesis of 2,3,9,10,16,17,23,24-Octakis(triisopropylsilylethynyl)tetrapyrazino-porphyrazine 1d. To a solution of **1b** (81 mg, 0.04 mmol) in THF (20 mL) was added *p*-toluenesulfonic acid (380 mg, 2.0 mmol). The reaction mixture was stirred for 5 min at 25 °C. After evaporation of the solvent, the crude product was washed several times with bidistilled water (5 × 20 mL) and dried in vacuo to afford **1d** as a deep green, analytically pure solid. Yield: 55 mg (0.03 mmol, 70%). Mp: >400 °C. IR (KBr): $\tilde{\nu}$ 3249 (w) (NH), 2943 (s) (CH), 2865 (s) (CH), 2144 (w) ($C{\equiv}C$), 1464 (m) (CH), 1318 (s) (CN). UV (CH_2Cl_2): λ_{max} (ϵ) 368 nm (141 000), 400 (sh, 65 100), 442 (sh, 46 200), 454 (sh, 40 700), 602 nm (28 200), 622 (37 900), 654 (125 900), 682 (176 600). ^1H NMR (250.13 MHz, THF/D_2O): δ 1.5−1.3 (m, 168H, CH, CH_3), −0.55 (s, 2H, NH). ^{13}C NMR (90.56 MHz, THF/D_2O): δ 147.0 (C), 146.3 (C), 142.3 (C), 104.7 (C), 101.9 (C), 18.5 (CH_3), 12.0 (CH). MALDI-TOF-MS: m/z 1966.5 (100) [MH^+]. Elemental analysis ($C_{112}H_{170}N_{16}Si_8$): calcd C 68.45, H 8.72, N 11.40; found C 68.44, H 8.67, N 10.78.

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