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Synthesis, structure and near-infrared luminescence of neutral 3d–4f bi-metallic monoporphyrinate complexes

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Received 6th June 2001, Accepted 10th August 2001
First published as an Advance Article on the web 27th September 2001

The interaction of cationic lanthanide complexes $[Ln(porp)(H_2O)_3]^+$ (Ln = Er or Yb; porp = porphyrinate) with sodium (cyclopentadienyl)tris(diethylphosphito)cobaltate (NaL_{OEt}) gives the neutral 3d–4f bi-metallic porphyrinate complexes, $[(L_{OEt})Ln(porp)]$. X-Ray structural analyses reveal that these complexes are seven-coordinate with the three oxygen atoms of the O_3-tripodal ligand, L_{OEt}, coordinated to the lanthanide metal behaving as a 6-electron donor. Photophysical measurements show that the porphyrinate ligand behaves as a sensitizer by absorbing visible light to excite the Ln(III) metal ions, producing near-infrared emission.

Introduction

Trivalent lanthanide ions are known for their unique optical properties such as line-like emission spectra and long luminescence lifetimes.[1] These unique properties have drawn considerable interest for their potential application as fluorescence imaging agents.[2] However, some lanthanide ions, such as Eu(III) and Tb(III), possess strongly emissive and long-lived excited states, but do not exhibit intense absorption bands.[3] Therefore, considerable effort has been devoted to the design of lanthanide complexes where light is absorbed by the ligands and the corresponding electronic energy then transferred to the emitting metal ions. Recently, there has been growing interest in the luminescence properties of erbium(III), ytterbium(III) and neodymium(III) polydentate complexes.[4–12] These lanthanide(III) ions, which emit in the near-infrared (NIR) region, a region where biological tissues and fluids are relatively transparent, have potential for chemosensor and fluoroimmuno essay applications. Investigations of sensitizers for NIR lanthanide luminescence have focused on conjugated organic molecules;[4–6] nevertheless, there are only a few examples of sensitizers that enable visible light excitation instead of near-UV excitation.[7–12] The ability of porphyrins to accumulate in malignant tumours and absorb strongly in the UV-vis region has made lanthanide(III) porphyrinate complexes ideal candidates for use as efficient photo-sensitizers[13] and luminescence imaging agents. Lanthanide(III) monoporphyrinate complexes were first reported in 1974.[14] However, since then only a few studies on these systems have appeared in the literature. Porphyrins as sensitizers for ytterbium(III) ions have been examined.[7,8] The use of the ytterbium(III) monoporphyrinate complex as a luminescence contrasting agent was only briefly studied.[9] Recently, we reported the synthesis of cationic lanthanide(III) monoporphyrinate complexes[15] and their solid state NIR luminescence.[16] Kläui's O_3-tripodal ligand $\{L_{OR} = (\eta^5\text{-}C_5H_5)Co[P(=O)(OR)_2]_3\}$,[17] which is a monoanionic 6e donor isoelectronic with cyclopentadienyl ligands ($\eta^5\text{-}C_5R_5$), is known to stabilise metal ions in high oxidation states[18] and should be able to stabilise oxophilic metal ions such as Ln(III). Herein, we report the synthesis of a number of neutral 3d–4f bi-metallic monoporphyrinate lanthanide complexes of the general formula $[(L_{OEt})Ln(porp)]$ *via* the interaction of cationic lanthanide(III) porphyrinate complexes with sodium (cyclopentadienyl)-tris(diethylphosphito)cobaltate (NaL_{OEt}). The photophysical properties of some of these complexes are also discussed.

Results and discussion

Crystal structures

At room temperature, the anionic tripodal nucleophile (L_{OEt}) reacts readily with the cationic lanthanide porphyrinate complexes $[Ln(porp)(H_2O)_3]^+$ [Ln = Er or Yb; porp = tetrakis[3,4,5-tri(methoxy)phenyl]porphyrinate (TM_3PP), tetrakis(4-methoxyphenyl)porphyrinate (TMPP), tetrakis(phenyl)porphyrinate (TPP) or tetrakis(*p*-tolyl)porphyrinate (TTP)] to give the neutral 3d–4f bi-metallic porphyinate complexes $[(L_{OEt})Ln(porp)]$ (**1**, Ln = Er, porp = TM_3PP; **2**, Er, TMPP; **3**, Er, TPP; **4**, Yb, TTP; **5**, Yb, TMPP). These results are summarized in Scheme 1. Compounds **1**–**5** were isolated as air-stable purple crystals in good yield. They all exhibited electronic absorption spectra characteristic of metal porphyrin complexes.[13] Elemental analyses and positive FAB mass spectra, which exhibited the corresponding $(M + 1)^+$ molecular ion peak, confirmed that the products were 1 : 1 adducts of lanthanide monoporphyrinate and the O_3-tripodal ligand. In their ^{31}P NMR spectra, they exhibited a singlet at around δ −166 for Er(III) complexes and δ 65 for Yb(III) complexes. The structures of **1**, **3** and **5** were ascertained by X-ray crystallography.

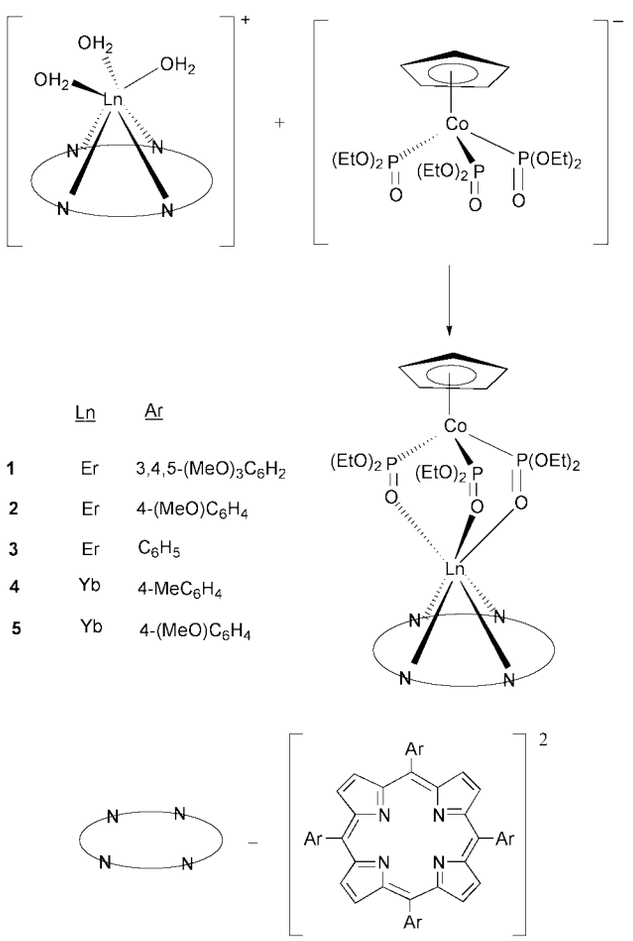
Crystals of **1**·$CHCl_3$, **3**·$CHCl_3$ and **5**·$0.75C_3H_6O$ suitable for X-ray diffraction studies were grown by slow evaporation of solutions of **1** and **3** in chloroform–hexane, and **5** in acetone. Perspective drawings of compounds **1**, **3** and **5** are shown in Fig. 1, 2 and 3, respectively. Their structures are isomorphous. Selected bond lengths and bond angles are given in Table 1. Crystal structure analyses revealed that the lanthanide(III) ions are seven-coordinate, surrounded by four N atoms of the porphyrinate dianion and three O atoms of the three phosphito groups. The Ln–N and Ln–O distances range over 2.358(3)–2.369(3) (Er–N) and 2.260(5)–2.309(5) Å (Er–O) for **1**,

 DOI: 10.1039/b104993n

Table 1 Selected bond lengths (Å) and bond angles (°) of compounds **1**, **3** and **5**

Compound **1**		Compound **3**		Compound **5**	
Er(1)–N(1)	2.358(3)	Er(1)–N(1)	2.348(8)	Yb(1)–N(1)	2.361(4)
Er(1)–N(2)	2.359(3)	Er(1)–N(2)	2.363(9)	Yb(1)–N(2)	2.350(4)
Er(1)–N(3)	2.369(3)	Er(1)–N(3)	2.388(13)	Yb(1)–N(3)	2.343(4)
Er(1)–N(4)	2.363(3)	Er(1)–N(4)	2.379(12)	Yb(1)–N(4)	2.355(3)
Er–N[a]	2.362	Er–N[a]	2.370	Yb–N[a]	2.352
Er(1)–O(13)	2.260(5)	Er(1)–O(1)	2.288(8)	Yb(1)–O(5)	2.285(4)
Er(1)–O(14)	2.297(5)	Er(1)–O(2)	2.276(7)	Yb(1)–O(6)	2.251(4)
Er(1)–O(15)	2.309(5)	Er(1)–O(3)	2.220(7)	Yb(1)–O(7)	2.270(4)
Er–O[b]	2.289	Er–O[b]	2.261	Yb–O[b]	2.269
O(13)–Er(1)–O(14)	76.1(4)	O(1)–Er(1)–O(2)	77.2(3)	O(5)–Yb(1)–O(6)	79.4(2)
O(13)–Er(1)–O(15)	75.8(4)	O(1)–Er(1)–O(3)	80.2(4)	O(5)–Yb(1)–O(7)	76.8(2)
O(14)–Er(1)–O(15)	75.9(4)	O(2)–Er(1)–O(3)	78.4(3)	O(6)–Yb(1)–O(7)	80.6(2)
N(1)–Er(1)–N(2)	75.7(1)	N(1)–Er(1)–N(2)	76.2(3)	N(1)–Yb(1)–N(2)	75.7(1)
N(1)–Er(1)–N(3)	119.9(1)	N(1)–Er–N(3)	118.5(3)	N(1)–Yb(1)–N(3)	120.4(1)
N(1)–Er(1)–N(4)	75.1(1)	N(1)–Er(1)–N(4)	73.8(3)	N(1)–Yb(1)–N(4)	76.2(1)
N(2)–Er(1)–N(3)	74.9(1)	N(2)–Er(1)–N(3)	76.9(4)	N(2)–Yb(1)–N(3)	77.0(1)
N(2)–Er(1)–N(4)	119.7(1)	N(2)–Er(1)–N(4)	119.5(2)	N(2)–Yb(1)–N(4)	122.2(1)
N(3)–Er(1)–N(4)	76.0(1)	N(3)–Er(1)–N(4)	73.5(4)	N(3)–Yb(1)–N(4)	75.5(1)
O(13)–Er(1)–N(1)	91.1(2)	O(1)–Er(1)–N(1)	74.5(3)	O(5)–Yb(1)–N(1)	132.1(2)
O(14)–Er(1)–N(1)	164.0(2)	O(2)–Er(1)–N(1)	135.0(3)	O(6)–Yb(1)–N(1)	75.2(1)
O(15)–Er(1)–N(1)	87.1(2)	O(3)–Er(1)–N(1)	129.0(4)	O(7)–Yb(1)–N(1)	135.8(2)
O(13)–Er(1)–N(3)	131.5(2)	O(1)–Er(1)–N(3)	162.9(4)	O(5)–Yb(1)–N(3)	89.8(2)
O(14)–Er(1)–N(3)	75.9(2)	O(2)–Er(1)–N(3)	85.7(3)	O(6)–Yb(1)–N(3)	164.3(2)
O(15)–Er(1)–N(3)	134.6(2)	O(3)–Er(1)–N(3)	97.3(5)	O(7)–Yb(1)–N(3)	85.9(2)

[a] Average bond distances of the metal to the N atoms of the porphyrin ring. [b] Average bond distances of the metal to the O atoms of the O_3-tripodal L_{OEt} ligand.



Scheme 1

2.348(9)–2.388(13) (Er–N) and 2.220(7)–2.288(8) Å (Er–O) for **3**, and 2.343(4)–2.361(4) (Yb–N) and 2.251(4)–2.285(4) Å (Yb–O) for **5**. The average Ln–N and Ln–O distances of **1** (Er–N 2.362, Er–O 2.289 Å), **3** (Er–N 2.370, Er–O 2.261 Å) and **5** (Yb–N 2.352, Yb–O 2.269 Å) are longer and shorter, respectively, than those of the cationic precursor complexes $[Ln(TMPP)(H_2O)_3]^+$ (Ln–N is 2.329 for Er and 2.301 Å for Yb; Ln–O is 2.391 for Er and 2.307 Å for Yb).[15] These data indicate that the lanthanide metals form stronger bonds with the O atoms of the phosphito groups than with the O atoms of the aqua ligands. The displacement of the lanthanide atoms from the N_4 and O_3 mean planes are, respectively, 1.185 and 1.565 Å for **1**, 1.201 and 1.540 Å for **3**, and 1.153 and 1.540 Å for **5**. The three mean planes (C_5 of the cyclopentadienyl ring, N_4 of the porphyrinate 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, respectively, 2.1, 3.0 and 3.9° for **1**, 4.8, 1.6 and 4.1° for **3**, and 0.5, 2.3 and 1.9° for **5**. The angle formed between the Ln · · · Co line and the normal of the N_4 plane is 2.3° for **1**, 2.3° for **3**, and 3.0° for **5**. The dihedral angles between the N_4 mean plane and the phenyl rings are 87.8 [C(6–14)], 128.6 [C(20–28)], 114.7 [C(34–42)] and 127.2° [C(48–56)] for **1**; 64.9 [C(21–26)], 93.6 [C(27–32)], 112.3 [C(33–38)] and 70.3° [C(39–44)] for **3**; and 63.9 [C(21–26)], 67.5 [C(28–33)], 117.5 [C(35–40)] and 82.7° [C(42–47)] for **5**. For compound **1**, the diethylphosphito groups were found to be disordered around the pseudo Er–Co axis. Two sets of bridging P and O atoms were found between Er and Co, with the site occupancy refined to 0.5 for each set. There was only one set of ethoxy groups in the phosphito ligand. For compound **5**, a similar disorder problem to that in **1** was also encountered for the phosphito groups. A two-site model with occupancy factors of 0.8 for one set and 0.2 for the other set was used. Furthermore, there were two highly disordered acetone molecules in the asymmetric unit, with assigned site occupancies of one-half and one-quarter.

Photophysical properties

The photophysical properties of compounds **1** and **5** have been examined and are summarized in Table 2. The room temperature solution electronic absorption and emission spectra of compounds **1** and **5** in the UV-vis region are almost identical and are characteristic of intra-ligand transitions of metal porphyrinate complexes.[13] Fig. 4(a) shows the absorption spectrum

Table 2 Photophysical data for compounds **1** and **5**[a]

Compound	Absorption λ_{max}/nm [log(ε/dm^3 mol^{-1} cm^{-1})]	Excitation λ_{exc}/nm	Emission λ_{em}/nm (τ, $\Phi_{em} \times 10^3$)[b]
1	601 (3.41), 561 (3.84) 431 (5.21), 411 (4.70)	420	652 (9.1 ns, 4.08) 1531[c,d]
5	601 (3.74), 561 (4.17) 431 (5.27), 411 (4.75)	420	652 (8.3 ns, 1.52) 921 (16 μs)[c]

[a] Photophysical measurements were made in $CHCl_3$ solution at room temperature. [b] Quantum yields were determined relative to $[Ru(bipy)_3]Cl_2$ in air-equilibrated water ($\Phi = 0.028$). [c] Due to the limitations of the instrument, we were unable to determine the quantum yields of the NIR luminescence of compounds **1** and **5**. [d] Due to the limitations of the instrument, we were unable to measure the lifetime of the NIR luminescence of compound **1**.

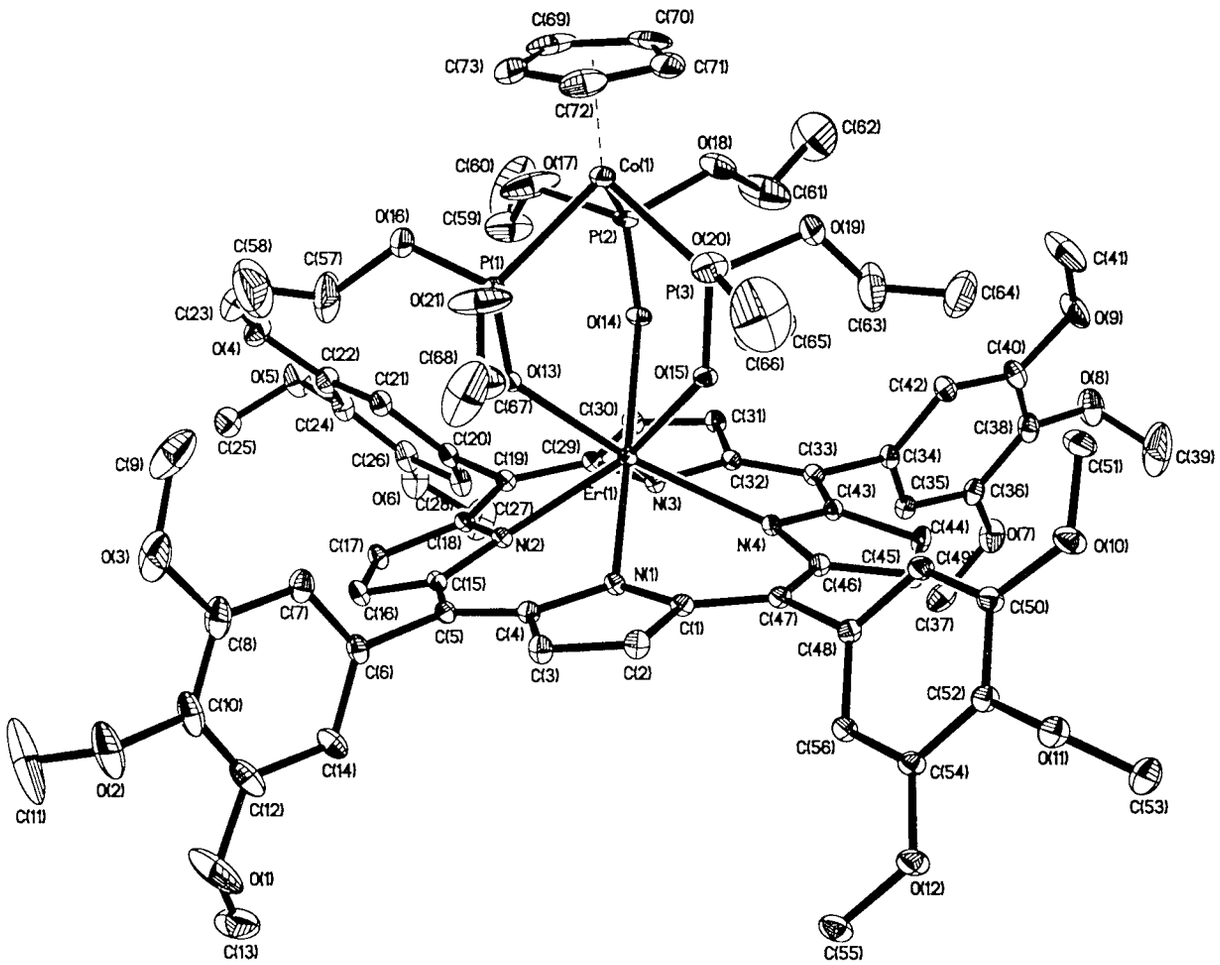


Fig. 1 A perspective drawing of compound **1**. Hydrogen atoms were omitted for clarity.

of **5** and the emission (excited at 325 nm) spectra of **5** and $[Yb(L_{OEt})_2(\eta^2\text{-}ONO_2)]$,[19] and Fig. 4(b) the absorption and excitation (monitored at 660 nm) spectra of **5**. The absorption bands at 411, 431, 561 and 601 nm and emission peak at 660 nm ($\tau = 9.1$ ns and $\Phi_{em} = 4.08 \times 10^{-3}$ for **1**; $\tau = 8.3$ ns and $\Phi_{em} = 1.52 \times 10^{-3}$ for **5**) can be assigned to the intra-ligand $\pi \longrightarrow \pi^*$ transitions of the porphyrinate ligand. The emission spectrum of $[Yb(L_{OEt})_2(\eta^2\text{-}ONO_2)]$ shows that the emissive peak ($\lambda_{em} = 410$ nm), which originates from the O_3-tripodal ligand L_{OEt}, overlaps with the absorption peak ($\lambda_{max} = 431$ nm) of the porphyrinate ligand of **5**. The excitation spectrum of **5** shows that the emission originated from the O_3-tripodal L_{OEt} ligand is absorbed by the porphyrinate ligand. The quantum efficiency of the metalloporphyrin is much lower than that of the corresponding porphyrin free base. For example, the quantum yield of **5** is only about 5% of the porphyrin free base H_2TMPP ($\Phi_{em} = 2.84 \times 10^{-2}$). Other than the visible emission, both compounds also exhibit emissions corresponding to the lanthanide(III) ion in the near-infrared region. The solution NIR emission spectra of **1** and **5** upon excitation at 600 nm are shown in Fig. 5(a). The emission peaks centred at 921 and 1531 nm can be assigned to the $^2F_{5/2} \longrightarrow {}^2F_{7/2}$ transition of Yb(III) and $^4I_{13/2} \longrightarrow {}^4I_{15/2}$ transition of Er(III), respectively. The spectral shape for **5** shows many well split peaks in the range 920–1060 nm, and this is probably the spectrum with the richest fine structure for a Yb(III) complex at room temperature. Excitation bands of **5** in chloroform solution at 298 K (monitored at 921 nm) are observed at about 560 and 600 nm, and closely resemble the low-energy absorption bands, indicative of their similar origin [Fig. 5(b)]. This clearly shows that the excitation of the Yb(III) ion originates from the $\pi \longrightarrow \pi^*$ transitions of the porphyrinate antenna. Due to the limitations of our equipment, we were unable to measure the excitation (monitored at 1531 nm) spectrum and the NIR luminescence lifetime of **1**. However, we were able to measure the NIR luminescence lifetime of **5**, which is 16 μs and is much longer than the lifetime of the porphyrinate emission.

Conclusion

In this paper we have shown that cationic lanthanide(III) porphyrinate complexes are good precursor complexes for the

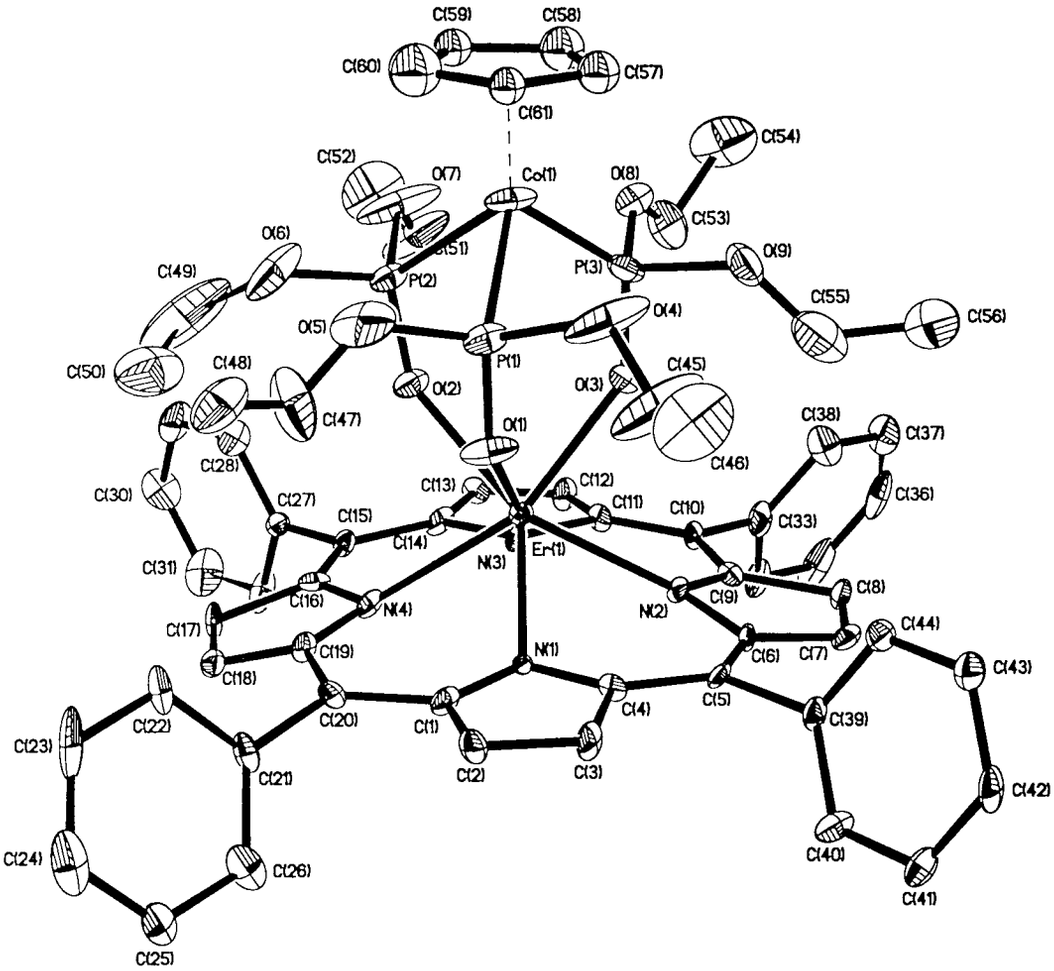


Fig. 2 A perspective drawing of compound **3**. Hydrogen atoms were omitted for clarity.

preparation of neutral 3d–4f bi-metallic porphyrinate complexes, and that porphyrinate ligands can behave as an antenna, transferring absorbed visible light energy to the encapsulated lanthanide(III) metal ion. We are now exploring the possibility of using cationic lanthanide porphyrinates as precursor complexes for the preparation of other cationic, neutral and anionic lanthanide porphyrinate complexes, with a view to examining their photophysics.

Experimental

Procedures

All reactions were carried out in an atmosphere of dry nitrogen or *in vacuo*. Solvents were dried by standard procedures, distilled and deaerated prior to use. All chemicals used were of reagent grade, obtained from the Aldrich Chemical Company and, where appropriate, degassed before use. 5,10,15,20-Tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphyrin (H_2TMPP), 5,10,15,20-tetrakis[3,4,5-tri(methoxy)phenyl]-21*H*,23*H*-porphyrin (H_2TM_3PP), 5,10,15,20-tetrakis(*p*-tolyl)-21*H*,23*H*-porphyrin (H_2TTP), 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (H_2TPP),[20] sodium (cyclopentadienyl)tris(diethylphosphito)-cobaltate (NaL_{OEt})[21] and [Ln(porp)$(H_2O)_3]^+$Cl (Ln = Er or Yb)[15] were prepared according to literature methods. Microanalyses were performed by the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. Electronic absorption spectra in the UV-vis region were recorded on a Hewlett Packard 8453 UV-visible spectrophotometer, steady-state visible fluorescence and PL excitation spectra on a Photon Technology International (PTI) Alphascan spectrofluorimeter and visible decay spectra on a pico-N_2 laser system (PTI Time Master) with λ_{exc} = 337 nm. NIR emission was detected by a liquid nitrogen cooled InSb IR detector (EG & G) with a preamplifier and recorded by a lock-in amplifier system as the third harmonics. The 355 nm line of a Nd : YAG laser (Quantel Brilliant B) was used as the excitation source and also to pump the OPO (Opotek MagicPrism VIR) to provide a continuously tunable laser source from 410–670 nm with a pulse width of 4 ns. NIR decay spectra were detected by an Oriel 77343 photomultiplier and monitored by a HP54522A 500 MHz oscilloscope. Quantum yields were computed according to the literature method[22] using $[Ru(bipy)_3]Cl_2$ as the reference standard (Φ = 0.028 in air-equilibrated water).[23] The IR spectra (KBr pellets) were recorded on a Nicolet Magna-IR 550 spectrometer and NMR spectra on a JEOL EX270 spectrometer. ^{1}H NMR chemical shifts were referenced to internal deuteriated solvents and then recalculated to TMS (δ 0.00) and those from the $^{31}P\{^1H\}$ NMR spectra to external 85% H_3PO_4. Low-resolution mass spectra were obtained on a Finnigan MAT SSQ-710 or MAT 95 spectrometer in FAB (positive ion) mode and reported as *m*/*z*.

Preparations

Compounds **1**–**5** were prepared by the same method. A typical procedure is given for **1**.

$[(L_{OEt})Er(TM_3PP)]$ 1. A solution of $[Er(TM_3PP)(H_2O)_3][Cl]$ (0.060 g, 0.050 mmol) and NaL_{OEt} (0.030 g, 0.052 mmol) in tetrahydrofuran (15 cm^3) was stirred under nitrogen at room temperature. The progress of the reaction was monitored by ^{31}P NMR spectroscopy. After stirring for 48 h, the reaction mixture was filtered. The solvent was removed from the filtrate *in vacuo* to give a purple residue, which was washed with methanol (2 × 10 cm^3) and hexane (2 × 5 cm^3). The crude product was

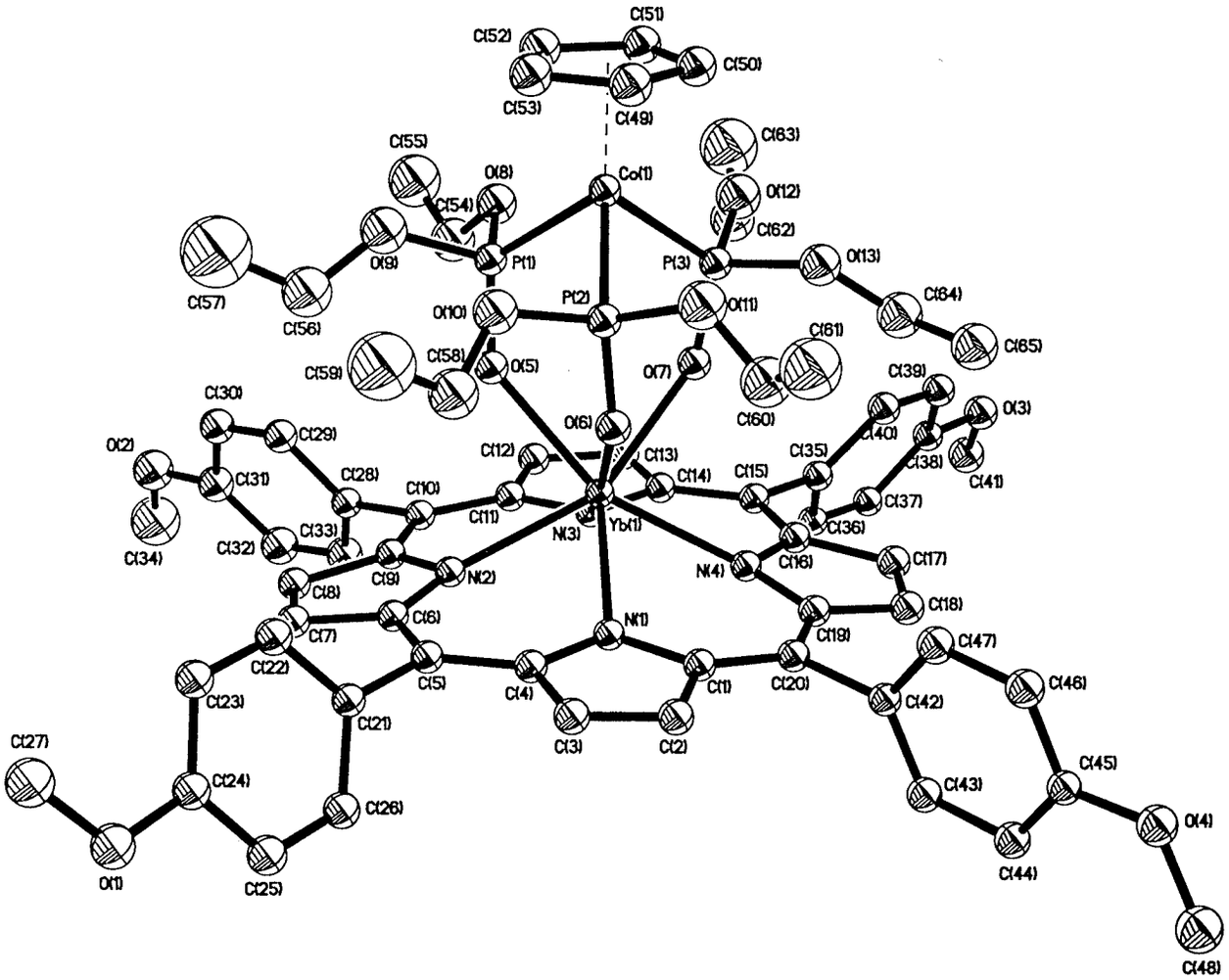


Fig. 3 A perspective drawing of compound **5**. Hydrogen atoms were omitted for clarity.

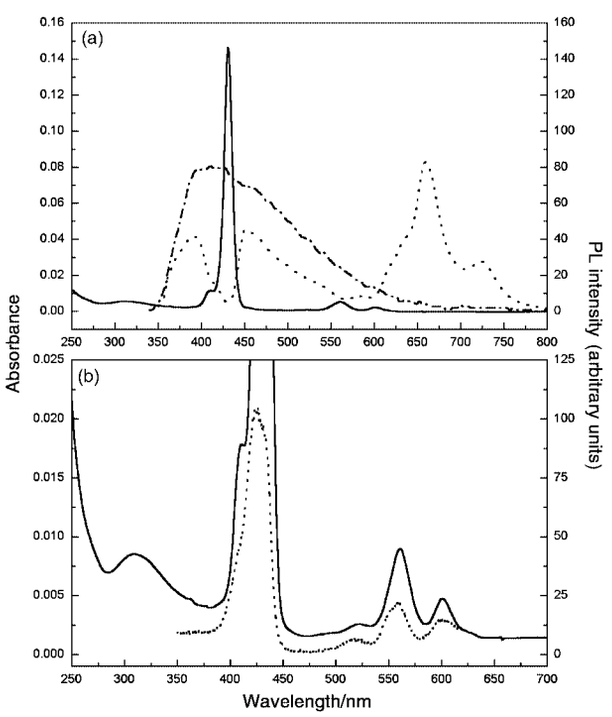


Fig. 4 (a) Room temperature absorption spectrum of **5** (——) and emission spectra excited at 325 nm of **5** (· · · · · ·) and [Yb(L_{OEt})$_2$-(η^2-ONO_2)] (—·—) in $CHCl_3$. (b) Absorption (——) spectrum and excitation (· · · · · ·) spectrum monitored at 660 nm of **5** in $CHCl_3$.

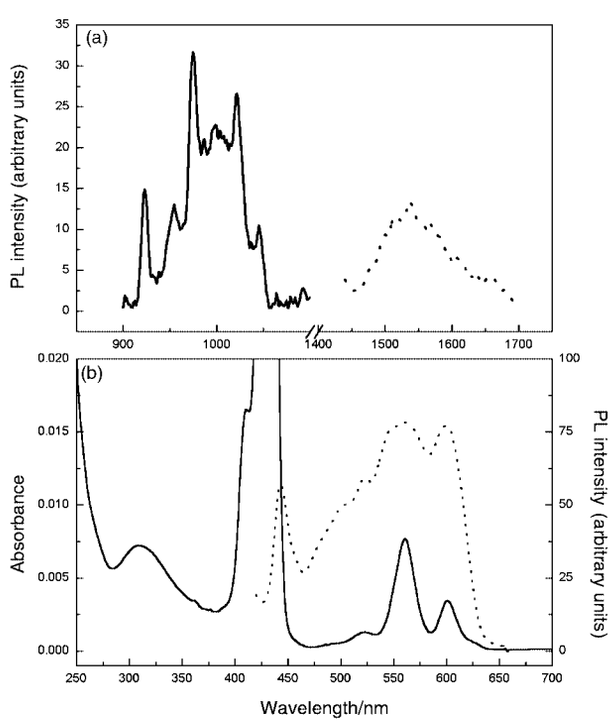


Fig. 5 (a) Room temperature NIR luminescence spectra of **1** (· · · · · ·) and **5** (——) in $CHCl_3$ upon excitation at 600 nm. (b) Room temperature absorption (——) spectrum and excitation (· · · · · ·) spectrum monitored at 921 nm of **5** in $CHCl_3$.

Table 3 Crystallographic data for compounds **1**, **3** and **5**

Compound	**1**	**3**	**5**
Empirical formula	$C_{73}H_{87}CoErN_4O_{21}P_3\cdot CHCl_3$	$C_{61}H_{63}CoErN_4O_9P_3\cdot CHCl_3$	$C_{65}H_{71}CoYbN_4O_{13}P_3\cdot 0.75C_3H_6O$
Formula weight	1794.93	1434.62	1484.70
Colour and habit	Purple block	Purple block	Dark red plate
Crystal size/mm	0.10 × 0.10 × 0.20	0.10 × 0.10 × 0.15	0.08 × 0.38 × 0.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	Cc	$P\bar{1}$ (no. 2)
a/Å	17.279(1)	13.283(3)	12.827(3)
b/Å	17.425(1)	21.498(4)	14.337(3)
c/Å	26.680(2)	23.681(5)	22.294(5)
α/°	90	90	79.35(3)
β/°	95.33(1)	104.78(3)	86.77(3)
γ/°	90	90	74.81(3)
V/Å^3	7997.9(9)	6538(2)	3888(2)
Z	4	4	2
D_{calc}/g cm^{-3}	1.491	1.457	1.268
Absorption coefficient/mm^{-1}	1.482	1.780	1.527
$F(000)$	3676	2908	1518
θ range/°	1.66–27.58	1.78–26.00	1.92–25.53
Reflections collected	45956	17477	12368
Independent reflections	17950 (R_{int} = 0.0667)	10438 (R_{int} = 0.0337)	11575 (R_{int} = 0.0411)
Goodness-of-fit on F^2	1.025	1.001	1.053
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.046, $wR2$ = 0.129	$R1$ = 0.051, $wR2$ = 0.127	$R1$ = 0.057, $wR2$ = 0.164
R indices (all data)	$R1$ = 0.0569, $wR2$ = 0.142	$R1$ = 0.067, $wR2$ = 0.139	$R1$ = 0.061, $wR2$ = 0.169

purified by column chromatography on silica gel using 1 : 1 chloroform–hexane as the eluent. The purple band was collected and the solvent removed to give a purple solid, which was recrystallized from chloroform–hexane *via* slow evaporation in air to afford purple crystals. Yield: 0.069 g, 83%. M.p. > 300 °C. IR (cm^{-1}, KBr): 2963m, 1579m, 1503m, 1407m, 1261s, 1123m, 1125s, 1100vs, 1022vs, 939m, 800vs, 722m, 584m. ^{31}P NMR ($CDCl_3$): δ −163.6 (s). UV-vis data in $CHCl_3$, 20 °C, λ_{max}/nm, [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 411 (4.70), 431 (5.21), 561 (3.84), 601 (3.41). Fluorescence data in $CHCl_3$, 20 °C, λ_{exc}/nm: 420; λ_{em}/nm: 1531, 652. MS (FAB, +ve) *m*/*z*: 1674 (M + 1)$^+$ for ^{166}Er. Anal. calc. (found) for $C_{73}H_{87}N_4O_{21}P_3CoEr$: C, 52.33 (52.95); H, 5.20 (5.27); N, 3.34 (3.38%).

[(L_{OEt})Er(TMPP)] 2. [Er(TMPP)(H_2O)$_3$]Cl (0.060 g, 0.060 mmol) and NaL_{OEt} (0.036 g, 0.062 mmol) were used. The reaction was carried out for 48 h. Yield: 64 mg, 75%. M.p. > 300 °C. IR (cm^{-1}, KBr): 2924m, 1606s, 1519s, 1507s, 1480w, 1463w, 1457w, 1439w, 1328w, 1290w, 1247vs, 1173s, 1138vs, 1038s, 930s, 986s, 840w, 804m, 798m, 728m, 585m. ^{31}P NMR ($CDCl_3$): δ −166.0 (s). UV-vis data in $CHCl_3$, 20 °C, λ_{max}/nm, [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 411 (3.97), 431 (5.03), 560 (3.72), 600 (3.47). MS (FAB, +ve) *m*/*z*: 1434 (M + 1)$^+$ for ^{166}Er. Anal. calc. (found) for $C_{65}H_{71}N_4O_{13}P_3CoEr\cdot 2H_2O$: C, 53.06 (53.08); H, 5.10 (5.15); N, 3.80 (3.41%).

[(L_{OEt})Er(TPP)] 3. [Er(TPP)(H_2O)$_3$]Cl (0.060 g, 0.070 mmol) and NaL_{OEt} (0.040 g, 0.072 mmol) were used. The reaction was carried out for 48 h. Yield: 70 mg, 76%. M.p. > 300 °C. IR (cm^{-1}, KBr): 3450w, 1652m, 1595m, 1558m, 1473m, 1440m, 1349m, 1139vs, 1033m, 1001m, 986m, 965s, 932m, 794vs, 747m, 728m, 700s, 585m. ^{31}P NMR ($CDCl_3$): δ −166.2 (s). UV-vis data in $CHCl_3$, 20 °C, λ_{max}/nm, [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 411 (3.98), 430 (5.03), 558 (3.74), 598 (3.44). MS (FAB, +ve) *m*/*z*: 1314 (M + 1)$^+$ for ^{166}Er. Anal. calc. (found) for $C_{61}H_{63}N_4O_9P_3CoEr$: C, 55.70 (55.79); H, 4.79 (4.83); N, 4.26 (4.25%).

[(L_{OEt})Yb(TTP)] 4. [Yb(TTP)(H_2O)$_3$]Cl (0.020 g, 0.020 mmol) and NaL_{OEt} (0.012 g, 0.022 mmol) were used. The reaction was carried out for 48 h. The product was recrystallized from a chloroform–ethanol mixture. Yield: 20 mg, 75%. M.p. > 300 °C. IR (cm^{-1}, KBr): 2995m, 2361m, 1635m, 1559m, 1521m, 1139vs, 1041s, 1023m, 988m, 833w, 798s, 724m, 670w, 585m. ^{31}P NMR ($CDCl_3$): δ 65.1 (s). UV-vis data in $CHCl_3$, 20 °C, λ_{max}/nm, [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 411 (4.10), 430 (5.12), 560 (3.86), 598 (3.59). MS (FAB, +ve) *m*/*z*: 1378 (M + 1)$^+$ for ^{174}Yb. Anal. calc. (found) for $C_{65}H_{71}N_4O_9P_3CoYb\cdot CH_3CH_2OH\cdot 2H_2O$: C, 55.14 (55.48); H, 5.55 (5.47); N, 3.83 (3.59%).

[(L_{OEt})Yb(TMPP)] 5. [Yb(TMPP)(H_2O)$_3$][Cl] (0.248 g, 0.193 mmol) and NaL_{OEt} (0.094 g, 0.194 mmol) were used. The reaction was carried out for 48 h. The product was crystallized from an acetone solution. Yield: 0.25 g, 91%. M.p. > 300 °C. IR (cm^{-1}, KBr): 2972w, 2924m, 1606m, 1519s, 1507s, 1482m, 1440m, 1290m, 1246vs, 1173s, 1139vs, 1038s, 986s, 930s, 804m, 797m, 727m, 622w, 597m, 584m. ^{31}P NMR ($CDCl_3$): δ 65.4 (s). UV-vis data in $CHCl_3$, 20 °C, λ_{max}/nm, [log(ε/dm^3 mol^{-1} cm^{-1}) in parentheses]: 411 (4.75), 431 (5.27), 561 (4.17), 601 (3.74). Fluorescence data in $CHCl_3$, 20 °C, λ_{exc}/nm: 420; λ_{em}/nm: 921, 652. MS (FAB, +ve) *m*/*z*: 1442 (M + 1)$^+$ for ^{174}Yb. Anal. calc. (found) for $C_{65}H_{71}N_4O_{13}P_3CoYb\cdot 0.75C_3H_6O$: C, 54.40 (54.24); H, 5.13 (5.16); N, 3.77 (3.73%).

X-Ray crystallography

Pertinent crystallographic data and other experimental details are summarized in Table 3. Crystals suitable for X-ray diffraction studies were grown by slow evaporation of solutions of the respective compounds in chloroform–hexane for **1** and **3**, and in acetone for **5**. The crystals were wrapped in epoxy glue to prevent them from losing solvent, and mounted on a thin glass fibre. No decay in intensity was encountered during the data collection. Intensity data for **1** and **3** were collected at 293 K on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data for **5** were collected at 294 K on an MSC/Rigaku RAXIS IIC imaging plate diffractometer using Mo-Kα radiation (λ = 0.71073 Å). For **1** and **3**, the collected frames were processed with the software SAINT[24] and an absorption correction was applied (SADABS)[25] to the collected reflections. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program.[26]

The space groups of each crystal were determined from the systematic absences and Laue symmetry checks and confirmed by successful refinement of the structures. The structures of all compounds were solved by direct methods (SHELXTL™[27] for **1** and **3**, SHELXTL PLUS[28] for **5**) and refined against F^2 by

full matrix least-squares analysis using SHELXL 93.[29] Except for the cyclopentadienyl ring in **3**, which was assigned with isotropic displacement parameters, all non-hydrogen atoms were refined anisotropically for the three structures. For **3**, constraints were placed on the C–C bond distances of the Cp and phenyl rings and the resulting model was refined to convergence with reasonable bond lengths and angles. Hydrogen atoms were generated in their idealized positions and allowed to ride on their respective parent carbon atoms.

CCDC reference numbers 155057, 155058 and 167524.

See http://www.rsc.org/suppdata/dt/b1/b104993n/ for crystallographic data in CIF or other electronic format.

Acknowledgements

Thanks are due to the Hong Kong Baptist University and the Hong Kong Research Grants Council (HKBU 2023/00P) for financial support.

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