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Article

Synthesis and Photophysical Properties of Meso-Substituted Bisporphyrins: Comparative Study of Phosphorescence Quenching for Dioxygen Sensing

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The 4,6-bis(10-mesityl-5,15-di-*p*-tolylporpyrinyl)dibenzothiophene (H_4DPSN) free base was obtained in five steps from commercially available materials. The metalation of DPSN^{2-} with zinc(II), copper(II), and palladium(II) led to three new homobimetallic systems, $(Zn)_2$DPSN, $(Cu)_2$DPSN, and $(Pd)_2$DPSN, respectively. The cofacial structures of these molecules offer the possibility of having dioxygen molecules inside the cavity for a period of time, allowing dynamic (collisional) phosphorescence quenching to be more efficient. The bimolecular excited-state deactivation rate constant for deactivation by dioxygen (k_Q: $(Pd)_2$DPB, 2.98×10^9; $(Pd)_2$DPSN, 3.99×10^9; $(Pd)_2$DPX, 6.94×10^9; (Pd)TPP, 8.95×10^9; $(Pd)_2$DPS, 8.95×10^9 M^{-1} s^{-1}) of $(Pd)_2$DPSN, which exhibits an intense phosphorescence at 699 nm, was compared to those observed for (Pd)TPP, $(Pd)_2$DPS, $(Pd)_2$DPX, and $(Pd)_2$DPB (TPP^{2-} = tetraphenylporphyrin dianion, DPS^{4-} = 4,6-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]dibenzothiophene tetraanion, DPX^{4-} = 4,5-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]-9,9-dimethylxanthene tetraanion, and DPB^{4-} = 1,8-bis[5-(2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrinyl)]biphenylene tetraanion). These collision-induced deactivation data were interpreted by estimating a series of physical parameters such as the surface area and bisporphyrin radii, the diffusion coefficient of the bismacrocycles, and the theoretical deactivation efficiency for the five compounds addressing the role of steric hindrance of the macrocycles on each other and the aryl groups at the meso positions. For sensing purposes, $(Pd)_2$DPX is characterized by a Stern–Volmer constant k_{SV} of 2.91×10^6 M^{-1}, placing the lower detection limit for [O_2] in solution at 0.58 ppm, which is better than that for (Pd)TPP ($k_{SV} = 2.31 \times 10^6$ M^{-1}; lower detection limit of 0.73 ppm), the classically used monoporphyrin complex.

Introduction

The chemistry of cofacial bisporphyrins is currently a topic of great interest, particularly because of their numerous applications in catalysis and their photophysical properties.[1,2] The first bisporphyrin systems maintained in a face-to-face configuration by flexible chains were reported by Collman and their collaborators to mimic hemoproteins.[3–7] Subsequently, Chang and collaborators have developed the "Pacman" concept, in which the two porphyrin rings are held together by a rigid spacer such as anthracenyl or biphenylenyl groups.[8–10] Thereafter, new rigid spacers such as DPO, DPX,

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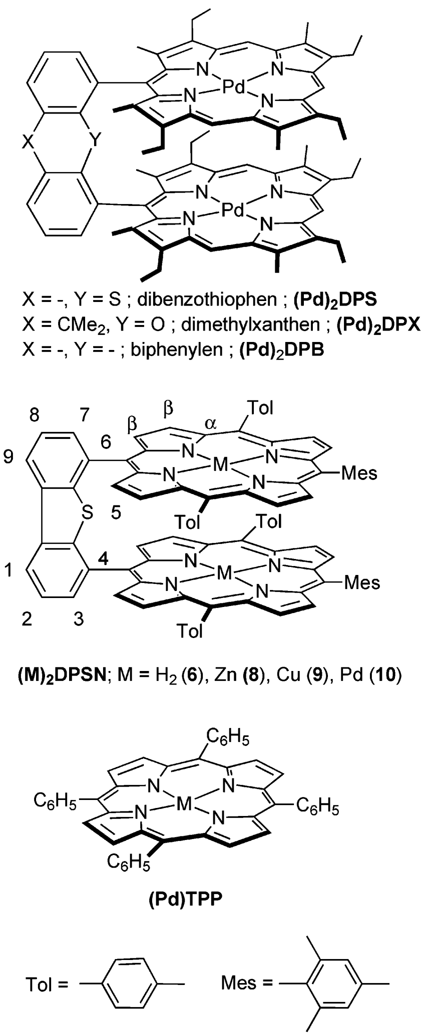
Scheme 1



X = -, Y = S ; dibenzothiophen ; **(Pd)$_2$DPS**
X = CMe$_2$, Y = O ; dimethylxanthen ; **(Pd)$_2$DPX**
X = -, Y = - ; biphenylen ; **(Pd)$_2$DPB**

(M)$_2$DPSN; M = H$_2$ (**6**), Zn (**8**), Cu (**9**), Pd (**10**)

(Pd)TPP

and DPS led to easier routes of synthesis (Scheme 1).[11−14] These spacers allowed researchers to vary the intermacrocycle C_{meso}−C_{meso} distance and the interplanar angle. According to a 14-step synthesis and an overall yield of about 0.3%, the synthesis of the free base H_4DPS, for instance, still has room for improvement.[13,15] In addition, very little research has been devoted to the synthesis of meso-substituted bisporphyrins. Recent works led to very original synthetic procedures that vary the nature of the bridge and the porphyrin meso substituents.[16]

Similarly, the study of palladium(II) monoporphyrins has shown their intense phosphorescence and their potential application for oxygen sensing at the parts per million level.[2,17−22] In this respect, the quest for more efficient sensors led us to investigate bismacrocycles, because the size of the cavity formed by the two macrocycles and the spacer allows small molecules to interact with the metal atoms in an endo position.[23−26] Taking advantage of a recent work by Lindsey and collaborators for the synthesis of meso-substituted porphyrins,[1,16,27,28] we have synthesized a new bisporphyrin free base, 4,6-bis(10-mesityl-5,15-di-*p*-tolylporphyrinyl)-dibenzothiophene, H_4DPSN, in five steps starting from commercially available materials, along with three homobimetallic complexes, including (Pd)$_2$DPSN. The photophysical properties of (Pd)$_2$DPSN and the bimolecular excited-state deactivation rate constant by oxygen, k_Q, are compared to those of four palladium(II) mono- and bisporphyrin systems. The data are analyzed using a theoretical approach, which consists of evaluating the quenching efficiency using an estimation of the efficient surface of the chromophores for O_2 interactions.

Experimental Section

Materials. Unless otherwise stated, all reagents and solvents were used as received. 1,3-Benzoxathiolium tetrafluoroborate[29] and 5-mesityldipyrromethane[30] **7** were synthesized according to literature methods. 2-MeTHF ($\geq$99%, anhydrous and under inert gas), DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone), and TMEDA (tetramethylethylenediamine) were purchased from Aldrich. HgO (yellow) was purchased from Janssen Chimica. Chromatographic purification of all compounds was performed with neutral alumina (Merck; usually Brockmann Grade III, i.e., deactivated with 6% water) and silica gel (Merck; 70−120 mm), and was monitored by thin-layer chromatography (Merck 60 F254 silica gel precoated sheets, 0.2 mm thick) and UV−vis spectroscopy.

Molecular Modeling. Connolly areas were calculated using Chem3D Ultra 8.0 software. The procedure consisted of computing a minimum energy structure at the MM2 level, followed by a second minimization using Gaussian 98 Semiempirical AM1 computation. Connolly areas[31] were obtained with ChemPropStd job. The radius r(2-MeTHF) was calculated using the Connolly molecular area of 2-MeTHF with probe radius set to 0.

Apparatus. ^{1}H NMR spectra were recorded on a Bruker DRX-500 AVANCE spectrometer at the Centre de Spectrométrie Mo-

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léculaire de l'Université de Bourgogne. All chemical shifts (δ) and coupling constants (J) are given in parts per million and hertz, respectively. The ^{1}H NMR assignments for the spacers refer to the numbering in Scheme 1. Microanalyses were performed at the Université de Bourgogne on a Fisons EA 1108 CHNS instrument. UV−vis spectra were recorded on a Varian Cary 50 spectrophotometer. Mass spectra were obtained in a linear mode with a Bruker Proflex III MALDI-TOF mass spectrometer using dithranol as matrix, and with a Kratos Concept 32 S spectrometer in EI mode. The EPR spectrum was recorded in solution on a Bruker ESP 300 spectrometer at the X-band (9.6 GHz), from the Centre de Spectrométrie Moléculaire de l'Université de Bourgogne, equipped with a double cavity and a liquid nitrogen cooling accessory. The EPR spectrum was referenced to 2,2-diphenyl-1-picrylhydrazyl (DPPH) ($g = 2.0036$). The IR spectrum was obtained on a Bruker Vector 22 FTIR spectrophotometer equipped with a high-pressure Diamond ATR system.

Emission and excitation spectra were obtained by using a double monochromator Fluorolog 2 instrument from Spex. Fluorescence lifetimes were measured on a Timemaster model TM-3/2003 apparatus from PTI. The source was a nitrogen laser equipped with a high-resolution dye laser (fwhm ~ 1500 ps), and the fluorescence lifetimes were obtained from deconvolution and distribution lifetime analysis.[32] All of the samples were prepared under an inert atmosphere (in a glovebox, $P(O_2) < 1-3$ ppm) by dissolution of the different compounds in 2-MeTHF in 1 cm^3 quartz cells equipped with a septum (298 K) or in standard 5 mm NMR tubes (77 K). Three different measurements (i.e., different solutions) were performed for each photophysical data type (quantum yields and lifetimes). The sample concentrations were chosen to obtain an absorbance of about 0.05. Each absorbance value was measured five times to gain better accuracy for determining the quantum yields. The quantum yield of H$_2$TPP ($\Phi = 0.11$) was used as a reference for the quantum yields measured at 298 K.[33−35] The quantum yield of H$_2$TPP ($\Phi = 0.11$) was also used as a reference for the quantum yields measured at 77 K, which itself was obtained using (Pd)TPP ($\Phi = 0.17$; 77 K; MCH = methylcyclohexane) as a reference.[36,37]

4,6-Diformyldibenzothiophene (2). **2** was synthesized using a modified literature method.[38] A solution of *n*-BuLi (166 mL, 2.5 M in heptane, 0.415 mol) in heptane was added dropwise to a solution of **1** (30 g, 0.163 mol) in heptane (1.2 L) and TMEDA (80 mL) under Ar over a period of 30 min. The reaction mixture was heated, and was stirred under reflux (70 °C) for 15 min. After the mixture was cooled in an ice bath, DMF (82 mL) was added, and the reaction mixture was stirred for 30 min at room temperature. The resulting solution was poured into cold water (6 L), and was stirred for an additional 2 h. A yellow solid was collected by filtration and dried under vacuum. Recrystallization in toluene afforded pure **2** (31 g, yield 79%) as a light yellow solid. ^{1}H NMR (DMSO): δ 10.58 (s, 2H, CHO), 9.10 (d, $J = 7.3$, 2H, H−C$_{3-7}$, or H−C$_{1-9}$), 8.55 (d, $J = 7.3$, 2H, H−C$_{3-7}$, or H−C$_{1-9}$), 8.11 (m, $J = 7.3$, 2H, H−C$_{2-8}$).

4,6-Bis[(2,2′-dipyrryl)methyl]dibenzothiophene (3). A solution of **2** (9 g, 37 mmol) and pyrrole (208 mL, 80 equiv) was degassed with Ar for 30 min until BF$_3$·OEt$_2$ (0.92 mL, 0.2 eq) was added. The reaction mixture was stirred for 1 h, quenched with 0.1 M NaOH, and extracted with CH$_2$Cl$_2$. The combined organic layers were washed with water and dried over MgSO$_4$, and the solvent was removed to afford a white solid. After the addition of CH$_2$Cl$_2$, the resulting solution was poured into cold pentane; the derivative **3** was collected by filtration as a white solid and dried under vacuum (16 g, yield 89%). ^{1}H NMR (CDCl$_3$): δ 8.05 (d, $J = 7.6$, 2H, H−C$_{3-7}$, or H−C$_{1-9}$), 7.97 (s, 4H, H−N), 7.40 (t, $J = 7.6$, 2H, H−C$_{2-8}$), 7.20 (d, $J = 7.6$, 2H, H−C$_{3-7}$, or H−C$_{1-9}$), 6.68 (d, 4H, H$_\alpha$), 6.15 (t, 4H, H$_\beta$), 6.00 (d, 4H, H$_\beta$), 5.74 (s, 2H, H$_{meso}$). ^{13}C NMR (CDCl$_3$): δ 126.7 and 125.6 (C$_{3-7}$ or C$_{1-9}$), 120.9 (C$_{2-8}$), 117.9 (C$_\alpha$), 108.9 (C$_\beta$), 108.2 (C$_\beta$), 43.6 (C$_{meso}$). MS (MALDI-TOF): *m/z* 472 (M$^+$), 471 calcd for C$_{30}$H$_{24}$N$_4$S. Anal. Calcd for C$_{30}$H$_{24}$N$_4$S·0.2H$_2$O: C, 75.66; H, 5.16; N, 11.77; S: 6.73. Found: C, 75.40; H, 5.56; N, 12.14; S: 6.43.

4,6-Bis[(2,2′-bis(1-(*p*-tolyl)-1,3-benzoxathiolyl)pyrryl)methyl]dibenzothiophene (4). To a solution of **3** (2 g, 4.2 mmol) in acetonitrile (360 mL) and pyridine (1.4 mL) was added 2-(*p*-tolyl)-1,3-benzoxathiolium tetrafluoroborate (5.27 g, 0.17 mmol). The reaction mixture was stirred for 30 min at room temperature, and then diluted with ethyl acetate (400 mL). The combined organic layers were washed with water and dried over MgSO$_4$, and the solvent was removed to obtain 2.8 g of a dark solid.

4,6-bis[(2,2′-bis(1-(*p*-methylbenzoyl)pyrryl))methyl]dibenzothiophene (5). HBF$_4$ (34% in water, 6 mL) was added to a solution of **4** (2.8 g, 2 mmol) in THF (260 mL) containing HgO (1.8 g, 8.4 mmol). The reaction mixture was stirred for 1.5 h at room temperature, and diluted with ethyl acetate (400 mL). The combined organic layers were washed with KI (10% in water), 0.1 M NaOH, and water, and then dried over MgSO$_4$. Removal of the solvent under vacuum gave a light red solid, which was dissolved in CH$_2$Cl$_2$/NEt$_3$ (99:1), and filtered through a pad of silica (CH$_2$Cl$_2$). The second collected derivative was the tetra-acyl compound (CH$_2$Cl$_2$ with 1% MeOH). Removal of the solvent followed by a recrystallization in CH$_2$Cl$_2$/heptane afforded an orange solid (1.2 g, 63%). ^{1}H NMR (CDCl$_3$): δ 11.08 (s, 4H, H−N), 8.13 (d, $J = 7.5$, 2H, H−C$_{3-7}$, or H−C$_{1-9}$), 7.67 (d, $J = 7.5$, 8H, tolyl), 7.49 (t, $J = 7.5$, 2H, H−C$_{2-8}$), 7.13 (m, 10H, H-tolyl, and H−C$_{3-7}$ or H−C$_{1-9}$), 6.61 (m, 4H, H$_\beta$), 6.06 (m, 6H, H$_\beta$, and H$_{meso}$), 2.34 (s, 12H, CH$_3$-tolyl). MS (MALDI-TOF): *m/z* 945 (M$^+$), 944 calcd for C$_{62}$H$_{48}$N$_4$O$_4$S. Anal. Calcd for C$_{62}$H$_{48}$N$_4$O$_4$S·0.2H$_2$O: C, 78.49; H, 5.14; N, 5.90; S, 3.38. Found: C, 78.23; H, 5.26; N, 6.07; S, 3.23. IR: $\nu_{C=O}$ 1598 cm^{-1}.

4,6-Bis(10-mesityl-5,15-di-*p*-tolylporphyrinyl)dibenzothiophene (6). Procedure A. A solution of ethylmagnesium bromide (1 M in THF, 25.2 mL, 10 equiv) was added dropwise to a solution of **3** (1.2 g, 2.8 mmol) in dry toluene (100 mL) under Ar placed in a cold bath of water. The reaction mixture was stirred for 30 min at room temperature, and a solution of *p*-toluoyl chloride (1.7 mL, 5 equiv) in 13 mL of toluene was added dropwise. The reaction mixture was stirred for an additional 10 min and, after being quenched with aq NH$_4$Cl, was extracted with ethyl acetate. The combined organic layers were washed with water and dried over MgSO$_4$, and the solvent was removed under vacuum to afford a red oil. Column chromatography (silica, CH$_2$Cl$_2$/methanol 96:4 with NEt$_6$) afforded a mixture of acylated products. CH$_2$Cl$_2$ was added, and the mixture was poured into cold pentane. A solid was collected by filtration. The solid (1 g), a mixture of acylated compounds as shown by mass spectroscopy, was then dissolved in dry THF (85 mL) and dry MeOH (15 mL), and was stirred under Ar before

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$NaBH_4$ (3 g, 80 equiv) was added step by step over 50 min. The reaction was monitored by IR spectrometry using as a marker the 1598 cm^{-1} $\nu_{C=O}$ band. The reaction mixture was poured into a saturated solution of NH_4Cl in water, and extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$, and the solvent was removed to afford a pale yellow solid. Acetonitrile (850 mL) was added with mesityldipyrromethane (0.615 g), and after the reaction mixture was degassed in the dark with Ar for 5 min, TFA was added. The reaction mixture was stirred for 3 min before we added DDQ (1.42 g, 5.4 mmol) and NEt_3 (6 mL). The mixture was stirred for an additional 1 h, and was filtered through a pad of alumina (eluted with CH_2Cl_2) until the eluent was no longer dark. Removal of the solvent afforded a dark solid, which was redissolved in CH_2Cl_2/heptane/NEt_3 (40:59:1) and filtered through a pad of silica (CH_2Cl_2). Removal of the solvent under vacuum followed by recrystallization in CH_2Cl_2/heptane afforded a purple solid (73 mg, yield 4%).

Procedure B. A solution of **5** (1 g, 1.05 mmol) in dry THF (85 mL) and dry MeOH (15 mL) was stirred under Ar. $NaBH_4$ (3 g, 0.085 mol, 80 equiv) was added step by step over 50 min. The reaction was monitored by IR spectrometry using as a marker the 1598 cm^{-1} $\nu_{C=O}$ band. The reaction mixture was poured into an aqueous saturated solution of NH_4Cl, and extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over $MgSO_4$, and the solvent was removed to afford a pale yellow solid. Acetonitrile (850 mL) was added with **7** (0.615 g), and the reaction mixture was degassed in the dark with Ar for 5 min before adding TFA (1.96 mL). The reaction mixture was stirred for 3 min, and DDQ (1.42 g, 5.4 mmol) and NEt_3 (6 mL) were added. The reaction mixture was stirred for an additional 1 h, and filtered through a pad of alumina (eluted with CH_2Cl_2) until the eluent was no longer dark. Removal of the solvent afforded a dark solid, which was redissolved in CH_2Cl_2/heptane/NEt_3 (40:59:1) and filtered through a pad of silica (CH_2Cl_2). Removal of the solvent under vacuum followed by recrystallization in CH_2Cl_2/heptane afforded a purple solid (50 mg, yield 3.4%). ^1H NMR ($CDCl_3$): δ 8.75 (d, $J = 8$, 2H, H-spacer), 8.55 (d, $J = 5.3$, 4H, H_β), 8.45 (d, $J = 5.3$, 4H, H_β), 8.41 (d, $J = 4.3$, 4H, H_β), 8.35 (d, $J = 4.3$, 4H, H_β), 8.11 (d, $J = 8$, 2H, H-spacer), 7.92 (t, $J = 8$, 2H, H-spacer), 7.66 (d, $J = 6.4$, 4H, H-tolyl), 7.43 (d, $J = 6.4$, 4H, H-tolyl), 7.18 (d, $J = 6.4$, 4H, H-tolyl), 7.12 (s, 2H, H-mesityl), 7.05 (s, 2H, H-mesityl), 7.01 (d, 4H, H-tolyl), 2.49 (s, 6H, CH_3-mesityl), 2.47 (s, 12H, CH_3-tolyl), 1.69 (s, 6H, CH_3-mesityl), 1.36 (s, 6H, CH_3-mesityl), −3.11 (s, 4H, N−H). MS (MALDI-TOF): *m/z* 1397 (M^+), 1397 calcd for $C_{98}H_{76}N_8S$. UV−vis (CH_2Cl_2) λ (nm) (ϵ 10^{-3} M^{-1} cm^{-1}): 416 Soret (560), 517 (30), 547 (11), 591 (11), 646 (10). Anal. Calcd for $C_{98}H_{76}N_8S \cdot 0.3H_2O$: C, 83.88; H, 5.50; N, 7.99; S, 2.29. Found: C, 83.63; H, 5.74; N, 8.29; S,1.86.

4,6-Bis(zinc(II)-10-mesityl-5,15-di-*p*-tolylporphyrinyl)dibenzothiophene (8). Under Ar, **6** (30 mg, 0.02 mmol) was dissolved in CH_2Cl_2 (15 mL) and NEt_3 (0.5 mL), and a saturated solution of zinc acetate in MeOH (1 mL) was added. The mixture was stirred under reflux for 15 min. Removal of the solvent under vacuum gave a purple solid, which was redissolved in CH_2Cl_2 (1% NEt_3) and filtered through a pad of silica (CH_2Cl_2). The first band was collected, and the solvent was evaporated. Recrystallization in CH_2Cl_2/MeOH afforded a purple solid (29 mg, yield 88%). ^1H NMR ($CDCl_3$): δ 8.79 (d, $J = 7.5$, 2H, H-spacer), 8.64 (d, $J = 4.3$, 4H, H_β), 8.62 (d, $J = 4.3$, 4H, H_β), 8.60 (d, $J = 4.3$, 4H, H_β), 8.47 (d, $J = 4.3$, 4H, H_β), 8.19 (d, $J = 7.5$, 2H, H-spacer), 7.96 (t, $J = 8$, 2H, H-spacer), 7.85 (d, $J = 7.5$, 4H, H-tolyl), 7.70 (d, $J = 7.5$, 4H, H-tolyl), 7.39 (d, $J = 7.5$, 4H, H-tolyl), 7.36 (d, $J = 7.5$, 4H, H-tolyl), 7.14 (s, 2H, H-mesityl), 7.06 (s, 2H, H-mesityl), 2.63 (s, 12H, CH_3-tolyl), 2.51 (s, 6H, CH_3-mesityl), 1.71 (s, 6H, CH_3-mesityl), 1.30 (s, 6H, CH_3-mesityl). MS (LSIMS): *m/z* 1520 (M^+), 1520 calcd for $C_{98}H_{72}N_8SZn_2$. UV−vis (CH_2Cl_2) λ (nm) (ϵ 10^{-3} M^{-1} cm^{-1}): 417 Soret (618), 551 (29), 591 (7). Anal. Calcd for $C_{98}H_{72}N_8SZn_2$: C, 77.21; H, 4.76; N, 7.35; S, 2.10. Found: C, 77.35; H, 4.52; N, 7.59; S, 1.86.

4,6-Bis(palladium(II)-10-mesityl-5,15-di-*p*-tolylporphyrinyl)dibenzothiophene (9). Under Ar, **6** (40 mg, 0.03 mmol) was dissolved in benzonitrile (15 mL), and $PdCl_2$ (20 mg, 3 equiv) was added. The mixture was stirred under reflux for 15 min. Removal of the solvent under vacuum gave a purple solid, which was redissolved in CH_2Cl_2 (1% NEt_3) and filtered through a pad of silica (CH_2Cl_2). The first band was collected, and the solvent was evaporated. The resulting solid was recrystallized in CH_2Cl_2/MeOH, and afforded an orange solid (28 mg, yield 61%). ^1H NMR ($CDCl_3$): δ 8.75 (d, $J = 8$, 2H, H-spacer), 8.49 (s, 8H, H_β), 8.47 (d, $J = 4.3$, 4H, H_β), 8.33 (d, $J = 4.3$, 4H, H_β), 8.16 (d, $J = 8$, 2H, H-spacer), 7.93 (t, $J = 8$, 2H, H-spacer), 7.75 (d, $J = 7.5$, 4H, H-tolyl), 7.65 (d, $J = 7.5$, 4H, H-tolyl), 7.45 (d, $J = 7.5$, 4H, H-tolyl), 7.32 (d, $J = 7.5$, 4H, H-tolyl), 7.13 (s, 2H, H-mesityl), 7.02 (s, 2H, H-mesityl), 2.59 (s, 12H, CH_3-tolyl), 2.49 (s, 6H, CH_3-mesityl), 1.74 (s, 6H, CH_3-mesityl), 1.21 (s, 6H, CH_3-mesityl). ^{13}C NMR ($CDCl_3$) (CH, CH_2, CH_3 only): δ 134.5 and 133 (CH-tolyl), 132.5, 121.5, and 124 (CH-spacer), 131.5 and 131.7 (CH-β-pyrrole), 129.5 (2 signals, CH-β-pyrrole), 127.9 and 127.7 (2 signals, CH-mesityl), 21.5 and 21.8 (CH_3-mesityl), 22 (CH_3-tolyl), 120−142 (7 signals). MS (MALDI-TOF): *m/z* 1604 (M^+), 1605 calcd for $C_{98}H_{72}N_8Pd_2S$. UV−vis (CH_2Cl_2) λ (nm) (ϵ 10^{-3} M^{-1} cm^{-1}): 412 Soret (481), 524 (51), 555 (7). Anal. Calcd for $C_{98}H_{72}N_8Pd_2S$: C, 73.26; H, 4.52; N, 6.98; S, 2.00. Found: C, 73.01; H, 4.20; N, 7.20; S, 2.30.

4,6-Bis(copper(II)-10-mesityl-5,15-di-*p*-tolylporphyrinyl)dibenzothiophene (10). Under Ar, **6** (30 mg, 0.02 mmol), K_2CO_3 (100 mg), and $Cu(OAc)_2 \cdot H_2O$ were dissolved in 20 mL of $CHCl_3$/MeOH (80:20). The mixture was stirred under reflux for 15 min. Removal of the solvent under vacuum gave a purple solid, which was redissolved in CH_2Cl_2, washed with water, and dried over $MgSO_4$. The solvent was removed. Recrystallization in CH_2Cl_2/MeOH afforded a purple solid (32 mg, yield 100%). MS (MALDI-TOF): *m/z* 1519 (M^+), 1518 calcd for $C_{98}H_{72}Cu_2N_8S$. UV−vis (CH_2Cl_2) λ (nm) (ϵ 10^{-3} M^{-1} cm^{-1}): 410 Soret (409.0), 540 (17.2), 577 (2.5). Anal. Calcd for $C_{98}H_{72}Cu_2N_8S$: C, 77.40; H, 4.77; N, 7.37; S, 2.11. Found: C, 77.67; H, 5.02; N, 7.07; S, 2.01.

Results and Discussion

Syntheses. The syntheses of cofacial meso-substituted bisporphyrins have already been described. Three routes of synthesis are possible.

One approach consists of the monoprotection of the corresponding bisaldehyde spacer, allowing the construction of a first porphyrin macrocycle, according to Lindsey's procedure.[1] This step is followed by the deprotection and construction of the second ring as developed by Collman and co-workers[39−42] and other groups.[43] The drawbacks are the extra protection/deprotection steps and the purification of the monoaldehyde intermediates.

A second strategy was developed independently by Therien and co-workers[44,45] and by Kobuke and co-workers,[46] and

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(39) Collman, J. P.; Tyvoll, D. A.; Chng, L. L.; Fish, H. T. *J. Org. Chem.* **1995**, *60*, 1926.

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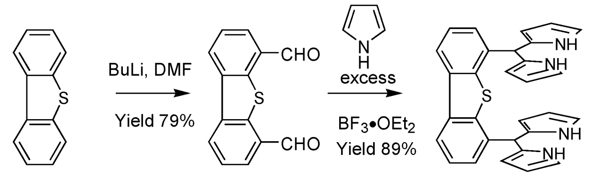
consists of the formation of a linear porphyrin−spacer−porphyrin triad, in which the spacer can be chemically altered in a way that leads to a cofacial arrangement.

The last method is the direct coupling between a functionalized spacer and two appropriately substituted porphyrin macrocycles. Examples of such strategies are those using the Sonogashira coupling.[47−50] Similarly, the Suzuki coupling was employed by Nocera and co-workers[14] for this purpose.

Attempts to synthesize the desired products using simpler procedures and requiring fewer steps were made. The direct reaction between pyrrole, monoaldehyde, and dialdehyde spacer, as previously attempted by Collman and co-workers, was not successful.[39] The condensation of 4,6-bis[(2,2′-dipyrryl)methyl]dibenzothiophene **3** with dialdehyde phenyldipyrromethane did not lead to the targeted product, despite the use of various experimental conditions as previously reported in the literature.[51−54] The coupling between **3** and diacetylate phenyldipyrromethane as already described for the syntheses of monoporphyrins was also not successful.[1,27,55−60] Presumably, the H in the α-position of the pyrrole N−H's may be not reactive enough in compound **3**.

On the basis of previous procedures reported by Lindsey and co-workers for mono- and multiporphyrin systems,[1,27,61,62] we report the procedure leading to the desired meso-substituted bisporphyrin **6**, H_4DPSN. The highly stable compound **3** is prepared in a high yield from the condensation of four pyrrolic units onto the dibenzothiophene spacer **2** using $BF_3{\cdot}OEt_2$ as a catalyst (Scheme 2). Experimental conditions show that the use of higher-purity diformyl compound **2** allows the synthesis of **3** without chromatography. However, **2** is purified by recrystallization in toluene prior use. Two routes for the synthesis of bisporphyrin **6** (H_4DPSN) starting from **3** have been investigated (Scheme 3). The first one, called A, consists of reacting **3** with EtMgBr to replace the α H's on the pyrrole residues, which can be functionalized by tolylcarbonyl groups.[1,27,61,62] Unfortunately, the target intermediate **5** has not been isolated in pure form. The solid, a mixture of acylated compounds obtained after reaction of bisdipyrromethane **3** with *p*-toluoyl chloride, is reduced by $NaBH_4$ and reacted with mesityl-dipyrromethane **7**. Subsequently, oxidation of the macrocycle ring is obtained by adding DDQ. H_4DPSN **6** was isolated, and purified by column chromatography.[27,61] The second route (B), developed by Barbero and co-workers,[29,63] involves the use of a benzoxathiol compound to generate the intermediate **4**, which was not isolated from the reaction mixture. This derivative was converted into **5** by reacting **4** with HgO. Fortunately, **5** was isolated and purified by column chromatography. The reduction by $NaBH_4$ followed by condensation with dipyrromethane **7** and oxidation by DDQ led to the desired bisporphyrin **6**. Both routes give an overall yield of 3−4% from **3**, and about 1.4% from the commercially available starting materials (five steps). This yield is higher than that reported for β-substituted H_4DPS (0.3%),[16] which utilizes a 14-step procedure. The use of acylated bisdipyrromethane intermediates represents a significant advance in the preparation of cofacial bisporphyrin systems.

Scheme 2



1 2 3

The metalation step proceeds as described in the literature, and involves the direct complexation with the desired cation.[10,11,64,65] Scheme 4 exhibits the one-step syntheses of three metal complexes of **6**, leading to products **8** ($(Zn)_2$-DPSN), **9** ($(Pd)_2$DPSN), and **10** ($(Cu)_2$DPSN), which were obtained in good yields. Compound **8** was synthesized with the aim of X-ray characterization. Unfortunately, all attempts to grow suitable crystals for X-ray analysis stubbornly failed. Compound **9**, which exhibits strong phosphorescence properties (see below) was also prepared. Compound **10** was investigated because the Cu−Cu distance is easily determined by EPR methods. Unfortunately, no evidence for Cu(II)−Cu(II) interaction at half-field transition has been detected by EPR. This absence of signal led us to conclude that the Cu−Cu distance is greater than 6−7 Å.[9] Table 1 compares ^{1}H NMR for the N−H protons for various cofacial bisporphyrin systems.[14] For H_4DPSN **6**, the δ value resembles that of other "open" bisporphyrin for which the $C_{meso}-C_{meso}$ distance is 6.3 Å (or greater). Comparison of the δ values

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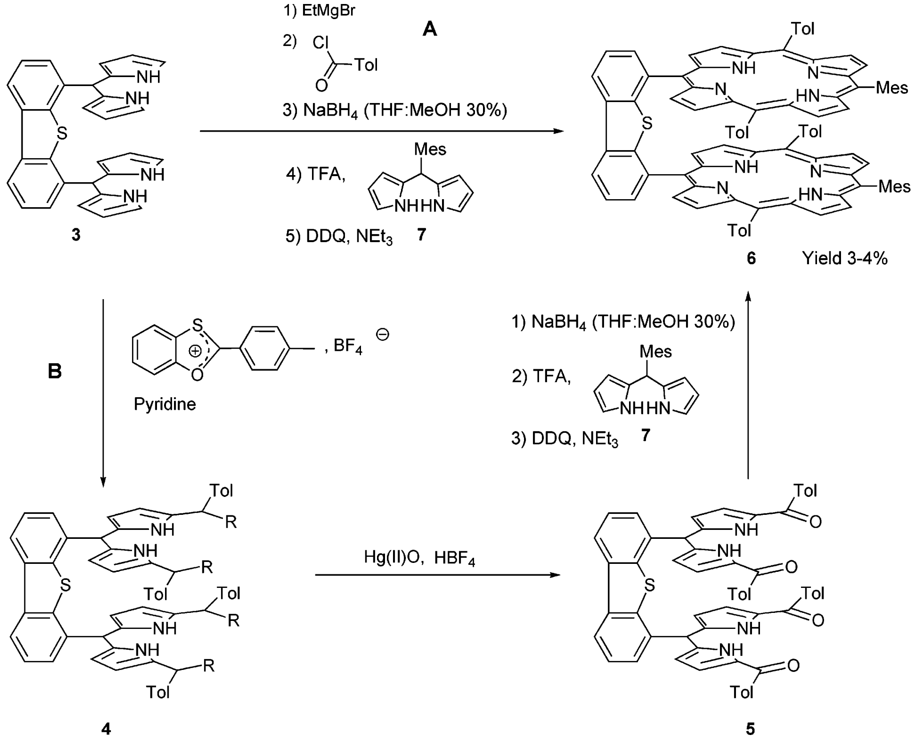
Scheme 3



Scheme 4

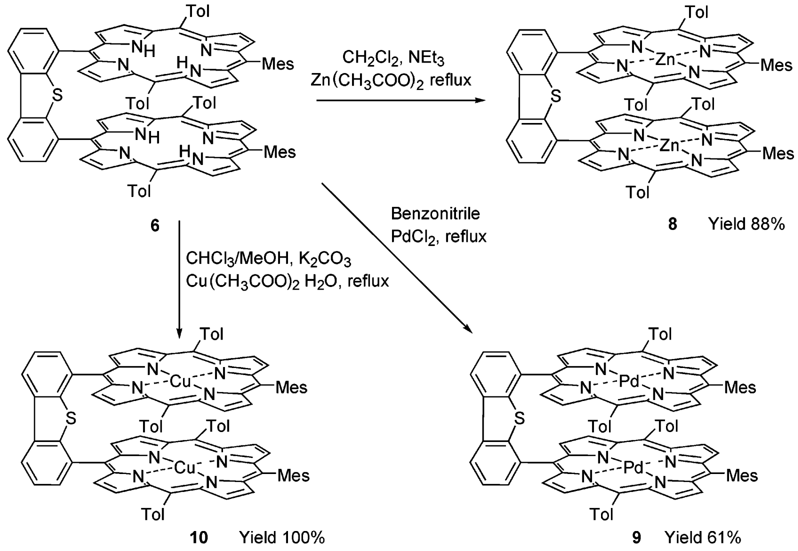


Table 1. $C_{meso}-C_{meso}$ Distances and Chemical Shifts of N−H Protons for Cofacial Free Base Bisporphyrins

	DPB	DPX	DPA	DPO	DPS	DPXN[a]	DPSN	DPON[b]
$d(C_{meso}-C_{meso})$ (Å)	3.80	4.32	4.94	5.53	6.3			
δ^c	−7.6	−6.42, −6.80	−4.98	−3.8, −3.91	−3.68,−3.75	−3.30	−3.11	−3.07
ref	9, 13	11, 67	8, 68	12, 13, 67	69	14		14

[a] DPXN: 4,5-bis[5-(10,15,20-trimesitylporphyrinyl)]-2,7-di-*tert*-butyl-9,9-dimethylxanthene. [b] DPON: 4,6-bis[5-(10,15,20-trimesitylporphyrinyl)]dibenzofuran. [c] ^{1}H NMR in CDCl$_3$.

of H$_4$DPXN ($\delta = -3.30$) to those of H$_4$DPX ($\delta = -6.42$ and -6.80) clearly shows that the use of bulky substituents at the meso position induces a larger cavity size.

Photophysical Data. Figure 1 and Figure 2 exhibit the absorption spectra of **6**, and **8**−**10**. The Soret band for **6** is strong and narrow ($\lambda_{max} = 416$ nm), which is characteristic for weakly or noninteracting meso-substituted porphyrins in a face-to-face configuration (i.e., no excitonic coupling).[15] Table 2 compares the UV−vis data between meso- and β-substituted mono- and bisporphyrins (H$_2$TPP vs H$_4$DPSN, H$_2$P vs H$_4$DPB, H$_4$DPS, and H$_4$DPX), and shows that the Soret band for meso-substituted macrocycles is more intense

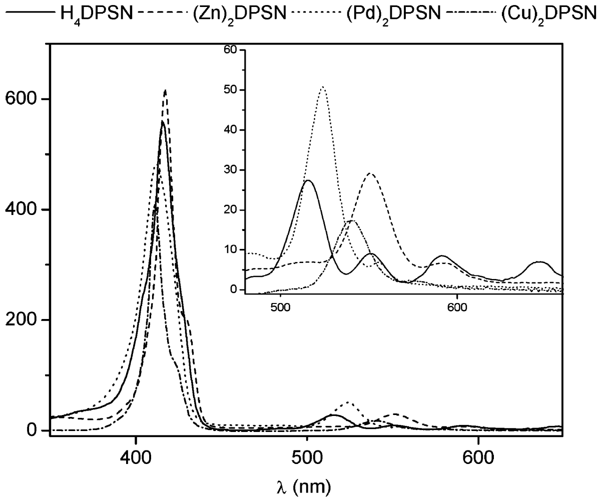


Figure 1. Absorption spectra of H_4DPSN, $(Zn)_2DPSN$, $(Pd)_2DPSN$, and $(Cu)_2DPSN$ in CH_2Cl_2 at 298 K.

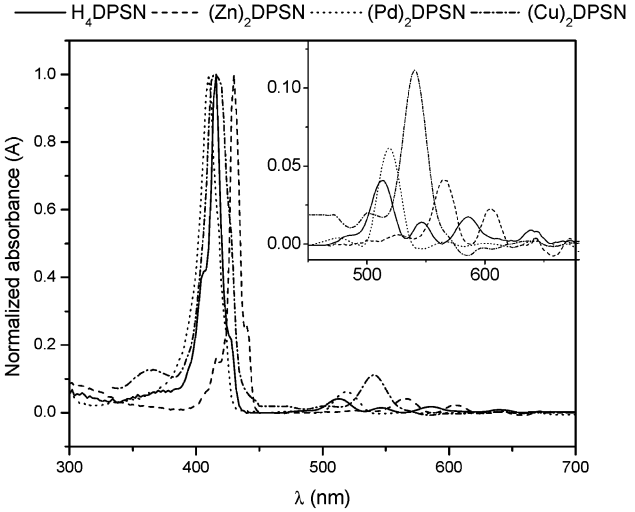


Figure 2. Absorption spectra of H_4DPSN, $(Zn)_2DPSN$, $(Pd)_2DPSN$, and $(Cu)_2DPSN$ in 2-MeTHF at 77 K.

Table 2. UV−Vis Absorption Data in CH_2Cl_2 at 298 K

	λ_{max} (nm) ($\epsilon \times 10^{-3}$ M^{-1} cm^{-1})				
compound	Soret region	Q-bands			
H_4DPSN	416 (556)	513 (28)	551 (9)	591 (9)	646 (7)
$(Zn)_2DPSN$	417 (619)	552 (29)			594 (6)
$(Pd)_2DPSN$	412 (482)	524 (50)			555 (7)
$(Cu)_2DPSN$	411 (408)				540 (17)
$H_2TPP^{35,a}$		515 (19.8)			
$(Zn)TPP^{34,35,a}$	425	550 (23.3)			589
$(Pd)TPP^{34\ a}$	418	524			554
$(Cu)TPP^{34\ a}$	416	539			578
H_2P^b	402 (154)	502 (15)	532 (8)	578 (6)	626 (4)
$(Zn)P^b$	410 (270)	540 (18)			576 (11)
$(Pd)P^b$	398 (180)	504 (16)			538 (43.2)
H_4DPS	398 (309.9)	502 (29.6)	536 (15.0)	570 (14.2)	622 (6.8)
$(Zn)_2DPS$	402 (473.6)	536 (32)			572 (29)
$(Pd)_2DPS^{68}$	394 (256.9)	516 (23.5)	548 (50.5)		610 (0.29)

[a] In C_6H_6. [b] P^{2-} = 5-phenyl-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin dianion.

and red-shifted than that observed for the β species. The phosphorescence of the (Pd)P monoporphyrin (P^{2-} = 5-phenyl-2,8,13,17-tetraethyl-3,7,12,18-tetramethylporphyrin dianion) was too small to be measured at 298 K.[65] The emission spectra and photophysical data for the investigated compounds are presented in Figure 3 and Table 3, respectively. The emission maxima are similar for the mono- and bisporphyrins in all meso-substituted systems. At 298 K, the Φ_F values for the bisporphyrins are smaller compared to those of H_2TPP. Moreover, the Φ_P values for the Pd*P* chromophore in $(Pd)_2DPSN$ is smaller than that observed for (Pd)TPP. At 77 K, Φ_P's are expectedly larger for all molecules, but the meso-substituted systems exhibit a larger increase in Φ_P going from 298 to 77 K.

Bimolecular Excited-State Quenching by Oxygen. The k_Q values for five dipalladium bisporphyrins from this work and the literature are compared. Figure 4 exhibits the graphs of $\Phi_P{}^0/\Phi_P$ as a function of the diffusion time of O_2 in the solution, where $\Phi_P{}^0$ and Φ_P are the phosphorescence quantum yields in the absence and presence of oxygen, respectively, for $(Pd_2)DPS$, $(Pd)_2DPX$, $(Pd)_2DPB$, $(Pd)_2DPSN$, and (Pd)TPP. This graph is similar to Stern−Volmer plots. $[O_2]$ is determined using (Pd)TPP as a standard ($\Phi_P{}^0/\Phi_P{}^{air}$ = 4850, $[O_2]_{dissolved} = 2.1 \times 10^{-3}$ M under $P_{O_2} = 0.21$ atm[20,37]), allowing for the determination of k_Q according to

$$\frac{\Phi_0}{\Phi} = 1 + k_Q\tau_P[O_2] = 1 + k_{SV}[O_2] \qquad (1)$$

where k_{SV} is the Stern−Volmer constant and τ_P is the phosphorescence lifetime (see Table 4). Comparison of the data can be made according to Table 5. $(Pd)_2DPX$ and $(Pd)_2DPB$ are the most and least sensitive to oxygen, respectively, (i.e., largest and smallest observed k_{SV} values). k_{SV} depends on both k_Q and τ_P (eq 1). In a previous paper,[65] it was demonstrated that τ_P is a function of the $C_{meso}-C_{meso}$ distance. As this distance decreases, τ_P decreases (τ_P: $H_4DPX > H_4DPB$), witnessing the presence of excited-state deactivation due to internal conversion processes promoted by intermacrocycle collisions or interactions. The incorporation of bulky tolyl and mesityl groups at meso positions should greatly reduce these interactions. Indeed, $\tau_P((Pd)_2DPSN) > \tau_P((Pd)_2DPS)$, and in fact, the former bismacrocycle exhibits the largest τ_P of the series. On the other hand, k_Q is small and just larger than that measured for $(Pd)_2DPB$, which is the bismacrocycle that exhibits the smallest cavity.

A qualitative analysis of the k_Q data is given below. Theoretically, k_Q arising from a collisional bimolecular process (dynamic quenching) is defined as

$$k_Q = f_Q k_0 \qquad (2)$$

where f_Q is the quenching efficiency and k_0 the diffusion-controlled bimolecular rate constant assuming that all collisions lead to excited-state deactivation. The fact that the absorption spectra are not modified by the presence of O_2 in solution confirmed that the observed phosphorescence

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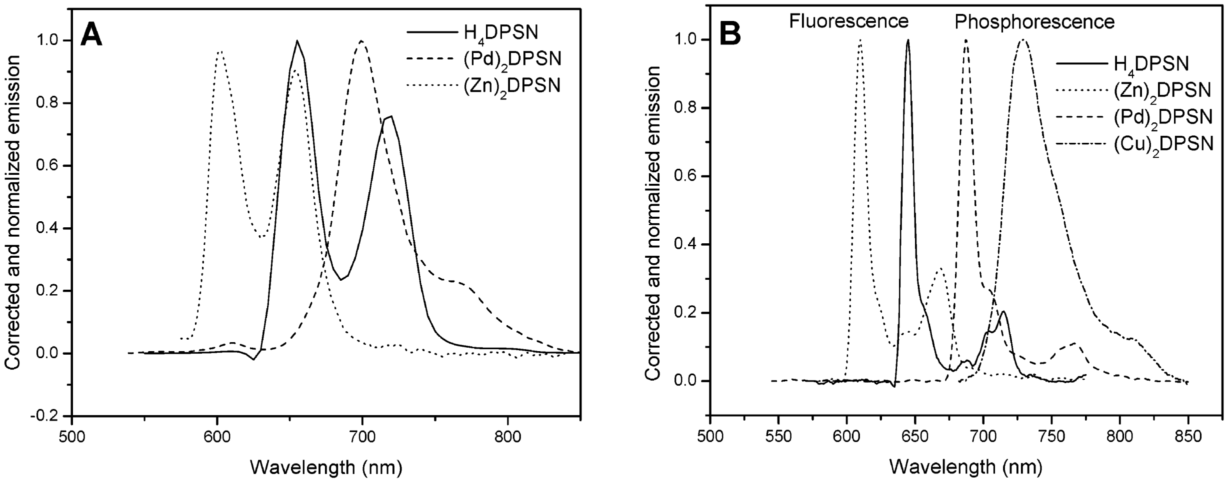


Figure 3. Emission spectra of H_4DPSN, $(Pd)_2DPSN$, and $(Zn)_2DPSN$ at 298 K (A) and 77 K (B), and of $(Cu)_2DPSN$ at 77 K (B) in 2-MeTHF.

Table 3. Emission Data[a]

compound	emission[b] λ_{max} (nm)		quantum yield[c,d]		lifetime[d,e] τ_F (ns), τ_P (μs)	
	298 K	77 K	298 K	77 K	298 K	77 K
H_4DPSN	655, 719	655, 715	0.06860 (Φ_F)	0.1310 (Φ_F)	12.43 (τ_F)	13.34 (τ_F)
$(Zn)_2DPSN$	602, 654	611, 670	0.02843 (Φ_F)	0.0574 (Φ_F)	2.46 (τ_F)	1.45 (τ_F)
$(Pd)_2DPSN$	699	688	0.03705 (Φ_P)	0.1551 (Φ_P)	506.00 (τ_P)	1388.00 (τ_P)
$(Cu)_2DPSN$		729		< 0.0001 (Φ_P)		45.5 (τ_P)
(Pd)TPP	696, 772	680, 755	0.02 (Φ_P)	0.17[f] (Φ_P)	258.67 (τ_P)	1320 (τ_P)

[a] In 2-MeTHF, $\lambda_{excitation} = 510$ nm for free and palladium porphyrins and 540 nm for copper and zinc derivatives; the quantum yield was evaluated by reference to H_2TPP (0.11,)[33−35] and the quantum yield for H_2TPP (0.11) at 77 K was verified by reference to (Pd)TPP (0.17; 77 K; MCH).[36,37] [b] The uncertainties in the values of λ_{max} are ±1 nm. [c] The uncertainties in the values of the quantum yields are ±10%. [d] F = fluorescence, P = phosphorescence. [e] The uncertainties in the values of the lifetimes are ±10%. [f] In methylcyclohexane (MCH).

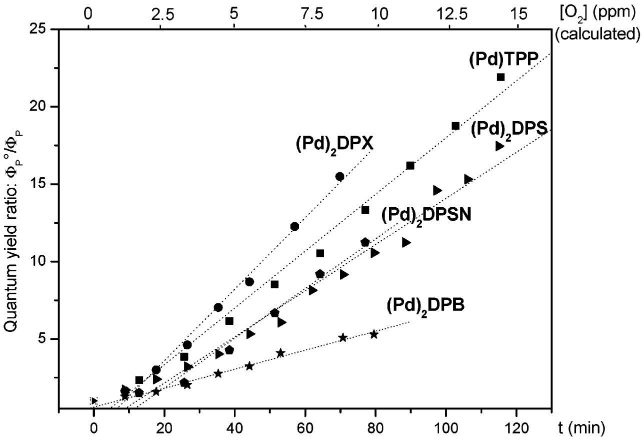


Figure 4. Graph of $\Phi_P{}^0/\Phi_P$ vs diffusion time of O_2 (lower scale) and vs $[O_2]$ (upper scale) of the Pd−porphyrin sensors.

quenching is due to a dynamic quenching process.[66] The collision frequency, Z, is defined as

$$Z = k_0[O_2] \qquad (3)$$

and k_0 can be expressed according to the Smoluchowski relation[37,66]

$$k_0 = 4\pi N R_P(D_{O_2} + D_P) \qquad (4)$$

where N is Avogadro's number, R_P is the collision radius, i.e., the sum of the radii of the emitting species (a single chromophore) and quencher (Scheme 5),[66] and D_{O2} and D_P are the diffusion coefficients of O_2 and the porphyrin species, respectively. The latter can be estimated using the Stokes−Einstein equation[37,66]

$$D = \frac{k_bT}{6\pi\eta r} \qquad (5)$$

Table 4. Photophysical Data of Palladium Bisporphyrins Compared to (Pd)TPP[a]

compound	τ_P (μs)	k_Q (10^9 M^{-1} s^{-1})	k_{SV} (10^6 M^{-1})	lowest detection[b] (ppm)
$(Pd)_2DPX$	440	6.94	2.91	0.58
(Pd)TPP	258	8.95	2.31	0.73
$(Pd)_2DPSN$	506	3.99	2.02	0.83
$(Pd)_2DPS$	210	8.95	1.88	0.90
$(Pd)_2DPB$	258	2.98	0.77	2.2

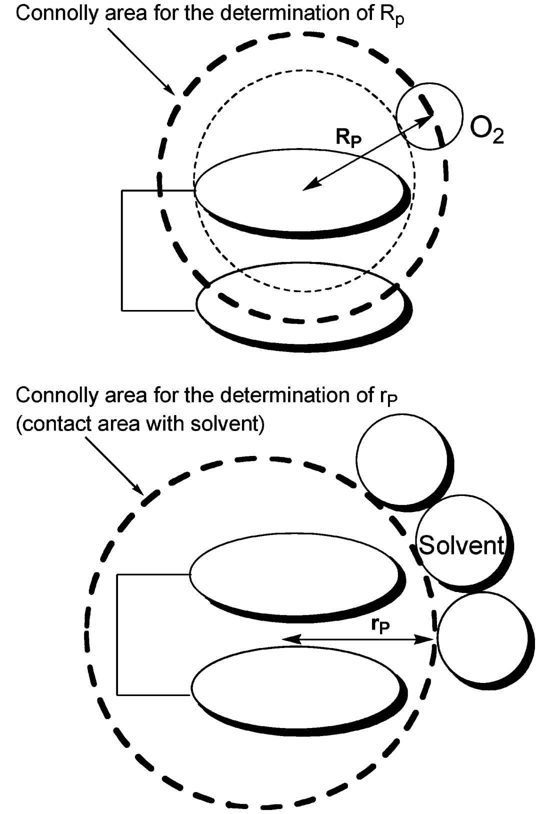
[a] τ_P values are phosphorescence lifetimes measured under an atmosphere of argon; k_Q values are excited-state deactivation constant; k_{SV} is the Stern−Volmer constant. [b] Lowest detection (5%) based on I = 0.95 I_0.

Table 5. Theoretical Parameters for O_2 Quenching, Quenching Efficiency, and Diffusion-Controlled Bimolecular Rate Constants for Palladium Bisporphyrins and (Pd)TPP

compound	r_P[a] (Å)	D_p[b] (10^{-9} m^2 s^{-1})	R_p[c] (Å)	k_0[d] (10^9 M^{-1} s^{-1})	k_Q[e] (10^9 M^{-1}s^{-1})	f_Q[f] (%)
$(Pd)_2DPX$	8.1	0.45	7.4	15.6	6.94	44
(Pd)TPP	6.6	0.56	8.8	19.4	8.95	46
$(Pd)_2DPSN$	9.5	0.39	8.6	17.7	3.99	22
$(Pd)_2DPS$	9.0	0.43	8.0	16.8	8.95	53
$(Pd)_2DPB$	7.9	0.46	7.3	15.4	2.98	19

[a] Porphyrin radius. [b] Diffusion coefficient of the bismacrocycle. [c] Sum of the molecular radius of the chromophore and dioxygen. [d] Theoretical diffusion-controlled deactivation constant. [e] Deactivation constant. [f] Deactivation efficiency.

Scheme 5



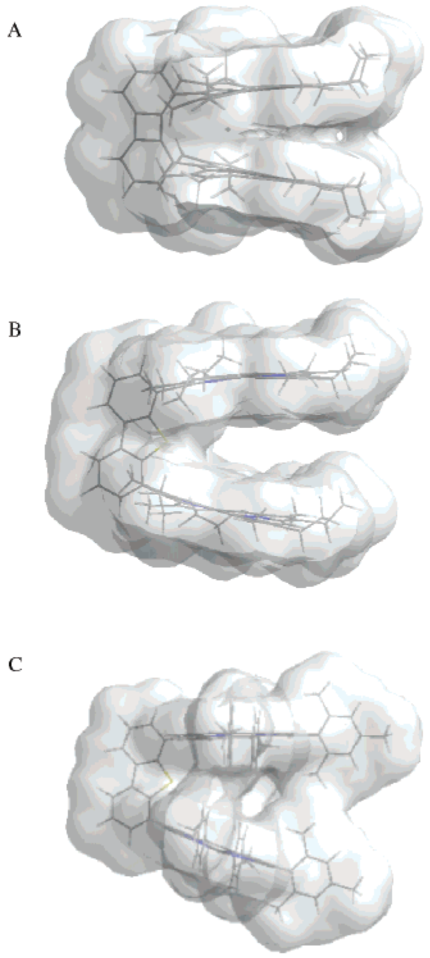


Figure 5. Examples of computed surfaces for $(Pd)_2DPB$ (A), $(Pd)_2DPS$ (B), and $(Pd)_2DPSN$ (C).

where k_b, η, and T are the Boltzman constant, the viscosity of the medium ($\eta = 0.575 \times 10^{-3}$ Pa for 2-MeTHF at 293 K),[37] and the temperature, respectively, r is the solvated molecular radius (i.e., r_P for the bisporphyrin, r_{O2} for O_2; Scheme 5). As molecules are not spherical systems, the molecular surfaces are computed according to the Connolly methodology.[31] The calculated surfaces are then used to extract r_P and r_{O_2} for a sphere model. This computer methodology requires knowledge of the solvent radius. In this work, r(2-MeTHF) was also estimated by computations using the van der Waals radii (r(2-MeTHF) = 2.89 Å). This approach represents a crude approximation. For O_2, $r_{O_2} =$ 1.6 Å and $D_{O_2} = 2.33 \times 10^{-9}$ m^2 s^{-1}.

Table 5 compares the calculated parameters and experimental k_Q allowing extraction of f_Q. Figure 5 shows three typical examples of computed surface envelopes used to determine r_P and R_P. As anticipated, r_P is greater for larger bismacrocycles (example: $r_P((Pd)_2DPSN) > r_P((Pd)_2DPB)$), and D_P's for the porphyrin molecules are smaller than that for O_2. Similarly, R_P's for β-substituted porphyrins are smaller than those for the meso-substituted chromophores, again consistent with the number of substituent C atoms attached on the porphyrin rings. k_0 is calculated from r_P, D_P, and R_P (eq 4). On the basis of the k_0 values, (Pd)TPP, $(Pd)_2DPSN$, and $(Pd)_2DPS$ are predicted to be the most efficient O_2 sensors if all collisions are efficient from a theoretical stand point. This basic model assumes that collisions with the porphyrin chromophore substituents lead to excited-state deactivation, which is not necessarily always the case. From the experimental k_Q's, we estimated and compared the f_Q's. The series can be separated into two groups: "open" ($(Pd)_2DPX$, $(Pd)_2DPS$) and "closed" ($(Pd)_2DPSN$, $(Pd)_2DPB$) systems. (Pd)TPP is characterized by an efficiency similar to that of the bisporphyrins with "open" cavities that are formed by the two macrocycles and the spacer.

The comparison of the f_Q values for $(Pd)_2DPX$, $(Pd)_2DPS$, and $(Pd)_2DPB$ shows that the smaller cavity in the biphenylenyl derivative (Figure 5) prevents efficient quenching by oxygen. The fact that the $f_Q((Pd)_2DPS)/f_Q((Pd)_2DPB)$ ratio is about 2 strongly suggests that the O_2 molecules do not penetrate inside the cavity in $(Pd)_2DPB$, and indicates that the two macrocycles screen each other. Similarly, comparison of the f_Q values for (Pd)TPP and $(Pd)_2DPSN$ indicates that the interior of the cavity of the latter system is cluttered. This can also be observed in Figure 5 when comparing $(Pd)_2DPS$ with $(Pd)_2DPSN$. Again, $f_Q((Pd)_2DPS)/f_Q((Pd)_2DPSN)$ and $f_Q((Pd)TPP)/f_Q((Pd)_2DPSN)$ ratios of about 2 are noted.

While the meso-substitution by aryl groups prevents the two macrocycles in a cofacial arrangement from deactivating each other, rendering τ_P longer, steric hindrance prevents O_2 from efficiently penetrating inside the cavity. As a consequence, the design for better sensors must take these parameters into account. It is interesting to note that $(Pd)_2DPX$ is the most sensitive of the porphyrin systems, but its synthesis requires many steps.

Conclusion

The results demonstrate the presence of a diffusion mechanism of O_2 toward the chromophore, contrasting with the static mechanism, which is the source of some controversy in the literature. In terms of efficiency vs cost, (Pd)-TPP definitely exhibits the best ratio in the studied series. However, the structural modification for molecular device improvement of this monoporphyrin complex is not flexible. Indeed, better sensitivity is obtained when one figures out a way to increase τ_P and Φ_P via structural modification. This was found in $(Pd)_2$DPX, for which τ_P was increased and both macrocycles remained clearly accessible to O_2. By reducing the number of steps of synthesis for $(Pd)_2$DPSN in this work, and choosing the appropriate substituents, we found it is possible that more effective O_2 sensing porphyrins could be prepared at a reasonable price. In this context, the construction of systems covalently anchored on solid support, both mono- and bisporphyrin systems, exhibits very interesting possibilities for future applications in this area.

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Supporting Information Available: Table comparing the λ_{max}, Φ_e, and τ_e for various related bisporphyrin systems; ^{1}H and ^{13}C-{^{1}H} NMR and MS (MALDI-TOF) and EPR spectra for **1**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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