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β-Fluorinated porpholactones and metal complexes: synthesis, characterization and some spectroscopic studies†

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We describe the synthesis of β-fluorinated porpholactones by oxidation of the fluorinated C=C bond of the pyrrolic subunit in porphyrin using the "$RuCl_3$ + Oxone®" protocol. The electron-withdrawing effects of β-fluorine on the absorption, fluorescence, phosphorescence and redox properties of the β-fluoroporpholactones were studied. A potential application of the β-fluoroporpholactones was demonstrated in sensitizing near-IR (NIR) emissive ytterbium, giving a high quantum yield (58%) and long luminescence time (525 μs) in CD_2Cl_2.

Introduction

Introducing electron-withdrawing groups into porphyrinate compounds is a preferred way to modulate the photophysical and redox potential properties as well as the reactivities of the molecules.[1–6] Among all the electron-withdrawing substituents, fluorine is a quite special one because of its strongest electronegativity (χ = 4), small atom radius (1.47 Å) and unique biological properties imparted when introduced into organic molecules.[7,8] In fact, introducing fluorine atoms, unlike its heavier counterparts chlorine and bromine,[9–12] into the β positions of tetrapyrrole molecules was once a difficult task and has been pursued intensively by many chemists.[13–19] For example, β-octafluorine-tetraaryl porphyrins were reported by the DiMagno group in 1997,[15,16] and then β-octafluorocorrole[17,18] and octafluoroporphyrin[19] were reported by the Chang group in 2003 and 2016 respectively, using the condensation of 3,4-difluoropyrrole[20,21] and an aldehyde in the presence of an acid catalyst. A significant electronic effect of β fluorination has been found on the reactivity of metal complexes. For instance, enhanced water splitting catalytic performance was observed on cobalt(III) hangman β-octafluorocorrole by Nocera and co-workers.[22] Increased low temperature preferential oxidation of carbon monoxide was achieved with rhodium(III) β-octafluoroporphyrin by the DiMagno group.[23] These excellent studies stimulated us to expand such an approach to more tetrapyrrole derivatives.

Porpholactone, in which a porphyrin pyrrole unit is formally replaced by an oxazolone moiety, is an important type of porphyrinoid. Since the first report on porpholactone by Crossley *et al.*,[24] several strategies to convert a *meso*-arylporphyrin to porpholactone have been reported.[25–29] Their potential applications have been demonstrated in optical materials, biology and catalysis in recent years.[30–39] However, much less attention has been paid on the electronic structure of the macrocycle, and no β-fluorinated porpholactone has been reported yet, probably due to the limited synthetic methodology. A practical method to β-fluoroporpholactone would be direct modification of the β-fluoroporphyrin and the bottleneck of this approach lies in the high stability of the C–F bond (bond dissociation energy ~105 kcal mol^{-1}).[40,41] Inspired by recent work on the electrophilic activation of the C–F bond using high-valent metal oxo species,[42–46] we report here the transformation of β-fluoroporphyrin to β-fluoroporpholactone on β C–F bond cleavage catalysed by ruthenium under oxidative conditions. This protocol enables us to obtain the first perfluorinated tetraarylporpholactone and to investigate the electronic effect of β-fluorine on porpholactones as well as the potential application in sensitizing near-IR emissive ytterbium.

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Results and discussion

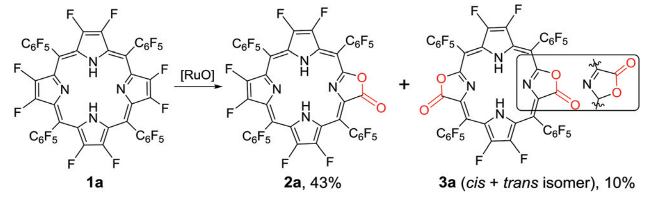
Synthesis of β-fluoroporpholactone

Our previous work showed that the "$RuCl_3$ + Oxone®" protocol was efficient in catalytically oxidizing porphyrin to porpholactone in one step.[28] The *in situ* generated high-valent [RuO] was believed to be the active intermediate. Enlightened by high-valent [FeO] and [CuO] in the hydroxylation of the C–F bond, we wonder whether the [RuO] species could show similar reactivity towards the β C–F bond of porphyrin. We started the investigation from the oxidation of 2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (**1a**). To our delight, after the optimization of the reaction conditions, porpholactone (**2a**, 43%) and porphodilactones (**3a**, a mixture of *cis* and *trans* isomers, 10%) were obtained with the "$RuCl_3$ + Oxone®" protocol (Scheme 1).

2a was fully characterized by NMR ($^1H/^{19}F/^{13}C$), HR-ESI-MS, IR, and UV-Vis spectrometry (see details in the ESI†). The characteristic carbon signal of the carbonyl moiety appears at 164.2 ppm in the ^{13}C NMR spectrum and at 1796 cm^{-1} in the FT-IR spectrum. The UV-vis absorption spectra of the products are shown in Fig. 1. A slight red shift of *ca.* 3 nm from 393 nm to 396 nm and a narrowed Soret band are observed upon introducing the lactone moiety on **1a** to give **2a** (Fig. 1). Four Q bands appear for **2a** as a result of the lowered symmetry compared to **1a**. These results are in line with our previously reported porpholactones.[28]

To examine the generality of this methodology, we used several β-octafluoroporphyrins with different *meso*-phenyl groups as substrates, including 2,6-difluorophenyl (**1b**), *p*-trifluoromethylphenyl (**1c**), *p*-chlorophenyl (**1d**) and phenyl (**1e**). Typical isolated yields are around 40%–50% with the optimal conversions of around 60%–70% (Table 1). The catalytic protocol shows good regioselectivity, leaving the *meso*-aryl C–F bond and trifluromenthyl group intact. Moreover, the metal complex **Zn-1a** could also be oxidized to the corresponding metalloporpholactone **Zn-2a**, albeit with low yield (20%) due to the significant disruption of the porphyrin macrocycle. The chemo-selectivity between β-C–F and C–H bonds was investigated using 2,3-difluoro-5,10,15,20-tetrapentafluorophenylporphyrin (**1f**) and 2,3,7,8-tetrafluoro-5,10,15,20-tetrapentafluorophenylporphyrin (**1g**) as substrates. The isolated products showed that the non-fluorinated pyrrole unit adjacent to the difluoropyrrole unit was selectively oxidized for both compounds, indicating that the C–H bond is more susceptible to oxidization than the C–F bond. Interestingly, for **1g**, the lactonized products are two isomers in 1 : 1 ratio, regarding the relative orientation of the lactone moiety with respect to the pyrrolic unit.

A preliminary reaction mechanism study was carried out according to the "breaking and mending strategy" developed



Scheme 1 Oxidation of **1a** by the "$RuCl_3$ + Oxone®" protocol. Conditions: **1a** 0.05 mmol, $RuCl_3 \cdot nH_2O$ 0.01 mmol, 2,2′-bipyridine 0.01 mmol, Oxone® 1 mmol, NaOH 1 mmol, 1,2-dichloroethane/H_2O = 1/1 (v/v) 60 mL, 80 °C, 1 h. See the ESI† for details.

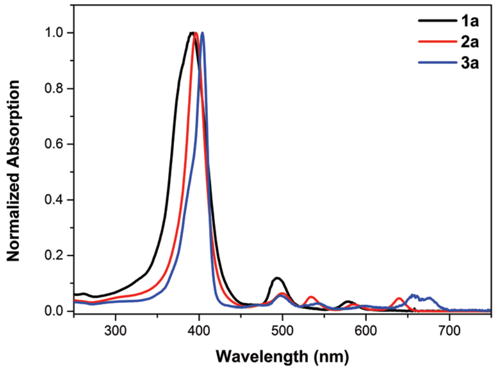
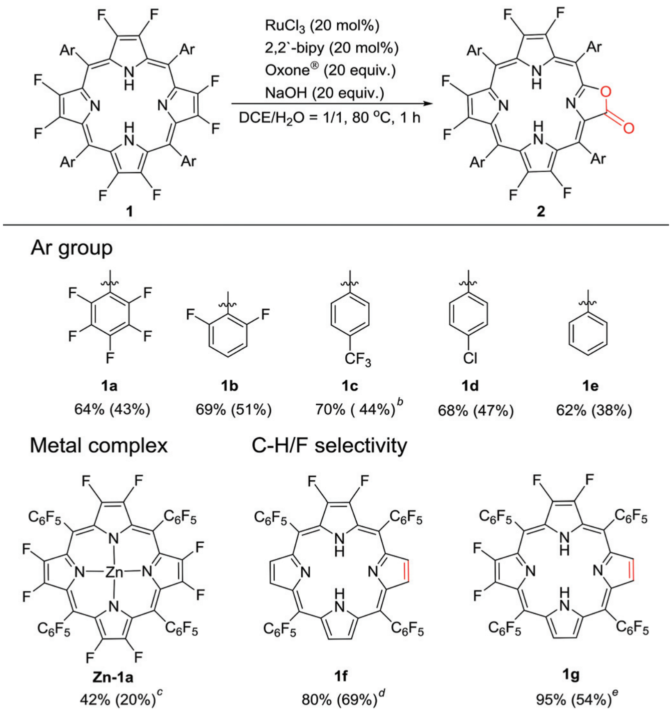
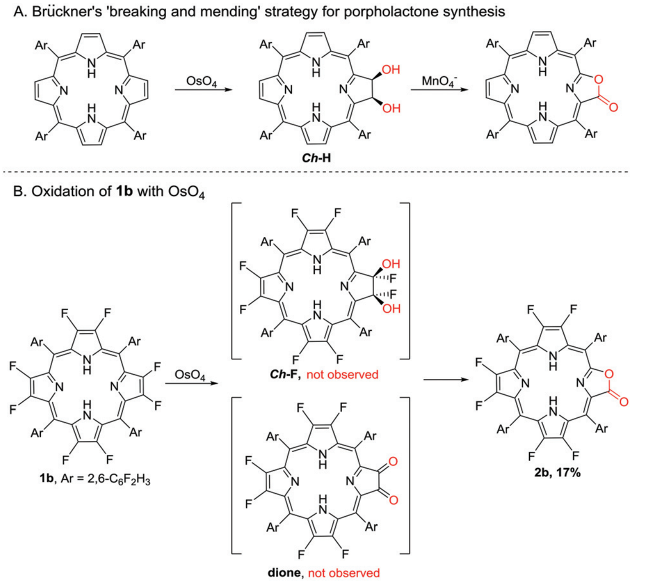


Fig. 1 UV-vis absorption spectra of porphyrin **1a** (black line), porpholactone **2a** (red line) and the mixture of porphodilactones **3a** (blue line) in CH_2Cl_2.

Table 1 Substrate scope of the ruthenium-catalysed synthesis of β-fluoroporpholactone[a]



[a] Conversion (isolated yields). See the ESI† for details. [b] 12 equiv. Oxone®. [c] 50 °C, 2 h. [d] 30 equiv. Oxone®, 15 min. [e] 16 equiv. Oxone®, 2 h, two porpholactone isomers in 1 : 1 ratio.

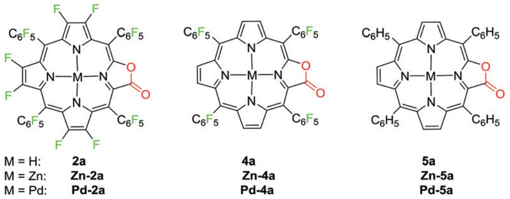


Scheme 2 The reactivity of porphyrin towards OsO_4.

by Brückner and co-workers.[30] A *cis*-Diol-substituted chlorin (***Ch*-H**), formed from the reaction of porphyrin with the mild oxidant OsO_4, could be converted to porpholactone in the presence of a strong oxidant such as MnO_4^- (Scheme 2A).[26,47–49] In this work, we attempted the dihydroxylation of **1b** with OsO_4, and however we could not obtain the desired dihydroxyl product (***Ch*-F**) but **2b** in 17% yield after the reaction for four days at room temperature (Scheme 2B).[47] It is well known that α-fluoroalcohols are highly unstable and undergo facile HF elimination to give carbonyl compounds.[50,51] Herrmann *et al.* reported that the catalytic oxidation of fluorinated olefins with OsO_4 gave dione products.[52] However, Crossley's seminal first paper on porpholactones showed that the oxidation of dione (β,β′-dioxoporphyrin) gave only a trace amount of porpholactone.[24] We therefore hypothesize that ***Ch*-F** is prone to oxidization to porpholactone even by the weak oxidant OsO_4 without the intermediation of dione, in contrast to its hydrogenated congener ***Ch*-H** with high stability.

Metalation of perfluoroporpholactone 2a

To demonstrate the coordination ability of β-fluorinated porpholactones towards transition metals, in this work, we chose **2a** as an example and investigated the metalation with zinc(II) and palladium(II) ions. The new porpholactone metal complexes **Zn-2a** and **Pd-2a** were synthesized according to literature methods in 95% and 53% yield respectively (Scheme 3).[33] Metalation with zinc commenced immediately and was complete within minutes upon mixing **2a** and zinc acetate in 1 : 1 $CH_2CH_2 : CH_3OH$ solution. Palladium insertion was accomplished by refluxing **2a** and palladium acetylacetonate in benzonitrile. Complexes **Zn-4a**, **Zn-5a**, **Pd-4a** and **Pd-5a** were prepared as well for the discussion of electrochemical and photophysical properties in the context (Scheme 3).



Scheme 3 Porpholactone compounds studied in this work.

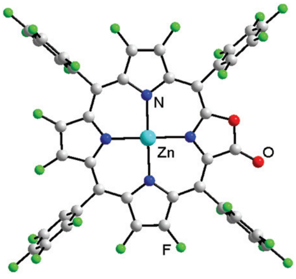


Fig. 2 Perspective drawing of the crystal structure of **Zn-2a** (the two axial pyridines and solvent molecules are omitted for clarity; the lactone moiety is crystallographically disordered, see the ESI†).

These complexes were characterized by multinuclear NMR, HR-ESI-MS and IR spectrometry (see the ESI†).

Importantly, a single crystal of **Zn-2a** suitable for X-ray analysis was obtained in $CHCl_3$/hexane (CCDC 1501201†). As shown in Fig. 2, the macrocyclic ring is essentially flat and the hexa-coordinate Zn (with two axial coordinate pyridine molecules) lies in the mean plane of four nitrogen atoms. The C=O bond length of **Zn-2a** is 1.27(1) Å, similar to that of its hydrogenated counterpart **Zn-5a** (1.25(4) Å).[26] The structure confirms the oxazolone moiety of porphyrin in **Zn-2a**, consistent with the above structure determination of β-fluorinated porpholactones.

Photophysical and electrochemical features

To show how fluorine groups at β positions regulate the electronic structures of porpholactones, the spectroscopic properties of the representative porpholactone free bases as well as the spectroscopic and electrochemical properties of metal complexes (Pd and Zn) were studied (Scheme 3). The absorption and emission data are given in Table 2 and the spectra are depicted in Fig. 3.

Fluorine substituents at both *meso* and β positions are effective in tuning the UV-vis absorption of porpholactones. A progressive blue shift occurs from **5a** to **2a**. Compound **2a** exhibits a Soret band at 396 nm in CH_2Cl_2, while **4a** at 409 nm and **5a** at 418 nm. The four Q bands of the three compounds show similar blue shifts upon fluorination except that the $Q_x(0,0)$ bands nearly appear at the same wavelength of around 641 nm. The corresponding Zn and Pd complexes show similar blue-shifted Soret bands upon fluorination, ranging from 415–422 nm and 399–418 nm respectively. However, compared to **Zn-4a** (542, 606 nm) and **Pd-4a** (542, 583 nm), the two

Table 2 Optical spectroscopy, fluorescence, and photophysics of porpholactones in CH_2Cl_2

Compound	Abs. [nm]	Em. [nm] (τ [ns or μs])[a]	Stokes shift [cm^{-1}]	QY[b]	k_{obs} [s^{-1}]	k_f [s^{-1}]
2a	396, 500, 534, 585, 640	644 (5.8), 714	97	0.075	1.7×10^8	1.3×10^7
4a[c]	409, 510, 545, 589, 642	643 (6.9), 710	24	0.13	1.4×10^8	1.9×10^7
5a[c]	418, 520, 558, 589, 641	644 (8.1), 709	73	0.065	1.2×10^8	0.8×10^7
Zn-2a	415, 556, 601	606 (0.84), 665	137	0.025	11.9×10^8	3.0×10^7
Zn-4a[c]	417, 542, 606	609 (0.86), 667	27	0.040	11.6×10^8	4.7×10^7
Zn-5a	422, 557, 602	605 (0.93), 664	82	0.035	10.8×10^8	3.8×10^7
Pd-2a	399, 536, 578	768 (367), 853	4280	0.046	2.7×10^3	12.5
Pd-4a[d]	407, 542, 583	770 (472), 847	4166	0.060	2.3×10^3	12.7
Pd-5a[e]	418, 537, 578	752 (300), 844	4003	0.061	3.3×10^3	20.3

[a] The emission lifetimes are in the nanosecond scale for free base and zinc complexes and are in the microsecond scale for palladium complexes. [b] Referenced to TPP in toluene ($\Phi = 0.11$) for free bases and to ZnTPP in toluene ($\Phi = 0.033$) for metal complexes. Errors for quantum yield values (±10%) are estimated. [c] Ref. 28. [d] Ref. 54. [e] Ref. 33.

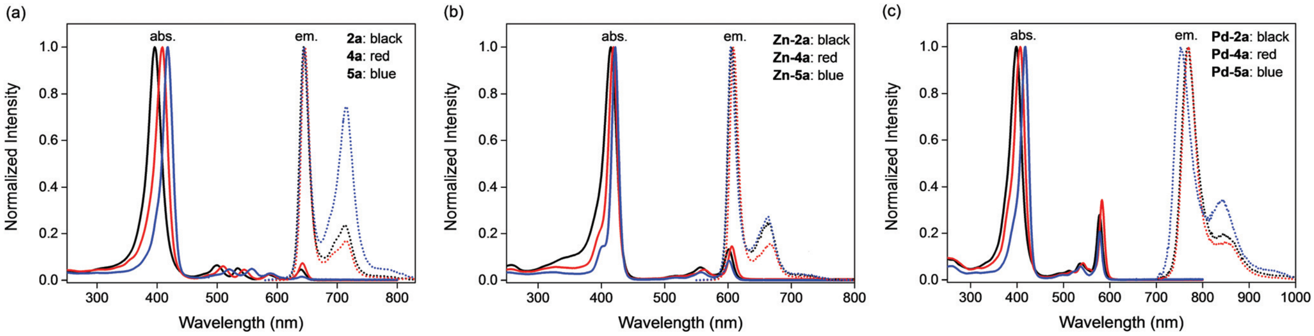


Fig. 3 UV-vis absorption (solid line) and emission spectra (dashed line) of (a) porpholactone free bases, (b) zinc complexes and (b) palladium complexes in CH_2Cl_2 solution at 298 K. The emission spectra of palladium complexes were recorded in degassed solution.

Q bands of **Zn-2a** (556, 601 nm) and **Pd-2a** (536, 578 nm) shift to lower energy, occurring at nearly identical wavelengths to those of **Zn-5a** (557, 602 nm) and **Pd-5a** (537, 578 nm) respectively.

The fluorescence spectra of the three porpholactone molecules and their zinc complexes are very similar, peaking at 644 and 605 nm respectively with well-resolved vibronic progressions. They all display good mirror image symmetry with their respective Q-band absorptions in intensity and spacing with a small Stokes shift (<150 cm^{-1}), indicating that the compounds do not undergo significant reorganization of nuclear coordinates in the excited states. The fluorescence lifetimes of the free bases decrease slightly from 8.1 to 5.8 μs in going from **5a** to **2a**. The corresponding zinc complexes also show a reduced fluorescence lifetime, yet to much less degree, from 0.93 to 0.84 ns upon perfluorination. The fluorescence quantum yields show an increase upon the first fluorination of *meso*-phenyl groups but a decrease upon further fluorination of β positions for both free bases and their zinc complexes. The deactivation rates of the excited state (k_{obs}) are calculated from lifetimes and are listed in Table 2. Increasing magnitudes of k_{obs} are observed for both free bases and zinc compounds upon fluorination. The radiative rates calculated from the S1 lifetimes and the quantum yields of fluorescence ($k_f = \Phi_f/\tau_f$) are also listed in Table 2. The radiative rate order follows the same order observed for the fluorescence quantum yield.

The three palladium complexes show intense phosphorescence at room temperature in degassed CH_2Cl_2 solutions (Fig. 3c). The emission profile of **Pd-2a** resembles that of **Pd-4a** with the maximum peak at 768 nm, showing a 16 nm blue-shift to that of **Pd-5a** at 752 nm. A similar trend was found in the corresponding platinum porphyrin complex series in an early report by Chang *et al.*[53] The lifetime of **Pd-2a** is 367 μs, longer than that of **Pd-5a** (300 μs), but shorter than that of **Pd-4a** (472 μs). In our hands the lifetime of **Pd-5a** and **Pd-4a** are longer than literature reports (157 and 296 μs respectively),[33,54] presumably resulted from the lower air concentration. The quantum yields of phosphorescence change little after *meso*-phenyl fluorination for **Pd-4a** (0.060), but diminish on further β fluorination for **Pd-2a** (0.046).

The electrochemical properties of the porpholactone free bases and the zinc complexes were investigated by cyclic voltammetry at 298 K using 0.1 M $n\text{Bu}_4\text{NPF}_6$ as the supporting electrolyte in CH_2Cl_2 and the data are tabulated in Table 3 (see the ESI† for figures). It is clearly shown that the fluorine substituents at both β positions and *meso*-phenyl groups are effective in tuning the redox potentials of the porpholactone compounds. For free bases, there is no oxidation peak observed for **2a** up to a potential of 1.8 V, while there is one irreversible peak for **4a** at 1.61 V and two quasi-reversible peaks for **5a** at 1.54 and 1.30 V respectively. The six fluorine substituents on the porphyrin ring bring about a 0.3 V shift to

Table 3 Electrochemical data for porpholactone compounds in CH_2Cl_2[a]

Compound	E_{ox2}	E_{ox1}	E_{red1}	E_{red2}	E_{red3}
2a	—	—	−0.23	−0.71	−1.66
4a	—	+1.61	−0.54	−0.99	—
5a	+1.54	+1.30	−0.89	−1.34	—
Zn-1a[b]	—	+1.70	−0.63	−1.04	—
Zn-2a	—	+1.59	−0.51	−0.94	—
Zn-4a[c]	+1.61	+1.33	−0.72	−1.16	—
Zn-5a	+1.10	+0.87	−1.14	−1.54	—

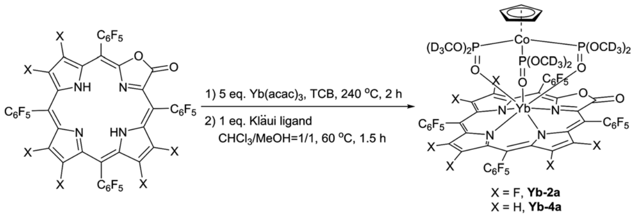
[a] Cyclic voltammetry conditions: compound concentration, 1 mM; sweep rate, 0.1 V s^{-1}; 0.1 M $n$$Bu_4PF_6$; Ag/AgCl reference. [b] Ref. 15. [c] Ref. 36.

the anode of the two reversible reduction waves (−0.23 and −0.71 V for **2a** *vs.* −0.54 and −0.99 V for **4a**), comparable to the 0.35 V shift brought by the twenty fluorines at *meso*-phenyl groups (*vs.* −0.89 and −1.34 V for **5a**). Besides, a third reduction peak appears at −1.66 V for **2a**, indicating the substantially decreased electron density of **2a**.

Similar trends were observed in the corresponding zinc complexes. Compared to **Zn-4a** and **Zn-5a**, **Zn-2a** shows a positive shift in potentials for both the porphyrinato oxidation and reduction, implying a decreased electron density of the macrocyclic ring by fluorination at *meso*-phenyl and β-pyrrolic positions. For **Zn-2a**, there is only one oxidation peak at 1.59 V up to a potential of 1.8 V, whereas there are two reversible oxidative peaks for **Zn-4a** (1.61 and 1.33 V) and **Zn-5a** (1.10 and 0.87 V) respectively. The two reduction waves of **Zn-2a** (−0.51 and −0.94 V) are anodically shifted from those of **Zn-4a** (−0.72 and −1.16 V) and **Zn-5a** (−1.14 and −1.54 V). Therefore, **Zn-2a** is easily reduced and resistant to oxidation relative to **Zn-4a** and **Zn-5a**. Compared to **Zn-1a**, introducing the lactone moiety results in catholically shifted oxidation waves and anodically shifted reduction waves.

NIR emissive ytterbium complex with enhanced quantum yield

To demonstrate the potential application of β-fluorinated porpholactones, we used them as an antenna ligand for NIR emissive lanthanides. NIR emitters such as Er, Nd and Yb complexes have many attractive potential applications in telecommunications, light-emitting devices and biological imaging but suffer from low quantum yields.[55–58] Our previous studies demonstrate that both porphyrin and porpholactone are good antenna ligands for Yb(III).[59,60] Replacing β hydrogens with fluorine substituents significantly increases the NIR emission efficiency of Yb as a result of the minimized non-radiative process caused by C–H bond vibrational quenching.[60] In this work, ytterbium complexes **Yb-2a** and **Yb-4a**, sandwiched by porpholactone and the partly deuterated Kläui ligand were prepared according to our previous procedure (Scheme 4).[60–63] These complexes were characterized by NMR, HR-ESI-MS, IR, and UV-Vis spectrometry and single crystal X-ray analysis (CCDC 1540175 (**Yb-2a**) and 1540176 (**Yb-4a**), see details in the ESI†).



Scheme 4 Synthesis of ytterbium porpholactone complexes.

As shown in Fig. 4a, the luminescence lifetime (τ) of **Yb-2a** (525 μs) is much longer than that of **Yb-4a** (75 μs) in CD_2Cl_2. The emission quantum yield (Φ) of **Yb-2a** (58%) is also much higher than that of **Yb-4a** (6.8%) in CD_2Cl_2 (Fig. 4b, referenced to Yb(TPP)(L_{OEt}), Φ = 2.4% in CH_2Cl_2, estimated uncertainty in Φ is 15%).[64] **Yb-2a** even shows comparable luminescence properties to our previously best results with **Yb-1a** (τ = 714 μs, Φ = 63% in CD_2Cl_2),[60] indicating that β-lactonization little affects the sensitization ability of porphyrin towards Yb. It is worth noting that, for the easy modification of the β-oxazolone moiety demonstrated by Brückner and us,[38,65–68] **Yb-2a** is anticipated to introduce flexibility to functionalize the Yb complexes. On the other hand, the remarkably higher value of the luminescence lifetime and quantum yield of **Yb-2a** than that of **Yb-4a** demonstrates the key role of the C–F bond in improv-

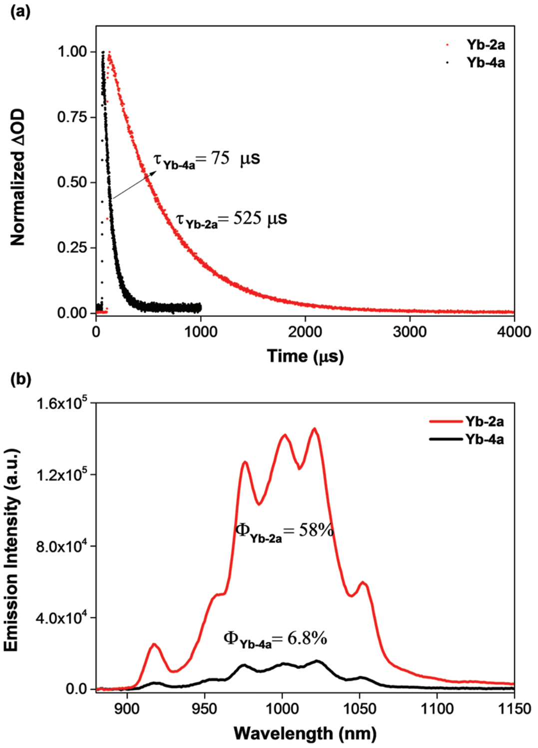


Fig. 4 (a) Decay of the NIR luminescence in the ytterbium complexes in CD_2Cl_2; (b) emission spectra of the ytterbium complexes under the same conditions (λ_{ex} = 425 nm, absorbance = 0.10) in CD_2Cl_2. The estimated uncertainty in quantum yields is 15%. Experimental relative errors: τ, ±2%; Φ, ±10%.

ing the NIR emission quantum yield of Yb by suppressing the vibrational quenching.[69]

Conclusion

In summary, we report here the synthesis of a new type of porpholactone with β-fluorine substituents, *via* the lactonization of β-fluorinated porphyrin. A high-valent ruthenium oxo intermediate generated from the protocol "$RuCl_3$ + Oxone®" was proposed as the active intermediate in the cleavage of the pyrrolic C–F bond. The perfluorinated porpholactone **2a** exhibits a similar coordination ability towards transition metals to porphyrin analogues. Comparative studies of photophysical and electrochemical properties with non-fluorinated counterparts show that β-fluorination leads to blue-shifted absorption bands and anodically shifted the redox potential of the porpholactone. As an example of the potential application of these molecules, we demonstrated that **2a** is an excellent antenna ligand for sensitizing NIR-emissive ytterbium, achieving a high luminescence quantum yield and a long lifetime.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Notes and references

1 B. Meunier, *Chem. Rev.*, 1992, **92**, 1411–1456.

2 D. Dolphin, T. G. Traylor and L. Y. Xie, *Acc. Chem. Res.*, 1997, **30**, 251–259.

3 C.-M. Che, V. K.-Y. Lo, C.-Y. Zhou and J.-S. Huang, *Chem. Soc. Rev.*, 2011, **40**, 1950–1975.

4 A. Giraudeau, H. Callot, J. Jordan, I. Ezhar and M. Gross, *J. Am. Chem. Soc.*, 1979, **101**, 3857–3862.

5 H. Fujii, *J. Am. Chem. Soc.*, 1993, **115**, 4641–4648.

6 T. G. Traylor, C. Kim, J. L. Richards, F. Xu and C. L. Perrin, *J. Am. Chem. Soc.*, 1995, **117**, 3468–3474.

7 D. O'Hagan, *Chem. Soc. Rev.*, 2008, **37**, 308–319.

8 N. V. S. D. K. Bhupathiraju, W. Rizvi, J. D. Batteas and C. M. Drain, *Org. Biomol. Chem.*, 2016, **14**, 389–408.

9 P. Bhyrappa and V. Krishnan, *Inorg. Chem.*, 1991, **30**, 239–245.

10 T. G. Traylor and S. Tsuchiya, *Inorg. Chem.*, 1987, **26**, 1338–1339.

11 T. Wijesekera, A. Matsumoto, D. Dolphin and D. Lexa, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1028–1030.

12 P. Ochsenbein, K. Ayougou, D. Mandon, J. Fischer, R. Weiss, R. N. Austin, K. Jayaraj, A. Gold, J. Terner and J. Fajer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 348–350.

13 J. Leroy and A. Bondon, *Eur. J. Org. Chem.*, 2008, 417–433.

14 S. G. DiMagno, J. C. Biffinger and H. Sun, in *Fluorine in Heterocyclic Chemistry Volume 1: 5-Membered Heterocycles and Macrocycles*, ed. V. Nenajdenko, Springer International Publishing, Cham, 2014, pp. 589–620.

15 E. K. Woller and S. G. DiMagno, *J. Org. Chem.*, 1997, **62**, 1588–1593.

16 J. Leroy, A. Bondon, L. Toupet and C. Rolando, *Chem. – Eur. J.*, 1997, **3**, 1890–1893.

17 H.-Y. Liu, T.-S. Lai, L.-L. Yeung and C. K. Chang, *Org. Lett.*, 2003, **5**, 617–620.

18 E. Steene, A. Dey and A. Ghosh, *J. Am. Chem. Soc.*, 2003, **125**, 16300–16309.

19 C. Kashi, C.-C. Wu, C.-L. Mai, C.-Y. Yeh and C. K. Chang, *Angew. Chem., Int. Ed.*, 2016, **55**, 5035–5039.

20 J. Leroy and C. Wakselman, *Tetrahedron Lett.*, 1994, **35**, 8605–8608.

21 E. K. Woller, V. V. Smirnov and S. G. DiMagno, *J. Org. Chem.*, 1998, **63**, 5706–5707.

22 D. K. Dogutan, R. McGuire and D. G. Nocera, *J. Am. Chem. Soc.*, 2011, **133**, 9178–9180.

23 J. C. Biffinger, S. Uppaluri, H. Sun and S. G. DiMagno, *ACS Catal.*, 2011, **1**, 764–771.

24 M. J. Crossley and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 920–922.

25 M. Gouterman, R. J. Hall, G. E. Khalil, P. C. Martin, E. G. Shankland and R. L. Cerny, *J. Am. Chem. Soc.*, 1989, **111**, 3702–3707.

26 C. Brückner, J. Ogikubo, J. R. McCarthy, J. Akhigbe, M. A. Hyland, P. Daddario, J. L. Worlinsky, M. Zeller, J. T. Engle, C. J. Ziegler, M. J. Ranaghan, M. N. Sandberg and R. R. Birge, *J. Org. Chem.*, 2012, **77**, 6480–6494.

27 H. Lv, B. Yang, J. Jing, Y. Yu, J. Zhang and J.-L. Zhang, *Dalton Trans.*, 2012, **41**, 3116–3118.

28 Y. Yu, H. Lv, X. Ke, B. Yang and J.-L. Zhang, *Adv. Synth. Catal.*, 2012, **354**, 3509–3516.

29 M. Sharma, E. Meehan, B. Q. Mercado and C. Brückner, *Chem. – Eur. J.*, 2016, **22**, 11706–11718.

30 C. Brückner, *Acc. Chem. Res.*, 2016, **49**, 1080–1092.

31 L. Costa, J. Costa and A. Tomé, *Molecules*, 2016, **21**, 320.

32 L. Liang, H. Lv, Y. Yu, P. Wang and J.-L. Zhang, *Dalton Trans.*, 2012, **41**, 1457–1460.

33 W.-P. To, Y. Liu, T.-C. Lau and C.-M. Che, *Chem. – Eur. J.*, 2013, **19**, 5654–5664.

34 Y. Ishigami, W. Waskitoaji, M. Yoneda, K. Takada, T. Hyakutake, T. Suga, M. Uchida, Y. Nagumo, J. Inukai, H. Nishide and M. Watanabe, *J. Power Sources*, 2014, **269**, 556–564.

35 J. Tang, J.-J. Chen, J. Jing, J.-Z. Chen, H. Lv, Y. Yu, P. Xu and J.-L. Zhang, *Chem. Sci.*, 2014, **5**, 558–566.

36 X.-S. Ke, Y. Chang, J.-Z. Chen, J. Tian, J. Mack, X. Cheng, Z. Shen and J.-L. Zhang, *J. Am. Chem. Soc.*, 2014, **136**, 9598–9607.

37 J. L. Worlinsky, S. Halepas, M. Ghandehari, G. Khalil and C. Brückner, *Analyst*, 2015, **140**, 190–196.

38 X.-S. Ke, J. Tang, J.-J. Chen, Z.-Y. Zhou and J.-L. Zhang, *ChemPlusChem*, 2015, **80**, 237–252.

39 Z.-Y. Wu, T. Wang, Y.-S. Meng, Y. Rao, S. Gao, J. Zheng, B.-W. Wang and J.-L. Zhang, *Chem. Sci.*, 2017, DOI: 10.1039/C7SC02073B.

40 M. F. Kuehnel, D. Lentz and T. Braun, *Angew. Chem., Int. Ed.*, 2013, **52**, 3328–3348.

41 J.-Y. Hu and J.-L. Zhang, *Top. Organomet. Chem.*, 2015, **52**, 143–196.

42 S. Sahu, M. G. Quesne, C. G. Davies, M. Dürr, I. Ivanović-Burmazović, M. A. Siegler, G. N. L. Jameson, S. P. de Visser and D. P. Goldberg, *J. Am. Chem. Soc.*, 2014, **136**, 13542–13545.

43 J. Serrano-Plana, I. Garcia-Bosch, R. Miyake, M. Costas and A. Company, *Angew. Chem., Int. Ed.*, 2014, **53**, 9608–9612.

44 C. Colomban, E. V. Kudrik, P. Afanasiev and A. B. Sorokin, *J. Am. Chem. Soc.*, 2014, **136**, 11321–11330.

45 S. Sahu, B. Zhang, C. J. Pollock, M. Dürr, C. G. Davies, A. M. Confer, I. Ivanović-Burmazović, M. A. Siegler, G. N. L. Jameson, C. Krebs and D. P. Goldberg, *J. Am. Chem. Soc.*, 2016, **138**, 12791–12802.

46 G. de Ruiter, N. B. Thompson, M. K. Takase and T. Agapie, *J. Am. Chem. Soc.*, 2016, **138**, 1486–1489.

47 C. Brückner, S. J. Rettig and D. Dolphin, *J. Org. Chem.*, 1998, **63**, 2094–2098.

48 J. R. McCarthy, H. A. Jenkins and C. Brückner, *Org. Lett.*, 2003, **5**, 19–22.

49 K. K. Lara, C. R. Rinaldo and C. Brückner, *Tetrahedron*, 2005, **61**, 2529–2539.

50 S. Andreades and D. C. England, *J. Am. Chem. Soc.*, 1961, **83**, 4670–4671.

51 C. J. Willis, *Coord. Chem. Rev.*, 1988, **88**, 133–202.

52 W. A. Herrmann, S. J. Eder and W. Scherer, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1345–1347.

53 S.-W. Lai, Y.-J. Hou, C.-M. Che, H.-L. Pang, K.-Y. Wong, C. K. Chang and N. Zhu, *Inorg. Chem.*, 2004, **43**, 3724–3732.

54 X.-S. Ke, H. Zhao, X. Zou, Y. Ning, X. Cheng, H. Su and J.-L. Zhang, *J. Am. Chem. Soc.*, 2015, **137**, 10745–10752.

55 J.-C. G. Bünzli and C. Piguet, *Chem. Soc. Rev.*, 2005, **34**, 1048–1077.

56 S. V. Eliseeva and J.-C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189–227.

57 J.-C. G. Bünzli, *Chem. Rev.*, 2010, **110**, 2729–2755.

58 L. Armelao, S. Quici, F. Barigelletti, G. Accorsi, G. Bottaro, M. Cavazzini and E. Tondello, *Coord. Chem. Rev.*, 2010, **254**, 487–505.

59 X.-S. Ke, B.-Y. Yang, X. Cheng, S. L.-F. Chan and J.-L. Zhang, *Chem. – Eur. J.*, 2014, **20**, 4324–4333.

60 J.-Y. Hu, Y. Ning, Y.-S. Meng, J. Zhang, Z.-Y. Wu, S. Gao and J.-L. Zhang, *Chem. Sci.*, 2017, **8**, 2702–2709.

61 C.-P. Wong, R. F. Venteicher and W. D. Horrocks Jr., *J. Am. Chem. Soc.*, 1974, **96**, 7149–7150.

62 W.-K. Wong, A. Hou, J. Guo, H. He, L. Zhang, W.-Y. Wong, K.-F. Li, K.-W. Cheah, F. Xue and T. C. Mak, *J. Chem. Soc., Dalton Trans.*, 2001, 3092–3098.

63 H. He, J. Guo, Z. Zhao, W. K. Wong, W. Y. Wong, W. K. Lo, K. F. Li, L. Luo and K. W. Cheah, *Eur. J. Inorg. Chem.*, 2004, **2004**, 837–845.

64 T. J. Foley, B. S. Harrison, A. S. Knefely, K. A. Abboud, J. R. Reynolds, K. S. Schanze and J. M. Boncella, *Inorg. Chem.*, 2003, **42**, 5023–5032.

65 J. Akhigbe, J. Haskoor, M. Zeller and C. Bruckner, *Chem. Commun.*, 2011, **47**, 8599–8601.

66 J. Ogikubo, E. Meehan, J. T. Engle, C. J. Ziegler and C. Brückner, *J. Org. Chem.*, 2012, **77**, 6199–6207.

67 Y. Yu, B. Czepukojc, C. Jacob, Y. Jiang, M. Zeller, C. Brückner and J.-L. Zhang, *Org. Biomol. Chem.*, 2013, **11**, 4613–4621.

68 X.-S. Ke, J. Tang, Z.-S. Yang and J.-L. Zhang, *J. Porphyrins Phthalocyanines*, 2014, **18**, 950–959.

69 J.-C. G. Bünzli, *Coord. Chem. Rev.*, 2015, **293**, 19–47.