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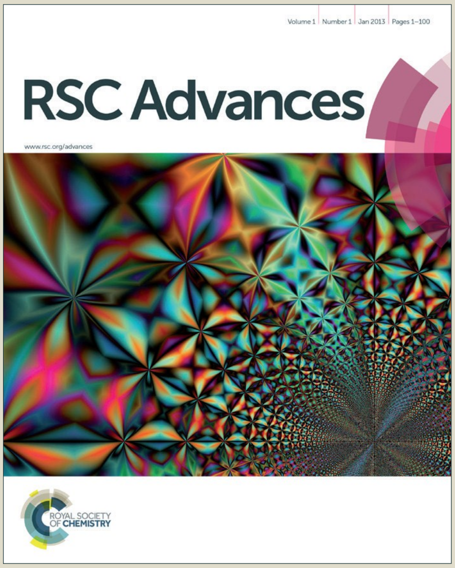

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Effects of Peripheral Substitutions on the Singlet Oxygen Quantum Yields of Monophthalocyaninato Ytterbium(III) Complexes

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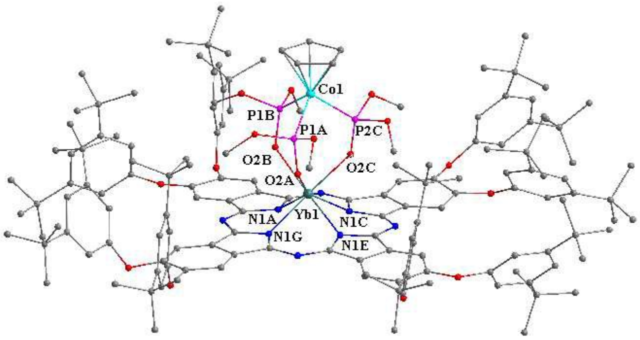
A new monophthalocyaninato ytterbium(III) complex **5** with eight 3,5-di-*t*-butylphenoxyl substituents at peripheral positions has been prepared and characterized. The effects of substituents on the relative singlet oxygen quantum yields of monophthalocyaninato ytterbium(III) complexes have been investigated.



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FULL PAPER

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A new monophthalocyaninato ytterbium(III) complex **5** with eight 3,5-di-*t*-butylphenoxyl substituents at peripheral positions is synthesized. X-ray structural analysis of **5**·$CHCl_3$·MeOH reveals that the Yb^{3+} ion is seven-coordinate, surrounded by four nitrogen atoms from the phthalocyaninate dianion and three oxygen atoms from the anionic tripodal L_{OMe}^- ligand {L_{OMe}^- = [(cyclopentadienyl)tris(dimethylphosphito) cobaltate(III)]}. The effects of substituents on the relative singlet oxygen ($^1O_2$) quantum yields of monophthalocyaninato ytterbium(III) complexes are investigated through the comparison. It is found that the monophthalocyaninato ytterbium(III) complex has higher $^1O_2$ quantum yield than its corresponding phthalocyaninate ligand. The introduction of 3,5-di-*t*-butylphenoxy substituent on the microcycle can enhance the yield of singlet oxygen. Due to the heavy-atom of both iodine and lanthanide ions, the ytterbium(III) complex **4** based on *tert*-butyl and iodine substituted phthalocyanine ligand has the highest $^1O_2$ quantum yield (0.82).

Introduction

Photodynamic therapy is a noninvasive methodology used for the treatment of a variety of premalignant and malignant diseases.[1-4] This therapy requires a photosensitizer, visible light, and molecular oxygen. After irradiation of light with an appropriate wavelength in the presence of oxygen, the photosensitizer will induce cellular and tissue damage by generating reactive oxygen species (ROS), such as singlet oxygen and other radical species.[5] Evidence favors that singlet oxygen ($^1O_2$) is the key cytotoxic agent for photobiological activity.[6-7] The $^1O_2$ is produced by energy transfer from the photoexcited sensitizer to the ground-state oxygen. This is known as the Type II photosensitization mechanism.[8-9] As the first generation photosensitizers, porphyrin derivatives have been studied extensively and used in clinical work.[2,10] However, the efficiency of the treatment is limited by their small extinction coefficient at the body therapeutic window (650-900 nm).[11] Phthalocyanines have been proposed as the second-generation photosensitizers because of their many advantages such as the intense absorption in the red visible region, high efficiency to generate singlet oxygen, ease of chemical modification, and low dark toxicity.[11-14] However, one major drawback of phthalocyanines in PDT is their aggregation tendency,[15-17] which severely diminishes their photosensitizing ability. We have previously reported two novel monophthalocyaninato ytterbium(III) complexes.[18] These Yb(III) complexes with an organometallic tripodal ligand at axial position show no aggregation in solution. As the energy of the emissive $^2F_{5/2}$ state of Yb(III) is about the same as that of the phthalocyanine T_1 state, there is a significant back-energy transfer, only $^1O_2$ phosphorescence, not Yb(III) emission, was observed in the NIR region. Due to the heavy-atom effect of the Yb^{3+} ion enhances the intersystem crossing from the ligand-

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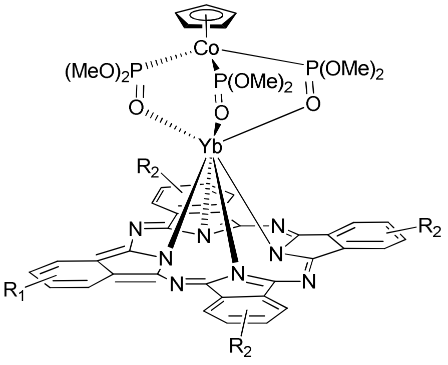
centered singlet state (^{1}LC) to the ligand-centered triplet state (^{3}LC), the monophthalocyaninato ytterbium(III) complexes have high ability to generate singlet oxygen than $H_2(t\text{-Bu})_4Pc$. However, the singlet oxygen quantum yields of these Yb(III) complexes were not reported.

It has been found that peripheral substituents can influence the electron delocalization, reduce aggregation, and enhance intersystem crossing in the case of heavy-atom substitution.[19-22] It is necessary to evaluate the structure-activity relationship of photosensitizers via variedly substituted monophthalocyaninato ytterbium(III) complexes. The main aim of this work is to explore the influences of peripheral substituents at the monophthalocyaninato ytterbium(III) complexes on the singlet oxygen quantum yields.



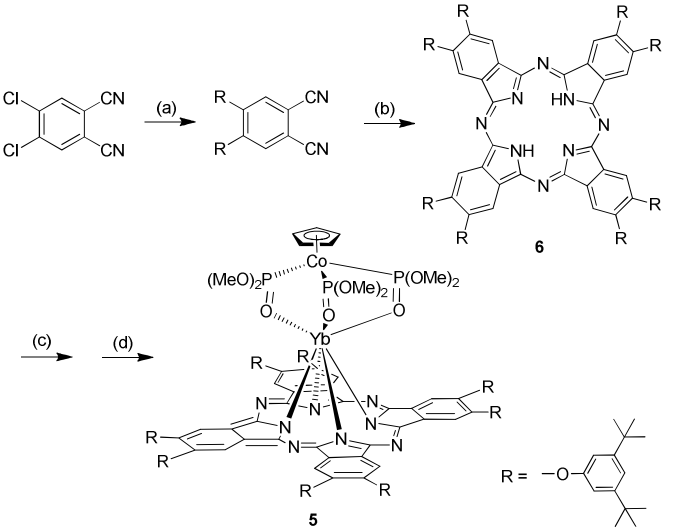
1 (R$_1$ = R$_2$ = H): PcYb
2 (R$_1$ = R$_2$ = *t*-Butyl): (*t*-Bu)$_4$PcYb
3 (R$_1$ = H, R$_2$ = *t*-Butyl): (*t*-Bu)$_3$PcYb
4 (R$_1$ = I, R$_2$ = *t*-Butyl): I(*t*-Bu)$_3$PcYb

Figure 1. Structures of monophthalocyaninato ytterbium(III) complexes **1**–**4**.

Recently, we reported four monophthalocyaninato ytterbium(III) complexes **1**–**4** shown in Figure 1.[18,23] As nonsubstituted phthalocyanine ligand is insoluble in organic solvent, identically structured nonsubstituted PcYb **1** was obtained in less than 10% yield. **2**–**4** were obtained in about 65% yield with the disadvantage of a mixture of place isomers. We hereby describe the synthesis, spectroscopic and photochemical properties of a new unique structured monophthalocyaninato ytterbium(III) complex **5** with eight 3,5-di-*t*-butylphenoxyl substituents at peripheral positions of the microcycle ring. The influences of peripheral substituents on the singlet oxygen quantum yields are discussed through the comparison.

Results and Discussion

The synthetic route for the monophthalocyaninato ytterbium(III) complex **5** is shown in Scheme 1. Following the procedure described in the literature,[24] the intermediate 4,5-dichloro-1,2-dicyanobenzene was prepared in three steps from 4,5-dichloro-1,2-benzenedicarboxylic acid via the anhydride, imide and diamide with an overall yield of 50%. The precursor 4,5-bis(3,5-di-*t*-butylphenoxy)phthalonitrile was prepared in 90% yield by the reaction of 3,5-di-*t*-butylphenol with 4,5-dichloro-1,2-dicyanobenzene in dry DMSO at 90°C in the presence of solid K_2CO_3. The phthalocyanine free-base (3,5-di-*t*-butylphenoxy)$_8$Pc **6** was synthesized in 43% yield by condensation of 4,5-bis(3,5-di-*t*-butyl-phenoxy)phthalonitrile in 1-pentanol in the presence of 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) under reflux for 24 h. Then the reaction of (3,5-di-*t*-butylphenoxy)$_8$Pc with $Yb[N(SiMe_3)_2]_3{\bullet}[LiCl(THF)_3]_x$ followed by addition of $Na(L_{OMe}^-)$ gave (3,5-di-*t*-butylphenoxy)$_8$PcYb **5** in 61% yield.



Scheme 1. Synthesis of (3,5-di-*t*-butylphenoxy)$_8$PcYb **5**: (a) 3,5-di-*t*-butylphenol, DMSO/K_2CO_3, 90°C; (b) DBU/1-pentanol, reflux, 48h; (c) $Yb[N(SiMe_3)_2]_3{\cdot}[LiCl(THF)_3]_x$, toluene, reflux; (d) NaL_{OMe}^-, room temperature.

The newly synthesized compound **5** was fully characterized by high resolution mass spectrometry, ^{1}H and ^{31}P NMR, UV/Vis absorption and fluorescence spectroscopy. The MALDI-TOF high-resolution mass spectrum (HRMS) of **5** showed the $[M]^+$ peak at 2770.2902, giving mass accuracy Δ_m of 0.5 ppm relative to their corresponding calculated *m/z* values of 2770.2916. The isotopic distribution pattern also matched the

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expected profile. **5** displayed a singlet at δ = 65.36 ppm (vs. 85% H_3PO_4) in their ^{31}P NMR spectra for the phosphito group of the anionic L_{OMe}^{-} ligand, The ^1H NMR spectrum (in $CDCl_3$) of **5** showed a singlet at δ = -5.90 ppm for the five cyclopentadienyl protons.

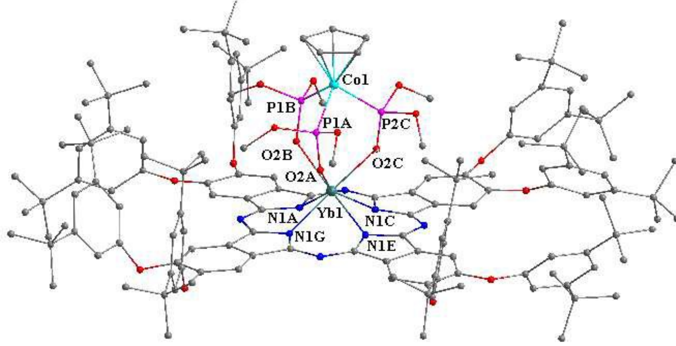

Figure 2. A perspective view of the host structure of compound $\mathbf{5}\cdot CHCl_3\cdot MeOH$. Hydrogen atoms, solvates and parts of substituted groups were omitted for clarity. Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths [Å] and bond angles [°]: Yb1-N1A 2.313(7), Yb1-N1C 2.314(6), Yb1-N1E 2.295(6), Yb1-N1G 2.286(6), Yb1-O2A 2.255(6), Yb1-O2B 2.242(6), Yb1-O2C 2.240(6); O2A-Yb1-O2B 78.4(2), O2A-Yb1-O2C 80.2(2), O2B-Yb1-O2C 83.6(2), N1A-Yb1-N1C 73.4(2), N1A-Yb1-N1E 118.4(2), N1C-Yb1-N1E 75.3(2), N1E-Yb1-N1G 74.9(2), N1C-Yb1-N1G 117.4(2), N1G-Yb1-N1A 74.7(2). The labels of A, B, C, D, E and G for N, O or P atoms with the same symmetric code as Co1 and Yb1 are used to discriminate different repeating portions of the phthalocyaninato ring and the tripodal ligand.

The solid-state structure of $\mathbf{5}\cdot CHCl_3\cdot MeOH$ was ascertained by X-ray crystallography. Complex $\mathbf{5}\cdot CHCl_3\cdot MeOH$ crystallizes in the triclinic space group $P\bar{1}$, in which the asymmetric unit is composed of one neutral molecular **5** and two solvates $CHCl_3$ and MeOH. As shown in Figure 2, it is evident that the Yb^{3+} ion is sandwiched between the phthalocyaninato ring and the anionic tripodal ligand and its seven-coordinate environment with a slightly distorted tricapped polygon prism is surrounded by four nitrogen atoms (N1A, N1C, N1E and N1G) from the phthalocyaninate dianion and three oxygen atoms (O2A, O2B and O2C) from the L_{OMe}^{-} anion as a cap. The bond lengths between Yb^{3+} and four N atoms of the phthalocyaninato ring and three O atoms of L_{OMe}^{-} are in the range of 2.286(6)-2.314(6) Å and 2.240(6)-2.255(6) Å, respectively, where the higher affinity of the Yb^{3+} ion to O atoms than that to N atoms endows relatively longer Yb-N distances than those of Yb-O bonds. The three mean planes (C_5 of the cyclopentadienyl ring, N_4 of the phthalocyaninate ligand, and O_3 of the phosphito groups) are almost parallel to one another. The dihedral angles formed between the C_5 and O_3 mean planes, O_3 and N_4 mean planes, and C_5 and N_4 mean planes are, 2.345(3)°, 3.531(2)°, and 5.587(3)°, respectively. The Yb^{3+} center is 1.186 (9) Å above the plane formed by the four phthalocyaninato N atoms and 1.489(3) Å below the plane formed by the three phosphito O atoms. The solvates $CHCl_3$ and MeOH exhibit no observed interaction with the host structure.

Table 1. Photophysical data of compounds 5 and **6**[a].

	Absorption, λ_{max}/nm [log(ε/dm^{3}mol^{-1}cm^{-1})]	Excitation λ_{ex}/nm	Emission at 298 K λ_{em}/nm (τ, Φ_{em} x 10^2)[b]
5	361(5.04), 613(4.70), 649(4.65), 680(5.52)	361	688(6.23ns, 1.0)
6	353(4.84), 605(4.52), 638(4.69), 667(5.22), 703(5.30)	667	707(-[c], 63), 741, 790

[a] Measurements were done in 1 x 10^{-6} M solution in toluene. [b] Quantum yield was measured relative to a 1 x 10^{-6} M solution of $H_2(t\text{-}Bu)_4Pc$ in toluene (Φ_{em} = 0.67). [c] Not detected.

The photophysical properties of **5** and **6** are summarized in Table 1. Figure 3 shows the absorption spectra of **5** and **6**. The UV/Vis spectrum of **6** shows two strong Q bands at 667 and 703 nm and two additional weak bands at 613 and 649 nm, and a strong B band at 353 nm. The Yb(III) complex **5** shows a strong Q band at 680 nm and two additional weak bands at 605 and 638 nm, and a strong B band at 361 nm. The absorption can be assigned to the π-π* transitions of the phthalocyaninate ligand. Figure 4 shows the room-temperature emission and excitation spectra of **5** in toluene. Complex **5** displays visible emission peak at 688 nm with lifetime (τ) of 6.23 ns and quantum yields (Φ_{em}) of 0.010. However, ligand-centered (LC) long-lived phosphorescence was not observed. The excitation spectrum of complex **5** monitored at 688 nm matched well with its absorption spectrum. Thus, the visible fluorescence of compounds can be assigned to the intraligand emission.

In order to evaluate the photosensitizing efficiency of monophthalocyaninato ytterbium(III) complexes **1**–**5**, the $^1O_2$ quantum yields (Φ_Δ) were determined by measuring the near-infrared (NIR) phosphorescence intensity of $^1O_2$ (at 1270 nm) produced from these compounds at irradiation at 675 nm, using unsubstituted zinc(II) phthalocyanine (ZnPc) as the reference (Φ_Δ = 0.58).[25] The relative $^1O_2$ quantum yields of these

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compounds and the reference ligands (3,5-di-*t*-butylphenoxy)$_8$Pc **6** are given in Table 2. The error in the determination of Φ_Δ was ～10% (determined from several Φ_Δ values).

Table 2. Singlet oxygen quantum yields of **1**–**6** in toluene.

Complex	**1**	**2**	**3**	**4**	**5**	**6**
Φ_Δ at 298K[a]	0.69	0.63	0.63	0.82	0.79	0.41

[a] Quantum yield of $^1O_2$ was measured relative to PcZn in toluene(Φ_Δ = 0.58)

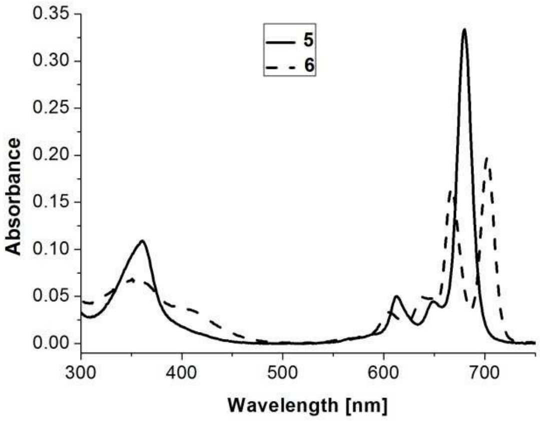

Figure 3. Absorption spectra of **5** and **6** solutions in toluene (1 × 10^{-6} M).

Compared to the phthalocyanine ligand **6**, those monophthalocyaninato ytterbium(III) complexes **1**–**5** show higher $^1O_2$ quantum yield (Φ_Δ) in the range of 0.63–0.82. This can be ascribed to the heavy-atom effect of the Yb^{3+} ion which, upon coordination with the phthalocyaninate ligand, enhances the intersystem crossing from the ^{1}LC to the ^{3}LC state. And the presence of heavy atom iodine at the phthalocyanice skelton can also enhances the intersystem crossing from the ground state to the triplet state of phthalocyanine ligand, resulting in the highest $^1O_2$ quantum yield. Complex **5** shows the second highest $^1O_2$ quantum yield (0.79), which might be explanined that the introduction of eight bulky 3,5-di-*t*-butylphenoxy substituents on the macrocycle provide a good shield from solvent induced nonradiative quenching and hense enhance the yield of singlet oxygen. This also indicates that singlet oxygen is produced by the energy transfer from the triple states of the photosensitizers and the ground state of molecular oxygen. Figure 5 shows the phosphorescence spectra of $^1O_2$ generated upon photoirradiation of an aerated solution of **1**–**6** in toluene (1.0 × 10^{-5} M) at 671, 678, 676, 682, 680 and 703 nm, respectively.

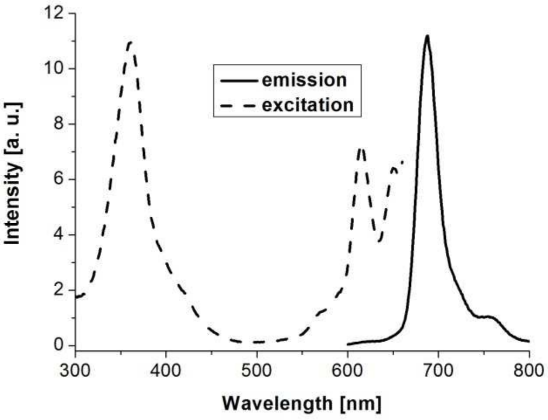

Figure 4. Room-temperature visible emission (excited at 361 nm) and excitation (monitored at 688 nm) spectra of complex **5** in toluene (1 × 10^{-6} M).

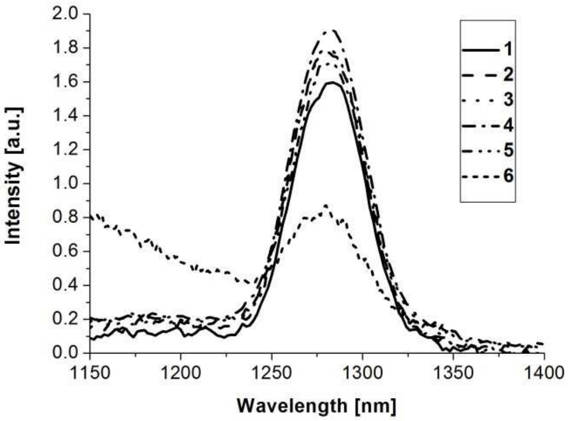

Figure 5. Phosphorescence spectra of $^1O_2$ generated from photoirradiation of complexes **1**–**6** in toluene (1.0 × 10^{-5} M) excited at the λ_{max} 671, 678, 676, 682, 680 and 703 nm, respectively.

Experimental Section

General:

All reactions were carried out under dry nitrogen atmosphere unless specified otherwise. Solvents were dried by standard procedures, distilled, and deaerated prior to use. All chemicals were obtained from Sigma-Aldrich Chemical Company and used without further purification. 4,5-dichloro-1,2-dicyanobenzene was prepared according to the literature methods.[25] Yb[N(SiMe$_3$)$_2$]$_3$•[LiCl(THF)$_3$]$_x$ was synthesized

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according to procedures in the literature.[26] Electronic absorption spectra in the UV/Vis region were recorded with a Varian Cary 100 UV/Vis spectrophotometer, steady-state visible fluorescence and photo-luminescence excitation spectra were recorded with a Photon Technology International (PTI) Alphascan spectrofluorimeter, and quantum yields of the visible emissions were determined according to the literature method[27] using $H_2(t\text{-Bu})_4Pc$ as reference standard (Φ_{em} = 0.67 in toluene).[28] NMR spectra were recorded with a Varian Unity Inova 400 MHz spectrometer. ^1H NMR chemical shifts were referenced to internal $CDCl_3$ and then re-referenced to TMS (δ = 0.00 ppm). High-resolution mass spectra, reported as *m/z*, were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer.

Singlet Oxygen quantum yield:

Singlet oxygen was detected directly by its phosphorescence emission at 1270 nm using an InGaAs detector on the PTI QM4 luminescence spectrometer. The singlet oxygen quantum yields (Φ_Δ) of all compounds were determined in toluene by comparing the singlet oxygen emission intensity of the sample solution to that of a reference material according to equation 1.[29]

$$\Phi_\Delta^{S} = \Phi_\Delta^{REF} \times \left(\frac{n_S}{n_{REF}}\right)^2 \frac{G_\Delta^{S}}{G_\Delta^{REF}} \times \frac{A_{REF}}{A_S} \qquad (1)$$

Where Φ_Δ is the singlet oxygen quantum yield, G_Δ is the integrated emission intensity, *A* is the absorbance at the excitation wavelength. *n* is the refractive index of the solvent. Superscripts REF and S correspond to the reference and sample, respectively. In all cases, the $^1O_2$ emission spectra were measured after excitation with the absorbance set at 0.05 in order to minimize re-absorption of the emitted light.

Preparations of [(3,5-di-*t*-butylphenoxy)$_8$PcYb] (5).

[4,5-bis(3,5-di-*t*-butylphenoxy)phthalonitrile].

Under a nitrogen atmosphere, 4,5-dichloro-1,2-dicyanobenzene (0.985 g, 5 mmol) and 3,5-di-*t*-butylphenol (6.18 g, 30 mmol) in dry DMSO (15 mL) were heated under stirring at 90°C. Anhydrous K_2CO_3 power (1.38 g, 10 mmol) was added in portions (8 × 1.25 mmol) every 5 min. The mixture was stirred at 90°C for additional 4 h and then after cooling added to 100 mL ice-water. The product was filtered, recrystallized from MeOH and dried in vacuum. The yield was 90% (2.40 g). ^1H NMR ($CDCl_3$): δ = 1.34 (s, 36H)，6.95 (s, 4H)，7.10 (s, 2H), 7.35 (s, 2H) ppm.

[(3,5-di-*t*-butylphenoxy)$_8$Pc] (6).

Under a nitrogen atmosphere, 4,5-bis(3,5-di-*t*-butylphenoxy) phthalonitrile (537 mg, 1 mmol) and DBU (0.15 mL) in dry amyl alcohol (20 mL) were heated at reflux for 48 h with stirring. After removing the most solvent, the mixture was poured into methanol (20 mL). The precipitate was collected by filtration and chromatographed on silica gel using hexane/DCM (v/v, 3:1) as the eluent. The yield was 43% (230 mg). MALDI-TOF HRMS: calcd. for $[M]^+$ 2148.3795; found 2148.3726. ^1H NMR ($CDCl_3$): δ = –0.38（s, 2H）1.32 (s, 144H), 7.13 (s, 16H), 7.24 (t, 8H), 9.02 (s, 8H) ppm.

[(3,5-di-*t*-butylphenoxy)$_8$PcYb] (5).

A solution of $Yb[N(SiMe_3)_2]_3 \bullet [LiCl(THF)_3]_x$ (5 mL, 0.8 mmol) was transferred to a Schlenk flask, and the solvent was removed under vacuum. The residue was redissolved in dichloromethane (10 mL) to give a suspension, which was centrifuged. The clear layer was then transferred to another Schlenk flask with dry compound **6** (0.107 g, 0.05 mmol) dissolved in toluene (15 mL). The resulting solution was heated at reflux for 3 h. Upon cooling the reaction mixture to 70°C, anhydrous NaL_{OMe}^{-} (0.040 g, 0.085 mmol) was added, and the solution was magnetically stirred for 1 h. After the reaction was complete, the solvent was removed under vacuum, and the residue was redissolved in chloroform, filtered, and chromatographed on silica gel using chloroform/hexane (v/v, 1:1) as the eluent. The yield was 61% (85 mg). MALDI-TOF HRMS: calcd. for $[M]^+$ 2770.2916; found 2770.2902. ^1H NMR ($CDCl_3$): δ = –5.90 (s, 5H), 1.86 (s, 144H), 7.61 (s, 18H), 7.92 (s, 8H), 8.66 (s, 16H), 14.12 (s, 8H) ppm. ^{31}P NMR ($CDCl_3$): δ = 65.36 ppm.

X-Ray Crystallography:

Single crystals of **5**$\cdot CHCl_3 \cdot$MeOH suitable for X-ray diffraction study were grown by slow evaporation of solutions of the compound in chloroform/methanol at room temperature. X-ray intensity data were collected with a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The collected frames were processed with the SAINT software[30] and an absorption correction was applied (SADABS[31]) to the collected reflections. The structures of these molecules were solved by

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direct methods and expanded by standard difference Fourier syntheses using the SHELXTL software.[32] Structure refinements were made on F^2 using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in their idealized positions and allowed to ride on the respective carbon atoms. Since there are disorders of *tert*-butyl groups in this compound, they were located and refined with restraints: DFIX, ISOR, SADI, SAME and SIMU. And some *tert*-butyl groups are split to two parts. Crystal data: $C_{157}H_{204}Cl_3CoN_8O_{18}P_3Yb$, MW=2922.51, triclinic, space group = $P\bar{1}$, a = 19.6111(18) Å, b = 19.6932(18) Å, c = 24.446(2) Å, α = 81.59(2)°, β = 70.14(2)°, γ = 60.83(2)°, V = 7751.4(12) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.252 $g{\cdot}cm^{-3}$.

CCDC-1044126 contains the supplementary crystallographic data for compound **5**·$CHCl_3$·MeOH. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

In summary, a new unique structured monophthalocyaninato ytterbium(III) complex **5** has been synthesized with high yield. The photophysical properties and the crystal structure of **5** have been examined. Compared to the phthalocyanine ligand **6**, those monophthalocyaninato ytterbium(III) complexes **1**–**5** show higher $^1O_2$ quantum yield (Φ_Δ) in the range of 0.63–0.82. This can be ascribed to the heavy-atom effect of the centered Yb^{3+} ion or heavy atom substitution iodine, which enhances the intersystem crossing from the ^{1}LC to the ^{3}LC state. In addition, the introduction of eight bulky 3,5-di-*t*-butylphenoxy substituents on the microcycle can provide a good shield from solvent induced nonradiative quenching and hense enhance the yield of singlet oxygen. The results offer new strategies for the design of efficient photosensitizer of phthalocyanine with high singlet oxygen quantum yield.

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Notes and references

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