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Axial Coordination of Porphyrinatocobalt(II) Complexes with Bis(pyridinolato)silicon(IV) Phthalocyanines

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Keywords: Phthalocyanines / Porphyrins / Axial coordination / UV/Vis spectroscopy

Treatment of dichlorosilicon(IV) phthalocyanine with 3- or 4-hydroxypyridine in the presence of pyridine in toluene gave the corresponding bis(pyridinolato)silicon(IV) phthalocyanine complexes SiPc(3-OPy)$_2$ (**1**) or SiPc(4-OPy)$_2$ (**2**), respectively, which were spectroscopically and structurally characterized. As shown by electronic absorption spectroscopy, these compounds axially bind to *meso*-tetraphenylporphyrinatocobalt(II) [Co(TPP) (**3**)] and *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrinatocobalt(II) [Co(TBPP) (**4**)] with the two pyridyl ligands forming the corresponding mixed phthalocyanine–porphyrin triads. The binding constants K_1 between the 4-pyridyl phthalocyanine **2** and the porphyrinatocobalt(II) complexes ($1.1–1.2 \times 10^4$ M^{-1}) are about threefold higher than those for the 3-pyridyl counterpart **1**. The heterodyads **2·3** and **2·4** were isolated by column chromatography and characterized by mass and absorption spectroscopy.

Introduction

Phthalocyanines and porphyrins are two important classes of functional dyes. Owing to their unique and intriguing properties, these macrocycles have found widespread applications in various disciplines ranging from materials science, catalysis, nanotechnology to medicine.[1] Despite their structural similarities, these two classes of π systems exhibit very different optical and electronic properties making them useful in different areas. A hybrid system containing both of these macrocycles may combine their advantageous properties and improve the overall performance. One obvious example is the complementary major absorptions of phthalocyanines (650–700 nm) and porphyrins (400–450 nm) in the visible region. Mixed phthalocyanine–porphyrin assemblies can absorb strongly over a large part of the solar spectrum, which can facilitate various light-induced processes. This property is important in applications such as light harvesting, photovoltaics, and molecular photonics.[2] A substantial number of mixed phthalocyanine–porphyrin arrays have been reported.[3] Apart from a covalent linkage the two types of macrocycles can also be linked by a metal center in the form of sandwich-type complexes,[4] by a bridging nitrido, oxo, chloro, or hydroxo ligand to form cofacial complexes[5] or by electrostatic interactions to form face-to-face aggregates.[3,6] The use of host-guest interactions to assemble these macrocycles has also been reported recently.[7] Although axial coordination has been widely used to construct various multiporphyrin systems,[8] the use of this strategy to build mixed phthalocyanine–porphyrin scaffolds remains little studied.[9] We have recently prepared the bis(4-pyridinolato)silicon(IV) phthalocyanine (**2**), which can axially bind to various tetrapyrrolatozinc(II) derivatives forming the corresponding 1:2 or 1:1 molecular assemblies.[9b] We describe herein an extension of this work using **2** as well as the 3-pyridyl analogue **1** as the cores to complex with porphyrinatocobalt(II) complexes. The relatively strong cobalt–pyridine binding interactions allow the isolation of the heterodyads.

Results and Discussion

The preparation of bis(3-pyridinolato)silicon(IV) phthalocyanine complex **1** was similar to that of the 4-pyridyl analogue **2** (Figure 1).[9b] It involved a ligand-substitution reaction of dichlorosilicon(IV) phthalocyanine with 3-hydroxypyridine in the presence of pyridine in toluene. Both **1** and **2** were soluble in common organic solvents and could be purified readily by column chromatography giving a comparable yield (75% and 72%, respectively). The porphyrinatocobalt(II) complexes Co(TPP) (**3**) and Co(TBPP) (**4**) (Figure 1) were prepared by cobaltation of the corresponding metal-free porphyrins.[10]

Both compounds **1** and **2** were fully characterized by using various spectroscopic methods and X-ray diffraction analyses. Single crystals of **1** were grown by slow diffusion of nitrobenzene into a CHCl$_3$ solution of **1**. The compound cocrystallized with two molecules of nitrobenzene in the triclinic system. As shown in part a of Figure 2, the structure contains an inversion center at the silicon center relating

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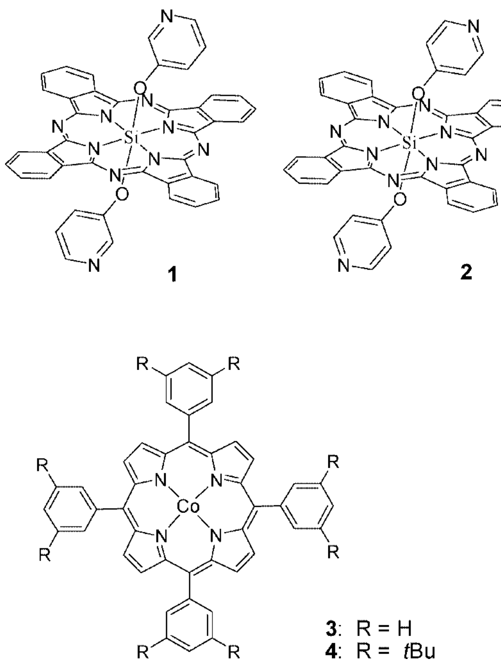

Figure 1. Structures of the bis(pyridyl) phthalocyanines **1** and **2**, and the porphyrinatocobalt(II) complexes **3** and **4**.

the two halves of the molecule. The silicon center is hexacoordinate with four isoindole nitrogen atoms of the phthalocyanine ring and two oxygen atoms of the pyridinolato ligands. The Si–O [1.740(2) Å] and average Si–N [1.912(4) Å] bond lengths as well as the other structural parameters are unexceptional.

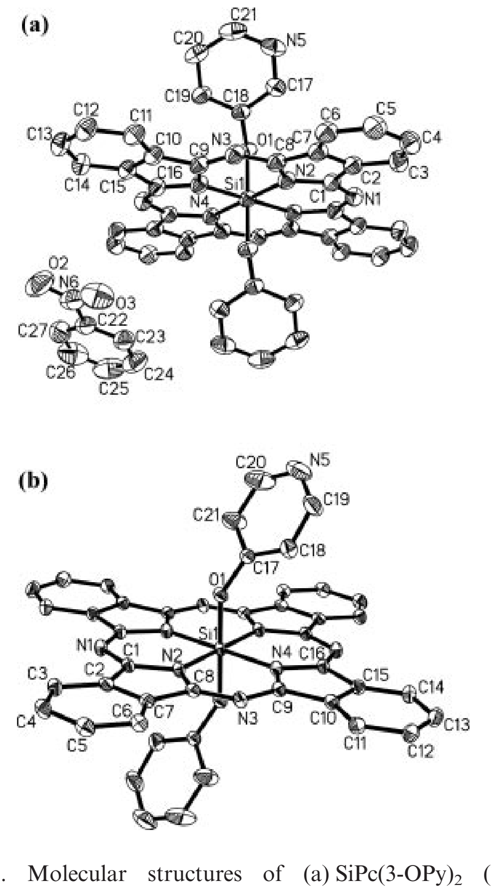

Figure 2. Molecular structures of (a) SiPc(3-OPy)$_2$ (**1**) and (b) SiPc(4-OPy)$_2$ (**2**) showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

Single crystals of **2** were grown by slow diffusion of MeOH into a $CHCl_3$ solution of **2**. The compound crystallized in the monoclinic system. The molecular structure of **2** (Figure 2, b) also contains an inversion center. The Si–O [1.715(2) Å] and average Si–N [1.910(4) Å] bond lengths are comparable with those of **1**. The phthalocyanine rings of **1** and **2** are essentially planar with a dihedral angle of 42.5° and 57.5°, respectively, between the phthalocyanine N(isoindole)$_4$ plane and the pyridyl ring. In both structures, particularly for **2**, the pyridyl-nitrogen atoms point outward favoring the complexation process.

The complexation of SiPc(4-OPy)$_2$ (**2**) and Co(TPP) (**3**) was first studied by electronic absorption spectroscopy. Figure 3 shows the UV/Vis spectra of mixtures of these two compounds in different ratios in $CHCl_3$, where the total concentration was fixed at 5.0 μM. It can be seen that as the mole fraction of SiPc(4-OPy)$_2$ (**2**) increases, the phthalocyanine B band at 354 nm, Q band at 684 nm, and vibronic band at 614 nm all increase in intensity. The porphyrin Soret band at 410 nm becomes attenuated and a new band at

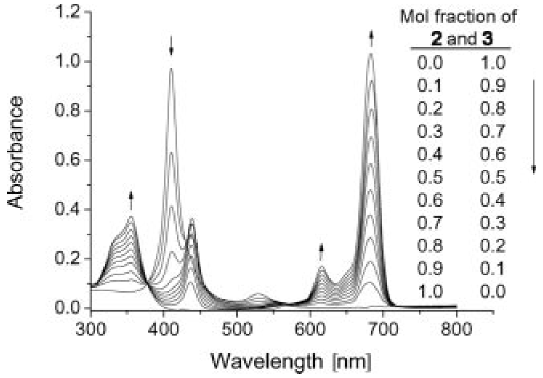

Figure 3. Absorption spectra of mixtures of SiPc(4-OPy)$_2$ (**2**) and Co(TPP) (**3**) in $CHCl_3$. The total concentration of the two compounds was fixed at 5.0 μM.

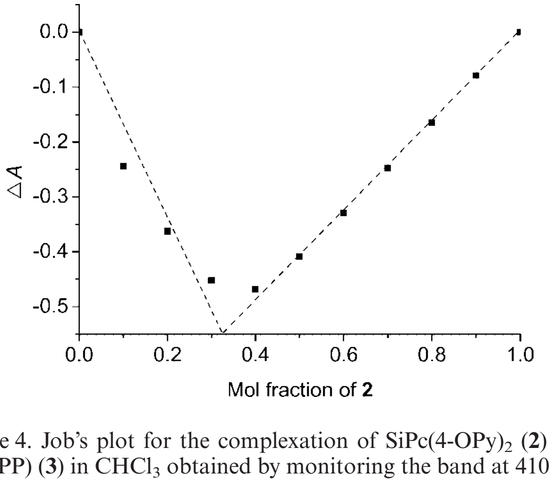

Figure 4. Job's plot for the complexation of SiPc(4-OPy)$_2$ (**2**) and Co(TPP) (**3**) in $CHCl_3$ obtained by monitoring the band at 410 nm.

435 nm appears, which can be attributed to the axially bound species. The corresponding Job's plot[11] (Figure 4), obtained by monitoring the band at 410 nm, shows a minimum when the mole fraction of **2** is about 0.34. This suggests a 1:2 stoichiometry for **2** and **3**, and the formation of the heterotriad $\mathbf{2}\cdot(\mathbf{3})_2$.

Figure 5 shows the changes of the Soret band of Co(TPP) (**3**), fixed at a concentration of 4.5 µM, upon titration with $\mathrm{SiPc(4\text{-}OPy)_2}$ (**2**) (from 75 to 260 µM) in $\mathrm{CHCl_3}$. The corresponding solution of **2** with the same concentration was used as the reference in recording the spectra. Under these conditions the phthalocyanine $\mathrm{SiPc(4\text{-}OPy)_2}$ (**2**) was in great excess. Therefore, the 1:1 complex was predominantly formed and the Benesi–Hildebrand equation [Equation (1)] could be applied to determine the binding constant K_1.[12]

$$\frac{b}{\Delta A}=\frac{1}{S_t K_1 \Delta\varepsilon[\mathrm{L}]}+\frac{1}{S_t \Delta\varepsilon} \qquad (1)$$

where b is the optical path length (1 cm); ΔA is the change in absorbance at 435 nm, where the largest change was observed; S_t is the total concentration of substrate (i.e. **3**); [L] is the concentration of ligand [i.e. **2**, which can be approximated as L_t (the total concentration of ligand) where $L_t >> S_t$]; and $\Delta\varepsilon = \varepsilon_{11} - \varepsilon_S - \varepsilon_L$, where ε_{11}, ε_S, and ε_L are the molar absorptivities of the 1:1 complex, **3**, and **2** at 435 nm, respectively. A plot of $1/\Delta A$ vs. $1/[\mathbf{2}]$ (inset of Figure 5) gave a straight line from which the value of K_1 was determined to be $(1.2 \pm 0.1) \times 10^4\ \mathrm{M^{-1}}$. Similarly, a linear relationship was also found in the Scott or Scatchard plot giving virtually the same K_1 value.[12]

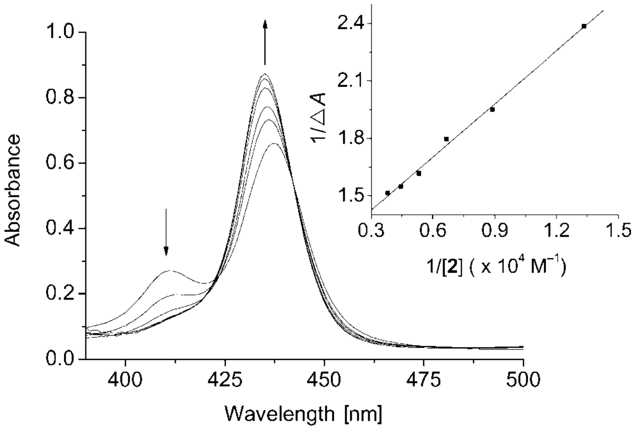

Figure 5. Changes in the UV/Vis spectrum of Co(TPP) (**3**) (4.5 µM) upon titration with $\mathrm{SiPc(4\text{-}OPy)_2}$ (**2**) (from 75 to 260 µM) in $\mathrm{CHCl_3}$. The inset shows the corresponding Benesi–Hildebrand plot obtained by monitoring the change in absorbance at 435 nm.

The complexation of other systems including $\mathrm{SiPc(4\text{-}OPy)_2}$ (**2**) with Co(TBPP) (**4**), as well as the 3-pyridyl analogue **1** with these two porphyrinatocobalt(II) complexes, was investigated by the same approach. All the systems gave very similar spectral changes except the complexation of $\mathrm{SiPc(3\text{-}OPy)_2}$ (**1**) with Co(TBPP) (**4**), for which the band ascribed to the axially bound species appeared as a shoulder at ca. 440 nm instead of a distinct signal (see Figure S1 in the Supporting Information). The results showed that both phthalocyanines **1** and **2** bind to porphyrinatocobalt(II) complexes **3** and **4** in a 1:2 manner proceeding in a stepwise fashion as shown in Figure 6.

Table 1 summarizes the binding constants (K_1) for these systems determined by absorption spectroscopy. The corresponding data for the complexation of 3- and 4-hydroxypyridine (3-OHPy and 4-OHPy) with Co(TPP) (**3**) were also determined by the same method and are included for comparison. It can be seen that the values for the 4-pyridinolato complex **2** are about three times larger than those of the 3-pyridinolato counterpart **1**. The addition of *tert*-butyl groups on the *meso*-phenyl substituents of porphyrin does not have a significant influence on the binding constants. The stronger binding for **2** compared with that of **1** can be attributed to the fact that the 4-pyridinolato ligand is a better σ donor than the 3-pyridinlolato analogue (because of the presence of the resonance form A as shown in Figure S2 in the Supporting Information). In addition, the 4-pyridin-

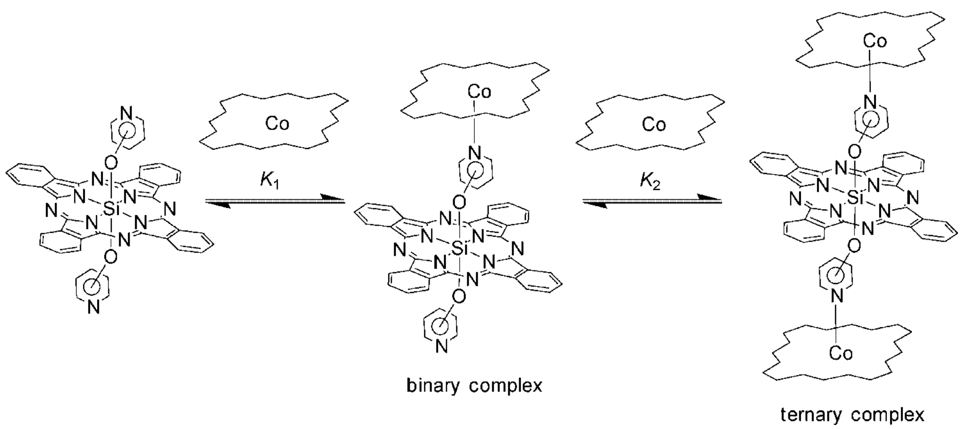

Figure 6. A schematic diagram showing the axial coordination porphyrinatocobalt(II) complexes **3** and **4** with bis(pyridyl) phthalocyanines **1** and **2**.

olato ligand can readily complex with the cobalt center, but for the 3-pyridinolato analogue complexation can only occur when the nitrogen atom is pointing away from the phthalocyanine plane (conformation B rather than C as shown in Figure S3 in the supporting information). However, since the K_1 value for 4-OHPy is also almost three times larger than that for 3-OHPy it seems that the electronic factor plays a dominant role. The binding constants determined for these systems are comparable with those reported for other porphyrinatocobalt(II) complexes and pyridine-type donor ligands.[13]

Table 1. Comparison of the binding constants.[a]

Ligand	Porphyrin	K_1 [M^{-1}]
SiPc(3-OPy)$_2$ (**1**)	Co(TPP) (**3**)	$(3.9 \pm 1.2) \times 10^3$
SiPc(3-OPy)$_2$ (**1**)	Co(TBPP) (**4**)	$(4.3 \pm 0.3) \times 10^3$
SiPc(4-OPy)$_2$ (**2**)	Co(TPP) (**3**)	$(1.2 \pm 0.1) \times 10^4$
SiPc(4-OPy)$_2$ (**2**)	Co(TBPP) (**4**)	$(1.1 \pm 0.2) \times 10^4$
3-OHPy	Co(TPP) (**3**)	$(3.6 \pm 0.4) \times 10^3$
4-OHPy	Co(TPP) (**3**)	$(1.4 \pm 0.1) \times 10^4$

[a] Determined by absorption spectroscopy in $CHCl_3$.

Because of the relatively large binding constants attempts were made to isolate the complexed species. By stirring a 1:2 (in mole) mixture of SiPc(4-OPy)$_2$ (**2**) and Co(TPP) (**3**) or Co(TBPP) (**4**) in $CHCl_3$ a new TLC spot with an R_f value of ca. 0.3 in $CHCl_3$/MeOH (v/v, 5:1) appeared. The new products could be isolated as a blue solid by silica-gel column chromatography using $CHCl_3$/MeOH (v/v, 9:1) as eluent. Mass and UV/Vis spectroscopic methods showed that they were the binary complexes **2·3** and **2·4**. The corresponding ternary complexes **2**·(**3**)$_2$ and **2**·(**4**)$_2$ could not be isolated, which is probably because of their small quantity (the binary complexes could only be isolated in ca. 5% yield). The MALDI-TOF mass spectra of the dyads showed an envelope peaking at m/z = 1399.0 or 1847.7, assignable to the corresponding molecular ion. For both signals, the isotopic pattern was in good agreement with the simulated spectrum. The identity of these complexes was further confirmed by accurate mass measurements (using ESI mass spectrometry).

Figure 7 compares the UV/Vis spectrum of the dyad **2·3** in $CHCl_3$ and the sum of the spectra of **2** and **3**, all at the same concentration. It can be seen that the porphyrin Soret band is redshifted from 410 nm to 435 nm upon complexation, while the absorptions of the phthalocyanine component are essentially unchanged. Similar results were obtained for the binary complex **2·4** (see Figure S4 in the Supporting Information). These observations supported the findings that the binary complexes were stable enough to be isolated, which is in contrast to the porphyrinatozinc(II) counterparts.[9b] Under the same conditions, the binary complexes of the 3-pyridyl analogue **1** and the porphyrinatocobalt(II) complexes **3** and **4** could not be isolated, which is in accord with their weaker binding interactions.

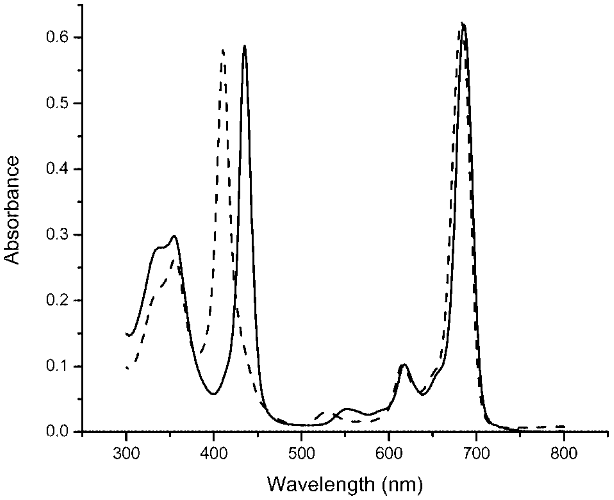

Figure 7. UV/Vis spectrum of the binary complex **2·3** (———) and the addition spectrum of **2** and **3** (-----) in $CHCl_3$. The concentrations of all the species were fixed at 3.2 μM.

Conclusions

In summary, the bis(pyridyl) phthalocyanines **1** and **2** serve as good building blocks for hetero phthalocyanine–porphyrin arrays. As shown by absorption spectroscopy, they formed 1:2 complexes with porphyrinatocobalt(II) **3** and **4** with binding constants K_1 in the range of 3.9×10^3 to 1.2×10^4 M^{-1}. The heterodyads **2·3** and **2·4** could also be isolated and spectroscopically characterized. It is envisaged that this axial coordination approach can be extended to construct larger mixed phthalocyanine–porphyrin arrays. This work is in progress.

Experimental Section

General: Reactions were performed under nitrogen. Toluene was distilled from sodium prior to use. *N*,*N*-Dimethylformamide (DMF) was predried with barium oxide and distilled under reduced pressure. The chloroform used in the UV/Vis studies was freshly distilled from CaH_2 under nitrogen. All other solvents and reagents were used as received. Chromatographic purifications were performed with silica gel (Macherey–Nagel, 70–230 mesh) columns with the indicated eluents. Compounds **2**,[9b] **3**,[10a] and the metal-free *meso*-tetrakis(3,5-di-*tert*-butylphenyl)porphyrin [H$_2$(TBPP)][10b] were prepared by previously described methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with a Bruker DPX 300 spectrometer (^{1}H NMR, 300; ^{13}C NMR, 75.4 MHz) in $CDCl_3$. Spectra were referenced internally using the residual solvent (^{1}H NMR: δ = 7.26 ppm) or solvent (^{13}C NMR: δ = 77.0 ppm) resonances relative to $SiMe_4$. MALDI-TOF mass spectra were recorded with a Bruker bench TOF mass spectrometer equipped with a standard UV-laser desorption source, using α-cyano-4-hydroxycinnamic acid as the matrix. FAB and ESI mass spectra were measured with a Thermo Finnigan MAT 95 XL mass spectrometer. UV/Vis spectra were recorded with a Cary 5G spectrophotometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, China.

SiPc(3-OPy)$_2$ (1): A mixture of dichlorosilicon(IV) phthalocyanine (1.0 g, 1.64 mmol), 3-hydroxypyridine (0.32 g, 3.36 mmol), and pyridine (2 mL) in toluene (50 mL) was heated at reflux overnight. The volatiles were then removed under reduced pressure and the residue was chromatographed on a silica gel column using $CHCl_3$/MeOH (v/v, 9:1) as eluent to give the product as a blue solid (0.89 g, 75%). ^{1}H NMR: δ = 9.64–9.67 (m, 8 H, Pc-H_α), 8.40–8.43 (m, 8 H, Pc-H_β), 6.98 (dd, J = 1.6, 4.8 Hz, 2 H, Py-H), 5.63 (dd, J = 4.8, 8.4 Hz, 2 H, Py-H), 3.92 (d, J = 1.6 Hz, 2 H, Py-H), 2.87 (d, J = 8.4 Hz, 2 H, Py-H) ppm. ^{13}C{^{1}H} NMR: δ = 149.7, 146.2, 139.2, 138.5, 135.2, 131.7, 125.6, 124.1, 122.0 ppm. UV/Vis ($CHCl_3$) [λ_{max} (log ε)]: 354 (4.89), 614 (4.59), 654 (4.53), 684 (5.36) nm. HRMS (FAB): calcd. for $C_{42}H_{25}N_{10}O_2Si$ [MH^+] 729.1931; found 729.1928. $C_{42}H_{24}N_{10}O_2Si \cdot MeOH$ (760.85): calcd. C 67.88, H 3.71, N 18.41; found C 67.81, H 4.01, N 18.54.

Co(TBPP) (4): A mixture of H_2(TBPP) (100 mg, 0.09 mmol) and anhydrous cobalt(II) chloride (20 mg, 0.15 mmol) in DMF (10 mL) was stirred at 120 °C for 8 h. The cooled dark red solution was then poured into MeOH (100 mL), and the precipitate was filtered off and washed with MeOH. The crude product was purified by column chromatography using $CHCl_3$ as eluent (92 mg, 87%). UV/Vis ($CHCl_3$) [λ_{max} (log ε)]: 411 (5.18), 528 (4.11) nm. HRMS (FAB): calcd. for $C_{76}H_{92}CoN_4$ [M^+] 1119.6653; found 1119.6638.

Heterodyad 2·3: A mixture of $SiPc(4\text{-}OPy)_2$ (**2**) (20 mg, 0.03 mmol) and Co(TPP) (**3**) (37 mg, 0.06 mmol) in $CHCl_3$ (50 mL) was stirred at room temp. overnight. After removing the solvent in vacuo the residue was chromatographed with $CHCl_3$/MeOH (v/v, 9:1) as eluent. The third blue band was collected and evaporated to give the product (2 mg, 5%). UV/Vis ($CHCl_3$) [λ_{max} (log ε)]: 355 (4.96), 435 (5.26), 553 (4.04), 618 (4.51), 686 (5.29) nm. MS (MALDI-TOF): an isotopic cluster peaking at m/z = 1399.0 [M^+]. HRMS (ESI): calcd. for $C_{86}H_{53}CoN_{14}O_2Si$ [MH^+] 1400.3577; found 1400.3574.

Heterodyad 2·4: According to the above procedure, $SiPc(4\text{-}OPy)_2$ (**2**) (20 mg, 0.03 mmol) complexed with Co(TBPP) (**4**) (66 mg, 0.06 mmol) in $CHCl_3$ (50 mL) to give the dyad **2·4** (3 mg, 6%). UV/Vis ($CHCl_3$) [λ_{max} (log ε)]: 351 (4.95), 437 (5.33), 551 (4.13), 619 (4.52), 688 (5.28) nm. MS (MALDI-TOF): an isotopic cluster peaking at m/z = 1847.7 [M^+]. HRMS (ESI): calcd. for $C_{118}H_{117}CoN_{14}O_2Si$ [MH^+] 1848.8584; found 1848.8052.

X-ray Crystallographic Analysis of 1 and 2: Crystal data and details of data collection and structure refinement are given in Table 2. For **1**, data were collected at 293 K with an MSC/Rigaku RAXIS IIc imaging-plate system using Mo-K_α radiation (λ = 0.71073 Å) from a Rigaku RU-200 rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{min}$ = 3°, $2\theta_{max}$ = 55°, 2–5° oscillation frames in the range 0–180°, exposure 12 min per frame).[14] A self-consistent semi-empirical absorption correction based on a Fourier coefficient fitting of symmetry-equivalent reflections was applied by using the ABSCOR program.[15] Crystallographic data of **2** were collected with a Bruker SMART CCD diffractometer with a Mo-K_α sealed tube (λ = 0.71073 Å) at 293 K, using a ω scan mode with an increment of 0.3°. Preliminary unit-cell parameters were obtained from 45 frames. Final unit-cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for the integration of the intensity of reflections and scaling;[16] SADABS for absorption corrections;[17] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.[18]

CCDC-644806 and CCDC-644807 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Absorption spectra of mixtures of $SiPc(3\text{-}OPy)_2$ (**1**) and Co(TBPP) (**4**) in $CHCl_3$; different resonance structures of the 3- and 4-pyridinolato ligands; schematic diagrams showing the complexation of $SiPc(3\text{-}OPy)_2$ (**1**) with porphyrinatocobalt(II) complexes. UV/Vis spectrum of the binary complex **2·4** and the addition spectrum of **2** and **4** in $CHCl_3$.

Table 2. Crystallographic data for **1** and **2**.

	1·$2C_6H_5NO_2$	**2**
Empirical formula	$C_{54}H_{34}N_{12}O_6Si$	$C_{42}H_{24}N_{10}O_2Si$
Formula mass [g mol^{-1}]	975.02	728.80
Crystal size [mm]	0.50 × 0.40 × 0.20	0.25 × 0.20 × 0.10
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a [Å]	8.6413(17)	9.613(3)
b [Å]	11.060(2)	19.394(5)
c [Å]	13.297(3)	9.945(3)
α [°]	94.96(3)	90
β [°]	101.70(3)	118.599(4)
γ [°]	110.34(3)	90
V [Å^3]	1149.6(4)	1627.8(8)
Z	1	2
F(000)	504	752
$D_{calcd.}$ [mg m^{-3}]	1.408	1.487
μ [mm^{-1}]	0.120	0.131
θ range [°]	2.33–25.53	2.10–25.02
Reflections collected	3613	7044
Independent reflections	3613	2867
Parameters	331	250
R_1 [$I > 2\sigma(I)$]	0.0556	0.0531
wR_2 [$I > 2\sigma(I)$]	0.1541	0.1138
Goodness-of-fit on F^2	1.067	1.038
Largest diff. peak and hole [e Å^{-3}]	0.350 and –0.229	0.318 and –0.284

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