DOI: 10.1002/adsc.201200720

Ruthenium-Catalyzed Oxidation of the Porphyrin β,β′-Pyrrolic Ring: A General and Efficient Approach to Porpholactones

Yi Yu,[a] Hongbin Lv,[a] Xiansheng Ke,[a] Boyan Yang,[a] and Jun-Long Zhang [a,*]

[a] Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, ChengFu Road 202, Beijing 100871, People's Republic of China
Fax: (+86)-10-6276-7034; e-mail: zhangjunlong@pku.edu.cn

Received: August 12, 2012; Revised: October 7, 2012; Published online: December 4, 2012

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201200720.

Abstract: We describe an efficient ruthenium-catalyzed oxidation of the β,β′-pyrrolic ring on the porphyrin periphery. Through the conversion of a β,β′-double bond to a lactone moiety, the direct preparation of porpholactones from porphyrins is achieved, which previously suffered from needing toxic reagents, multiple synthetic steps and low yields. The generality of this method has been investigated with various porphyrins with different electronic and steric effects, even some metalloporphyrins, and so represents a general and efficient approach for the synthesis of the intriguing porpholactone derivatives.

Keywords: β,β′-double bond; lactones; oxidation; porpholactones; porphyrins; ruthenium

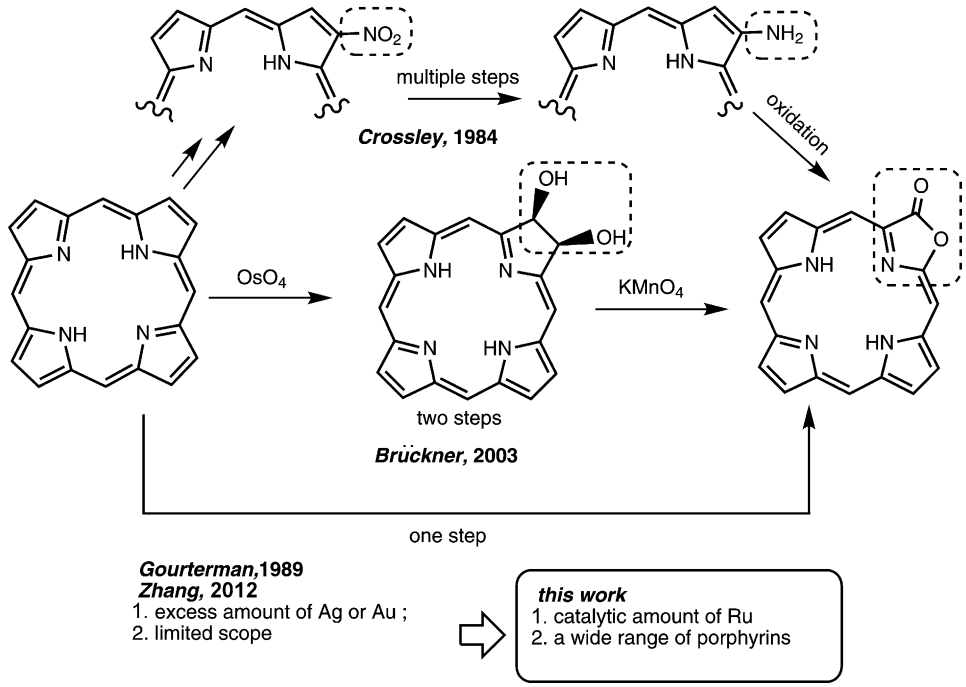
Introduction

Modification of the porphyrin periphery to tune the electronic nature of porphyrins has attracted considerable attention in material science, catalysis and biological applications.[1] Application of transition metal-catalyzed reactions, the so-called "marriage of porphyrin chemistry with metal-catalyzed reactions",[2] has begun to emerge as a recognized and valuable approach. This allows the synthesis of novel porphyrinoids which are difficult to realize by conventional methods. Thus, expanding the scope of metal-catalyzed reactions for the modification of the porphyrin periphery is of importance to enrich the repertoire of porphyrinoids with novel properties. However, there have been many challenges that diminish the scope of this approach, particularly with respect to the porphyrins susceptible to these transition metal-catalyzed reactions. Herein, we report the ruthenium-catalyzed oxidation of the β,β′-double bond to a lactone moiety on the porphyrinoid periphery, which represents the direct conversion of a range of *meso*-tetraarylporphyrins to the corresponding porpholactones.

Porpholactones, in which one β,β′-C=C bond is formally replaced by a lactone moiety, are a particular kind porphyrinoids with optical properties and electronic nature between those of porphyrins and chlorins.[3] Their potential applications have been demonstrated in optical materials, biology and catalysis in recent years.[4] Despite the great progress made, looking for an effective and general synthetic approachs still remains a challenge. In 1984, Crossley and King first reported the discovery of a porpholactone from the oxidation of β-aminoporphyrins through several steps as shown in Scheme 1[5].

Then porpholactones appeared as adventitious products in a variety of oxidation reactions of β-derivatized porphyrins. In 2003, Brückner and co-workers utilized the 'breaking and mending' strategy to synthesize porpholactones starting from *meso*-tetrakis-2,3-dihydroxy-2,3-chlorins, which were obtained from the β,β′-dihydroxylation of porphyrins by stoichiometric OsO_4.[6] This provides a way to explore the fundamental chemistry and the applications of porpholactones. However, due to the toxicity of OsO_4 and long reaction time (several days), work to investigate the direct conversion of a porphyrin to a porpholactone in an efficient way is still highly desirable.The serendipitous finding that silver nitrate mediated the oxidation of porphyrin to porpholatone by Gouterman and co-workers,[3a] encouraged us to move from silver salts to gold complexes.[7] Although the efficiency of the reaction is improved, the limited scope of porphyrins and the large amount of gold used retarded the practical applications.

To address this issue, we turned our attention to metal-catalyzed oxidation of alkenes, because porphyrins have a highly delocalized π system and pyr-



Scheme 1. Synthetic routes to porpholactones.

rolic C=C bonds. According to the mechanisms proposed by Brückner and others, β,β′-dihydroxylation of the pyrrolic C=C bond and generation of a dialdehyde are the key steps.[6,8] Previous studies demonstrated, next to OsO_4, that Fe and Ru complexes were efficient to catalyze the dihydroxylation of alkenes and the oxdiative cleavage of C=C bond as shown by Que,[9] Yang[10] and Che[11]. Thus, investigating the reactivity of Ru and Fe catalysts in oxidizing porphyrins to porpholactones is the starting point of our work.

Results and Discussion

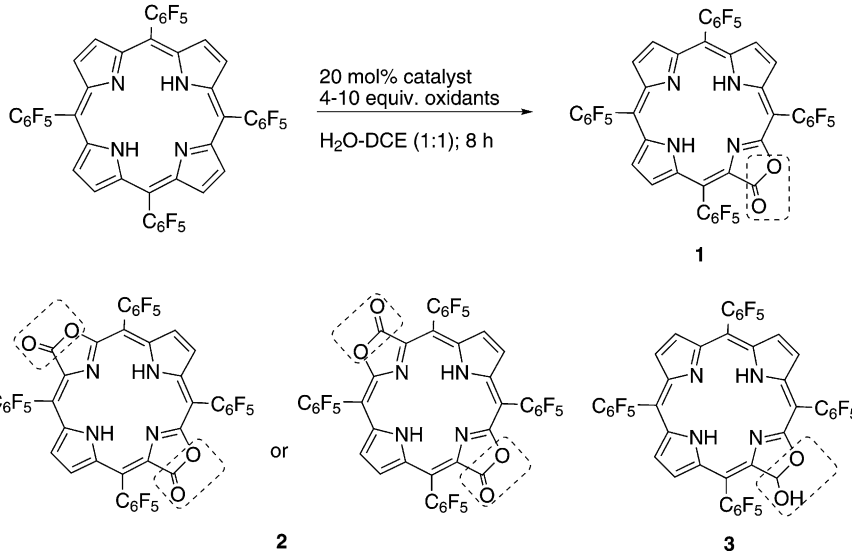
Optimization of Reaction Condtions

We chose *meso*-tetrakis(pentafluorophenyl) porphyrin (F_{20}TPP) as a substrate, and *meso*-tetrakis(pentafluorophenyl) porpholactone **1** (F_{20}TPPL) was obstained in an isolated yield of 20% using Yang's protocol "$RuCl_3$+$NaIO_4$" in mixed solvent of 1,2-dichloroethane and water (1:1) (Table 1, entry 1). Although the conversion of F_{20}TPP is >90%, side products such as porphodilactone **2** (F_{20}TPPDL)[3a] and porpholactol (F_{20}TPPLOH) **3** were isolated in the yields of 15 and 3%, respectively, together with unidentified products. Using Oxone®/$NaHCO_3$ as oxidant could improve the selectivity for F_{20}TPPL (32%) and the yields of F_{20}TPPDL and F_{20}TPPLOH decreased to 4% and 2% (Table 1, entry 2). Other oxidants such as H_2O_2, TBHP and $KMnO_4$ resulted in low conversions (< 5%) (Table 1, entries 3–5). When $FeCl_3$ was used as catalyst or in the absence of $RuCl_3$, the conversion of F_{20}TPP was 30%, but the main product was β-chlorotetrakis(pentafluorophenyl)porphyrin (Table 1, entry 6). It is worthy of note that, in the absence of Fe or Ru catalysts, no conversion of F_{20}TPP was observed (Table 1, entry 7). Thus, the catalyst $RuCl_3$ and the oxidant Oxone®/$NaHCO_3$ were used for further optimization.

We also examined the effect of catalyst loading on the reactivity and selectivity. As shown in Table 2, low catalyst loadings (5–10%, entries 1 and 2) afforded low conversions, although less overoxidation product **2** was obtained. Even with extending the reaction time to 24 h, the conversions of F_{20}TPP did not increase. High catalyst loadings (>50%, entries 3 and 4) resulted the decrease of chemoselectivity. Thus, we chose 20% catalyst loading for further optimization of the reaction conditions.

To improve the chemoselectivity, we employed different ligands to modify the catalytic system and the results are shown in Table 3. When bipyridine was used as a ligand and 20 mol% $RuCl_3$, the conversion of F_{20}TPP was 93% with a yield of 78% for F_{20}TPPL (entry 3), which is higher than with the other ligands such as pyridine, picolinic acid, 1,10-phenanthroline (phen), *N,N,N′N′*-tetramethylethane-1,2-diamine (TMEDA), 2,2′,2″-terpyridine (Terpy) and 2,6-dicarboxypyridine (2,6-Dipic) (Table 3, entries 1, 2 and 4–7). Low conversions were obtained when Terpy and 2,6-Dipic were used as ligands, probably due to the steric

Table 1. Screening for metals and oxidants.[a]



Entry	Catalyst	Oxidant	Conversion [%]	Yield [%][b]
1	$RuCl_3$	$NaIO_4$	93	20[c]
2	$RuCl_3$	Oxone®/$NaHCO_3$	90	32[d]
3	$RuCl_3$	H_2O_2	<5	<5[e]
4	$RuCl_3$	TBHP	<5	<5
5	$RuCl_3$	$KMnO_4$	<5	<5
6	$FeCl_3$	Oxone®/$NaHCO_3$	30	–[f]
7	–	Oxone®/$NaHCO_3$	–	–

[a] *Reaction conditions:* $H_2F_{20}TPP$: 0.04 mmol, catalyst: 0.008 mmol, oxidants 0.16–0.40 mmol at 40 °C.
[b] Isolated yields.
[c] Yield of **2** ($F_{20}TPPDL$) was 15%.
[d] Yields of **2** ($F_{20}TPPDL$) and **3** ($F_{20}TPPLOH$) were 3%.
[e] Yield of **3** ($F_{20}TPPLOH$) was 2%.
[f] β-Monochlorotetrakis(pentafluorophenyl)porphyrin was isolated.

hindance at the pyrrolic rings of porphyrins. Finally, we examined the base effect using sodium carbonate, sodium phosphate, and sodium hydroxide (Table 3, entries 8–10) and found that sodium hydroxide gave a higher yield (85%).

Table 2. Catalyst loading.[a]

Entry	Catalyst Loading [%]	Conversion [%]	Yield [%] of **1**[b]	Yield [%] of **2**[b]
1	5	28	10	–[c]
2	10	60	21	<5
3	20	90	32	<5
4	50	>95	22	11
5	100	>95	18	18

[a] *Reaction conditions:* $H_2F_{20}TPP$: 0.04 mmol, catalyst: as shown in Table 1, oxidant: Oxone®/$NaHCO_3$, for 6 h at 40 °C.
[b] Isolated yields.
[c] Trace of **2** and not isolated.

Table 3. Screening of ligands and bases.[a]

Entry	Ligand	Base	Conversion [%]	Yield [%][b]
1	pyridine	$NaHCO_3$	95	28
2	picolinic acid	$NaHCO_3$	92	57
3	Bipy	$NaHCO_3$	93	78
4	Phen	$NaHCO_3$	86	49
5	TMEDA	$NaHCO_3$	89	40
6	Terpy	$NaHCO_3$	20	8
7	2,6-Dipic	$NaHCO_3$	19	7
8	Bipy	Na_2CO_3	94	81
9	Bipy	Na_3PO_4	95	79
10	Bipy	NaOH[c]	94	85

[a] *Reaction conditions:* $H_2F_{20}TPP$: 0.04 mmol, $RuCl_3$: 0.008 mmol, ligands: 0.008 mmol, Oxone®: 0.2 mmol, base: 0.6 mmol.
[b] Isolated yield.
[c] NaOH: 0.2 mmol, reaction temperature 60 °C.

Substrate Scope

To evaluate the generality of our Ru-based catalytic system in the oxidation of the porphyrin β,β′-pyrrolic ring, a series of porphyrins with substituents, varied for different electronic effects, steric effects and biocompabiltiy, were examined. As shown in Figure 1, when the 4-position was substituted, the isolated yields of porphyrins increased along with decreasing electron-donating ability of substituents (4-CF_3 > 4-F > 4-Cl > 4-H > 4-OMe). For 4-H and 4-OMe substituents, complete conversion of the corresponding porphyrins needed heating to reflux and lower yields were observed than those with electron-withdrawing substituents. This electronic effect was similar to that previously reported for the Ru-catalyzed dihydroxylation system, in which the substrates with electron-withdrawing groups gave higher yields than those with electron-donating groups.[12]

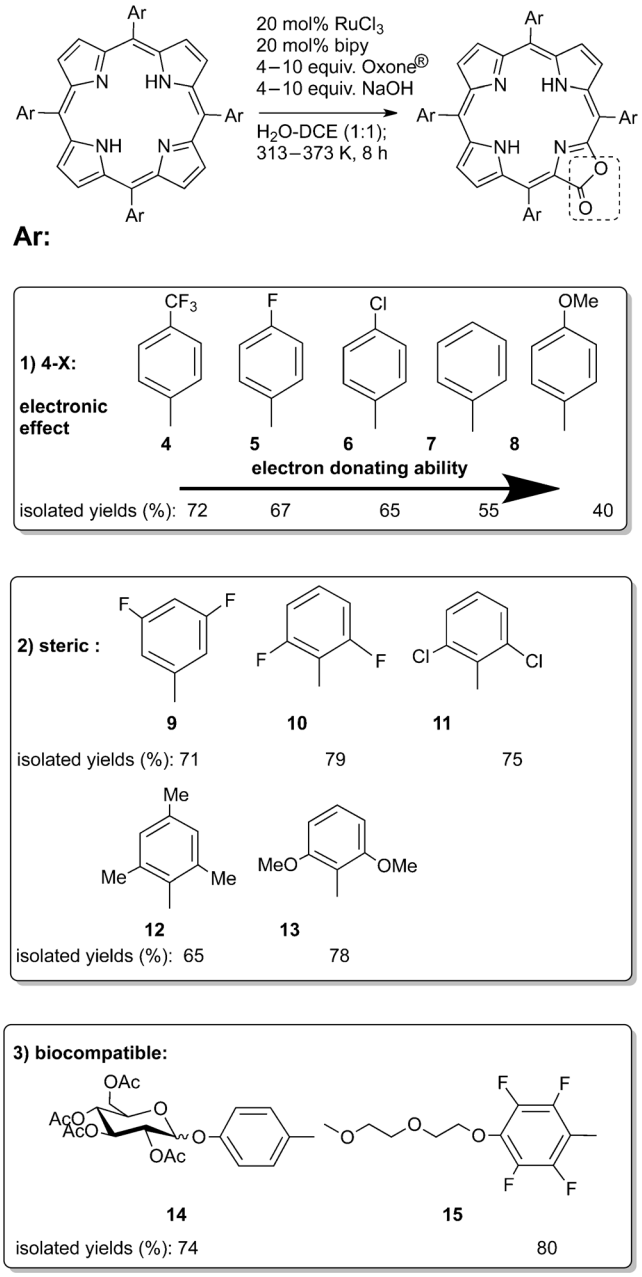


Figure 1. Scope of porphyrins that can be used in the Ru-catalyzed oxidation of the β,β′-pyrrolic ring.

The steric effect was investigated by using 3,5-F_2, 2,6-F_2, 2,6-Cl_2, 2,4,6-Me_3 and 2,6-di-MeO (**9**–**13**) substituted porphyrins and the isolated yields from 65–79% were obtained. There is no appreciable distinction between different steric effects of *meso*-phenyl, which are perpendicular to the tetrapyrrole planar ring. Although containing an electron-donating MeO group, porphyin **13** exhibits higher reactivity than porphyrin **8**, indicating that the substituent's position is also important to affect the reactivity. Most importantly, this investigation has demonstrated that the oxidation protocol can be applied to porphyrins with varied substituents and be scaled up to 400 mg with only slightly decreased yield.

We also applied this protocol to synthesize porpholactones with biocompatible groups such as glycosyl (**14**) and PEG (**15**), which are important to extend the applications in biological studies. As shown in Figure 1, the corresponding porpholactones can be obtained in yields of 74 and 80%, respectively, after a preparative HPLC purification. It is worthy of note that these reactions were carried out in pure water, and the yields were higher than or comparable to those of the analogous porphyrin **8** or F_{20}TPP.

Metalloporphyrins also proved susceptible to the oxidation conditions, providing metalloporpholactones. We used MF_{20}TPP (M = Ni, Cu, Zn, Pd, Pt and Au) as substrates. As shown in Figure 2, the transition metals such as Ni, Cu, Zn and Pd afforded high yields (78–85%) of the corresponding metalloporpholactones and no demetallation was observed. However, oxidation of PtF_{20}TPP gave a 30% yield of PtF_{20}TPPL and a 46% yield of free base porpholactones. For [AuF_{20}TPP]Cl, no gold(III) porpholactone was detected. We hypothesized that low conversion of Au and Pt porphyrins might be due to decreasing chelating ability for the replacement of pyrrole by the lactone moiety. To confirm this, we used a free base porpholactone ligand with $AuCl_3$ according to the previous procedure,[7] and no gold(III) porpholactone was obtained. These results suggested that the Ru-based catalytic system could be extended to the synthesis of metallophopholactones with 1st and 2nd row transition metals.

Mechanistic Considerations

To understand the mechanism, we isolated the intermediate under the optimized reaction conditions after 2 h, using F_{20}TPP as a substrate. Other than porphodi-

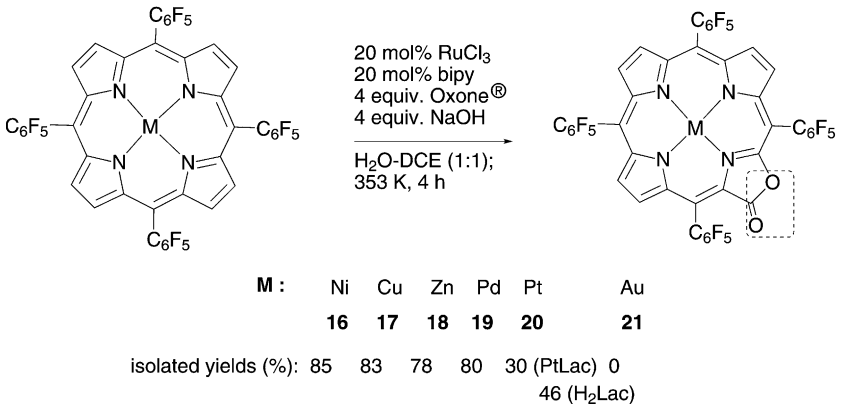


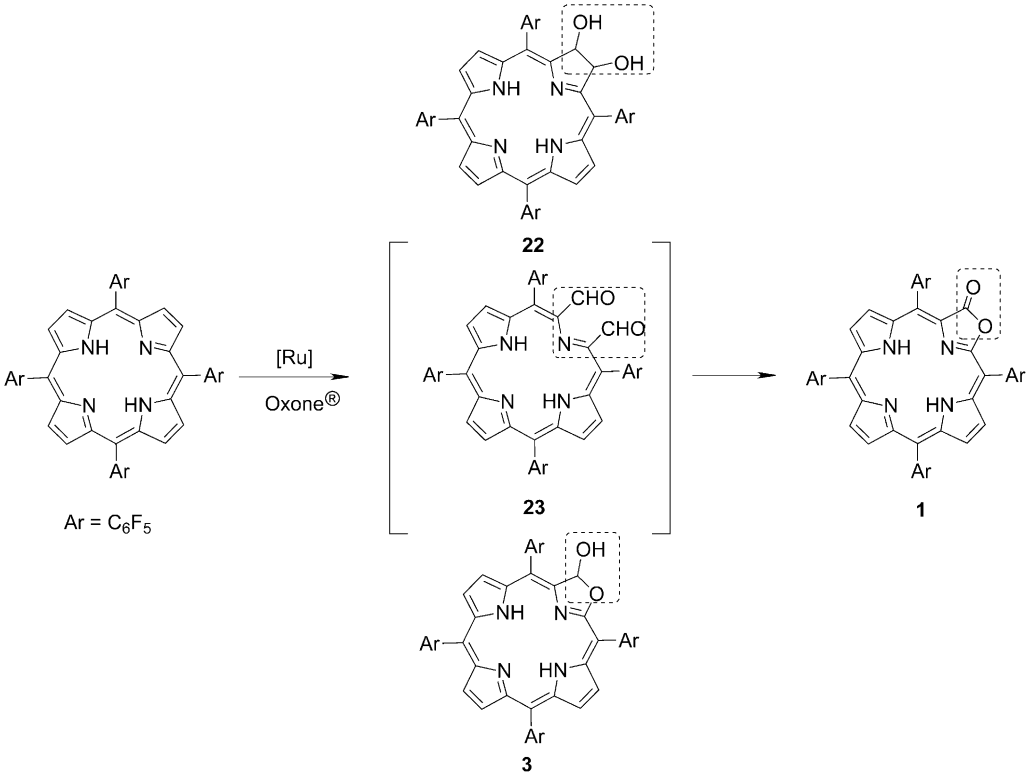
Figure 2. Ru-catalyzed the formation of metalloporpholactones.

lactone (F_{20}TPPDL) and porpholactol (F_{20}TPPLOH), small amounts of *meso*-dihydroxylchlorin **22** and secochlorin bisaldehyde **23** were isolated as shown in Scheme 2. According to the mechanisms proposed by Brückner, we assumed that the conversion of porphyrin to porpholactone *via* dihydroxylation, double bond cleavage and "mending", catalyzed by Ru complexes. The different oxidative porphyrinoid products obtained using Os and Ru catalysts is due to the different reactivity of these metal catalysts.

The Ru-catalyzed epoxidation or cleavage of alkenes and the related mechanism based on the reactivity of RuO_4 have been well studied by Griffth and co-workers more than 40 years ago.[13] Yang and co-workers reported that "$RuCl_3$ + Oxone® or $NaIO_4$" protocol was efficient to catalyze oxidative cleavage of the C=C bond. Thus, high-valent ruthenium oxo complexes generated in our catalytic system were the plausible active intermediates.

Conclusions

Taken together, we have reported an effective synthetic method to porpholactones catalyzed by a Ru-based oxidation system. Thanks to the elegant mechanistic studies on the formation of porpholactones by Brückner, this is the first report to employ high-valent ruthenium chemistry in the synthesis of porphyrinoids, which provides an example for the con-



Scheme 2. Proposed reaction pathway for the Ru-catalyzed oxidation of porphyrins.

cept of "marriage of porphyrin chemistry with metal-catalyzed reactions". More importantly, the generality of this protocol to oxidize various porphyrins with different electronic and steric effects and even some metalloporphyrins to the corresponding porpholactone derivatives is useful for further applications and transformations of porpholactones.

Experimental Section

General Information

Dichloroethane (A.R. Grade) was used without further purification. Commercially available reagents were used without further purification. Deuterium solvents were stored with 4 Å molecular sieves. UV/Vis spectra were recorded on an Agilent 8453 UV/Vis spectrometer equipped with a Agilent 89090 A thermostat (±0.1 °C). IR spectra were recorded on a Bruker VECTOR22 FT-IR spectrometer as KBr pellets. ESI-MS were recorded on a Bruker APEX IV Fourier Transform Ion Cyclotron Resonance Mass Spectrometer using electrospray ionization. ^{1}H and ^{19}F NMR spectra were recorded on a Bruker-400 MHz NMR spectrometer. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), all coupling constants are in Hz and measured relative to the signal for residual chloroform (7.26 ppm) in the deuterated solvent. For ^{19}F NMR spectra, $CFCl_3$ was used as the internal reference at 0 ppm.

General Procedure of the Synthesis of Porpholactones and Metalloporpholactones

To a stirred mixture of porphyrins/metalloporphyrins (0.02 mmol) and $RuCl_3$ (0.85 mg, 0.004 mmol) stock solutions in 1,2-dichloroethane (50 mL) and water (5 mL), respectively, a DCE solution (5 mL) of 2,2′-bipyridine (0.62 mg, 0.004 mmol) was added. The solution was heated to a certain temperature, then the mixture of Oxone (0.08–0.20 mmol) and NaOH (0.08–0.20 mmol) was added in 5 portions over a period of 4–8 h. The reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$, then the organic layer was separated and the aqueous layer was extracted by dichloromethane twice. The combined organic layer was dried by Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified through a silica column to give the product porpholactones.

5,10,15,20-Tetra(pentafluorophenyl)porpholactone (1): Following the general procedure with heating at 40 °C for 6 h, addition of 0.10 mmol Oxone® and 0.10 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.87 (m, 4H), 8.67 (d, J = 4.7 Hz, 1H), 8.59 (d, J = 4.7 Hz, 1H), −1.79 (s, 1H), −2.09 (s, 1H); ^{19}F NMR (471 MHz, $CDCl_3$): δ = −137.00–−137.33 (m, 4F), −137.53 (dd, J = 22.9, 7.3 Hz, 2F), −138.99 (dd, J = 23.2, 7.4 Hz, 2F), −150.87–−151.04 (m, 3F), −151.67 (t, J = 20.8 Hz, 1F), −161.11–−161.39 (m, 6F), −161.90 (td, J = 22.4, 7.1 Hz, 2F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 409 (5.18), 510 (3.95), 545 (3.81), 589 (3.60), 642 nm (4.03); fluorescence (CH_2Cl_2): λ_{max} = 643 nm, 710, ϕ = 0.13; IR: ν = 926, 991, 1502, 1517, 1774 (C=O), 1792 (C=O), 3341 cm^{-1}; ESI-MS: m/z = 993.04023, calcd. for $C_{43}H_9F_{20}N_4O_2$ $[M+H]^+$:993.04007.

5,10,15,20-Tetra(4-trifluoromethylphenyl)porphlactone (4): Following the general procedure with heating at 90 °C for 8 h, addition of 0.16 mmol Oxone® and 0.16 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (s, 2H), 8.67 (s, 1H), 8.54 (s, 2H), 8.48 (d, J = 4.2 Hz, 1H), 8.24 (m, 6H), 8.12–7.98 (m, 10H), −1.72 (s, 1H), −2.07 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −66.03–−67.32 (m, 12F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 417 (5.44), 518 (4.11), 556 (4.07), 589 (3.82), 641 nm (3.69); fluorescence (CH_2Cl_2): λ_{max} = 643, 710 nm, ϕ = 0.05; IR: ν = 802, 1020, 1069, 1109, 1128, 1171, 1323, 1616, 1784 (C=O), 3334 cm^{-1}; ESI-MS: m/z905.17860, calcd. for $C_{47}H_{25}F_{12}N_4O_2$ $[M+H]^+$: 905.17804.

5,10,15,20-Tetra(4-fluorophenyl)porpholactone (5): Following the general procedure with heating at 90 °C for 8 h, addition of 0.16 mmol Oxone® and 0.16 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77 (dd, J = 18.0, 8.3 Hz, 2H), 8.70 (d, J = 4.4 Hz, 1H), 8.58 (d, J = 3.6 Hz, 2H), 8.51 (d, J = 4.2 Hz, 1H), 8.08–8.03 (m, 6H), 7.91 (t, J = 6.0 Hz, 2H), 7.47–7.41 (m, 4H), −1.73 (s, 1H), −2.10 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −118.27–−118.57 (m, 4F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 417 (5.46), 519 (4.11), 557 (4.10), 589 (3.88), 641 nm (3.60); fluorescence (CH_2Cl_2): λ_{max} = 645, 710 nm, ϕ = 0.04; IR: ν = 797, 849, 1157, 1234, 1504, 1784 (C=O), 3331 cm^{-1}; ESI-MS: m/z = 705.19052, calcd. for $C_{43}H_{25}F_4N_4O_2$ $[M+H]^+$:705.19082.

5,10,15,20-Tetra(4-chlorophenyl)porpholactone (6); Following the general procedure with heating at 90 °C for 8 h, addition of 0.16 mmol Oxone® and 0.16 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83–8.74 (m, 2H), 8.70 (dd, J = 4.8, 1.7 Hz, 1H), 8.58 (t, J = 4.1 Hz, 2H), 8.52 (d, J = 4.7 Hz, 1H), 8.08–7.99 (m, 6H), 7.88 (d, J = 8.3 Hz, 2H), 7.75–7.70 (m, 8H), −1.76 (s, 1H), −2.12 (s, 1H); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 419 (5.52), 521 (4.15), 558 (4.17), 589 (3.92), 641 nm (3.64); fluorescence (CH_2Cl_2): λ_{max} = 644, 709 nm, ϕ = 0.03; IR: ν = 719, 798, 970, 1015, 1088, 1483, 1769, 3340 cm^{-1}; ESI-MS: m/z = 769.07148, calcd. for $C_{43}H_{25}C_{l4}N_4O_2$ $[M+H]^+$: 769.07261.

5,10,15,20-Tetraphenylporpholactone (7): Following the general procedure with heating at 100 °C for 8 h, addition of 0.20 mmol Oxone® and 0.20 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (ddd, J = 12.5, 5.0, 1.6 Hz, 2H), 8.62 (dd, J = 4.8, 1.7 Hz, 1H), 8.54–8.47 (m, 2H), 8.45 (d, J = 4.6 Hz, 1H), 8.10–7.98 (m, 6H), 7.89 (dd, J = 7.3, 1.8 Hz, 2H), 7.74–7.60 (m, 12H), −1.75 (s, 1H), −2.12 (s, 1H); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 418 (5.51), 520 (4.15), 558 (4.17), 589 (3.93), 641 nm (3.59); fluorescence (CH_2Cl_2): λ_{max} = 644, 709 nm, ϕ = 0.04; IR: ν = 704, 797, 970, 1445, 1764 (C=O), 3334 cm^{-1}; ESI-MS; m/z = 633.22847, calcd. for $C_{43}H_{29}N_4O_2$ $[M+H]^+$: 633.22850.

5,10,15,20-Tetra(4-methoxylphenyl)porpholactone (8): Following the general procedure with heating at 110 °C for 10 h, addition of 0.20 mmol Oxone® and 0.20 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.79–8.76 (m, *2*H), 8.71 (s, 1H), 8.63–8.59, 8.56 (d, J = 4.4 Hz, 1H), 8.06–8.01 (m, 6H), 7.89 (d, J = 8.3 Hz, 2H), 7.33–7.25(m, 8H), 4.07 (d, J = 10.7 Hz, 12H), −1.66 (s, 1H), −2.04 (s, 1H); UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) = 425 (4.78), 527 (3.37), 566 (3.48), 592 (3.30), 643 (2.63); fluorescence (CH_2Cl_2) λ_{max}, nm 647, 715, ϕ = 0.04; IR: ν = 802, 1033, 1176, 1250, 1291, 1509, 1607, 1762 (C=O), 1774 (C=O), 2834, 2851, 2927, 2955, 3342 cm^{-1}; ESI-MS: m/z = 753.27141, calcd. for $C_{47}H_{37}N_4O_6$ $[M+H]^+$: 753.27076.

5,10,15,20-Tetra(3,5-difluorophenyl)porpholactone (9): Following the general procedure with heating at 90 °C for 6 h, addition of 0.12 mmol Oxone® and 0.12 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, J = 6.7 Hz, 2H), 8.78 (d, J = 4.5 Hz, 1H), 8.65 (dd, J = 11.5, 4.3 Hz, 2H), 8.57 (d, J = 4.0 Hz, 1H), 7.69 (s, 4H), 7.63 (d, J = 6.2 Hz, 2H), 7.49 (d, J = 5.9 Hz, 2H), 7.35–7.16 (m, 4H), −1.84 (s, 1H), −2.19 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −114.80 (t, J = 7.9 Hz, 2F), −115.10–−115.22 (m, 4F), −115.32 (t, J = 7.9 Hz, 2F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 415 (5.47), 516 (4.21), 552 nm (4.16); fluorescence (CH_2Cl_2): λ_{max} = 643, 710 nm, ϕ = 0.06; IR: ν = 715, 790, 843, 868, 931, 988, 1120, 1321, 1362, 1430, 1591, 1620, 1762 (C=O), 1781 (C=O), 3329 cm^{-1}; ESI-MS: m/z = 777.15262, calcd. for $C_{43}H_{21}F_8N_4O_2$ $[M+H]^+$: 777.15313.

5,10,15,20-tetra(2,6-difluorophenyl)porpholactone (10): Following the general procedure with heating at 80 °C for 6 h, addition of 0.12 mmol Oxone® and 0.12 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.82 (d, J = 4.4 Hz, 1H), 8.78 (t, J = 4.8 Hz, 2H), 8.72 (d, J = 4.4 Hz, 1H), 8.63 (d, J = 4.3 Hz, 1H), 8.55 (d, J = 4.1 Hz, 1H), 7.81- 7.70 (m, 4H), 7.35 (dd, J = 14.3, 7.0 Hz, 8H), −1.67 (s, 1H), −2.00 (s, 1H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −109.05 (dt, J = 23.6, 6.3 Hz, 4F), −109.75 (t, J = 6.5 Hz, 2F), −111.04 (t, J = 6.4 Hz, 2F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 412 (5.44), 511 (4.16), 548 (4.04), 587 (3.83), 641 nm (4.06); fluorescence (CH_2Cl_2): λ_{max} = 643, 711 nm, ϕ = 0.09; IR: ν = 713, 784, 800, 963, 1004, 1236, 1465, 1623, 1772 (C=O), 1788 (C=O), 3344 cm^{-1}; ESI-MS: m/z = 777.15145, calcd. for $C_{43}H_{21}F_8N_4O_2$ $[M+H]^+$: 777.15313.

5,10,15,20-Tetra(2,6-dichlorophenyl)porpholactone (11); Following the general procedure with heating at 80 °C for 6 h, addition of 0.12 mmol Oxone® and 0.12 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, J = 4.8 Hz, 1H), 8.58 (dd, J = 9.2, 4.7 Hz, 2H), 8.51 (d, J = 4.6 Hz, 1H), 8.46 (d, J = 4.6 Hz, 1H), 8.37 (d, J = 4.5 Hz, 1H), 7.77 (t, J = 8.0 Hz, 8H), 7.73–7.63 (m, 4H), −1.51 (s, 1H), −1.85 (s, 1H); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 416 (5.34), 516 (4.05), 553 (3.89), 590 (3.70), 641 nm (3.82); fluorescence (CH_2Cl_2): λ_{max} = 646, 711 nm, ϕ = 0.01; IR: ν = 709, 717, 778, 803, 965, 978, 1192, 1428, 1559, 1776 (C=O), 1787 (C=O), 3339 cm^{-1}; ESI-MS: m/z = 904.91609, calcd. for $C_{43}H_{21}Cl_8N_4O_2$ $[M+H]^+$: 904.91672.

5,10,15,20-Tetramesitylporpholactone (12); Following the general procedure with heating at 80 °C for 6 h, addition of 0.12 mmol Oxone® and 0.12 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (d, J = 4.7 Hz, 1H), 8.51 (d, J = 4.4 Hz, 1H), 8.46 (d, J = 4.8 Hz, 1H), 8.41 (dd, J = 9.5, 4.5 Hz, 2H), 8.33 (d, J = 4.5 Hz, 1H), 7.24 (s, 8H), 2.60 (s, 6H), 2.57 (d, J = 3.7 Hz, 6H), 1.91 (s, 6H), 1.86 (d, J = 4.1 Hz, 12H), 1.83 (s, 6H), −1.48 (s, 1H), −1.86 (s, 1H); UV-vis (CH_2Cl_2): λ_{max}, (log ε) = 417 (5.48), 519 (4.12), 556 (4.12), 588 (3.90), 642 nm (3.66); fluorescence (CH_2Cl_2): λ_{max} = 642, 708 nm, ϕ = 0.06; IR: ν = 725, 803, 971, 1036, 1076, 1116, 1203, 1221, 1273, 1369, 1451, 1559, 1612, 1653, 1731 (C=O), 1771 (C=O), 2856, 2920, 3338 cm^{-1}; ESI-MS: m/z = 801.41578, calcd. for $C_{55}H_{53}N_4O_2$ $[M+H]^+$: 801.41630.

5,10,15,20-Tetra(2,6-dimethoxylphenyl)porpholactone (13): Following the general procedure with heating at 80 °C for 5 h, addition of 0.12 mmol Oxone® and 0.12 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (d, J = 4.9 Hz, 1H), 8.55–8.48 (m, 3H), 8.45 (d, J = 4.5 Hz, 1H), 8.36 (d, J = 4.5 Hz, 1H), 7.65 (t, J = 8.8 Hz, 4H), 6.94 (dd, J = 8.7, 4.7 Hz, 8H), 3.59 (s, 6H), 3.55 (s, 6H), 3.51 (d, J = 3.7 Hz, 12H), −1.49 (s, 1H), −1.86 (s, 1H). UV-vis (CH_2Cl_2): λ_{max} (log ε) = 419 (5.19), 518 (3.84), 554 (3.76), 588 (3.59), 642 nm (3.44); fluorescence (CH_2Cl_2): λ_{max} = 644, 710 nm, ϕ = 0.15; IR: ν = 724, 794, 961, 982, 1033, 1072, 1111, 1249, 1286, 1431, 1472, 1588, 1732 (C=O), 1767 (C=O), 2854, 2926, 2956, 3337 cm^{-1}; ESI-MS: m/z = 873.31153, calcd. for $C_{51}H_{45}N_4O_{10}$ $[M+H]^+$: 873.31302.

5,10,15,20-Tetra(4-glucosylphenyl)porpholactone (14): Following the general procedure with heating at 90 °C for 6 h, addition of 0.12 mmol Oxone® and 0.12 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, J = 4.8 Hz, 1H), 8.77 (d, J = 4.9 Hz, 1H), 8.71 (d, J = 4.8 Hz, 1H), 8.63–8.56 (m, 2H), 8.53 (d, J = 4.3 Hz, 1H), 8.05–8.01 (m, 6H), 7.92–7.86 (m, 2H), 7.37 (d, J = 7.8 Hz, 8H), 5.51–5.38 (m, 12H), 5.30 (dd, J = 13.1, 8.9 Hz, 4H), 4.45–4.37 (m, 4H), 4.36–4.23 (m, 4H), 4.11–3.94 (m, 4H), 2.20 (s, 12H), 2.15–2.07 (m, 36H), −1.73 (s, 1H), −2.09 (s, 1H); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 420 (5.78), 516 (4.35), 552 (4.10), 592 (3.85), 647 nm (3.79); fluorescence (CH_2Cl_2): λ_{max} = 644, 714 nm, ϕ = 0.05; IR: ν = 801, 963, 982, 1038, 1068, 1179, 1229, 1373, 1456, 1508, 1607, 1750, 2855, 2924, 2955, 3342 cm^{-1}; ESI-MS: m/z = 2017.58773, calcd. for $C_{99}H_{101}N_4O_{42}$ $[M+H]^+$: 2017.58849.

5,10,15,20-Tetra{4-[2-(2-methoxyethoxy)ethoxy]phenyl}-porpholactone (15): Following the general procedure with heating at 80 °C for 4 h, addition of 0.08 mmol Oxone® and 0.08 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (d, J = 4.5 Hz, 1H), 8.86 (d, J = 3.4 Hz, 2H), 8.88–8.84 (m, 2H), 8.68 (d, J = 4.1 Hz, 1H), 8.60 (d, J = 3.8 Hz, 1H), 4.79–4.66 (m, 8H), 4.08–4.01(m, 8H), 3.88–3.81 (m, 8H), 3.71–6.33 (m, 8H), 3.52–3.39 (m, 12H), −1.80 (s, 1H), −2.10 (s, 1H); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 408 (5.30), 510 (4.03), 546 (3.90), 587 (3.74), 641 nm (3.98); fluorescence (CH_2Cl_2): λ_{max} = 644, 710 nm, ϕ = 0.11; IR: 708, 755, 805, 853, 928, 982, 1067, 1109, 1140, 1248, 1356, 1374, 1397, 1430, 1492, 1501, 1651, 1771 (C=O), 2855, 2879, 2897, 2923, 3336 cm^{-1}; ESI-MS: m/z = 1393.32772, calcd. for $C_{63}H_{53}F_{16}N_4O_{14}$ $[M+H]^+$: 1393.32973.

[5,10,15,20-Tetra(pentafluorophenyl)porpholactone]-nickel(II) (16): Following the general procedure with heating at 80 °C for 4 h, addition of 0.08 mmol Oxone® and 0.08 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 12.7 Hz, 4H), 8.50 (d, J = 12.7 Hz,4H); ^{19}F NMR (282 MHz, $CDCl_3$): δ = −136.92–−137.85 (m, 6F), −138.78 (dd, J = 22.6, 6.7 Hz, 2F), −150.94 (dt, J = 42.6, 21.2 Hz, 3F), −151.68 (t, J = 20.9 Hz, 1F), −160.80–−161.41 (m, 6F), −161.84 (td, J = 21.7, 6.6 Hz, 2F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 404 (5.04), 549 (3.81), 592 nm (4.49); IR: ν = 767, 808, 881, 941, 953, 993, 1022, 1064, 1081, 1258, 1303, 1352, 1433, 1498, 1516, 1729 (C=O), 1761 (C=O), 1773 (C=O), 1782 cm^{-1} (C=O); ESI-MS: m/z = 1048.96022, calcd. for $C_{43}H_7F_{20}N_4NiO_2$ $[M+H]^+$: 1048.95976.

[5,10,15,20-Tetra(pentafluorophenyl)porpholactone]copper(II) (17): Following the general procedure with heating at 80 °C for 4 h, addition of 0.08 mmol Oxone® and 0.08 mmol NaOH. UV-vis (CH_2Cl_2): λ_{max} (log ε) = 383 (4.70), 410 (5.44), 556 (4.06), 599 nm (4.65); IR: ν = 769, 878, 939, 951, 988, 1018, 1057, 1078, 1293, 1325, 1347, 1364, 1457, 1493, 1519, 1561, 1755 (C=O), 1783 (C=O), 1805 cm^{-1} (C=

O); ESI-MS: $m/z = 1053.95328$, calcd. for $C_{43}H_7CuF_{20}N_4O_2$ $[M+H]^+$: 1053.95402,.

[5,10,15,20-Tetra(pentafluorophenyl)porpholactone]-zinc(II) (18): Following the general procedure with heating at 80 °C for 4 h, addition of 0.08 mmol Oxone® and 0.08 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.77$ (d, $J = 4.7$ Hz, 1H), 8.74–8.68 (m, 3H), 8.67–8.60 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -137.46$–-138.00 (m, 6F), −139.24 (dd, $J = 23.6$, 7.4 Hz, 2F), −151.29–−152.23 (m, 3F), −152.56 (t, $J = 21.0$ Hz, 1F), −161.60–−162.01 (m, 6F), −162.48 (td, $J = 23.5$, 8.0 Hz, 2F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 393 (4.52), 417 (5.24), 542 (3.59), 561 (3.87), 606 nm (4.40); fluorescence (CH_2Cl_2): $\lambda_{max} = 608$, 644 nm, $\phi = 0.03$; IR: ν = 764, 878, 940, 952, 989, 1017, 1060, 1078, 1294, 1325, 1346, 1365, 1433, 1454, 1494, 1516, 1559, 1755 (C=O), 1784 (C=O), 1804 cm^{-1} (C=O); ESI-MS: $m/z = 1054.95526$, calcd. for $C_{43}H_7F_{20}N_4O_2Zn$ $[M+H]^+$: 1054.95356.

[5,10,15,20-Tetra(pentafluorophenyl)porpholactone]palladium(II) (19): Following the general procedure with heating at 80 °C for 4 h, addition of 0.08 mmol Oxone® and 0.08 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.76$–8.73 (m, 4H), 8.68 (s, 4H); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta =$ −136.58–−138.08 (m, 6F), −138.74 (dd, $J = 22.9$, 7.0 Hz, 2F), −150.30–−151.22 (m, 3F), −151.48 (t, $J = 21.0$ Hz, 1F), −160.29–−161.48 (m, 6F), −161.79 (td, $J = 22.0$, 6.8 Hz, 2F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 378 (4.70), 407 (5.24), 542 (4.09), 555(3.89), 583 nm (4.77); fluorescence (CH_2Cl_2, degassed): $\lambda_{max} = 764$; IR: ν = 670, 891, 926, 943, 961, 991, 1024, 1067, 1080, 1304, 1332, 1360, 1435, 1458, 1496, 1521, 1559, 1774 (C=O), 1790 cm^{-1} (C=O); ESI-MS: $m/z = 1095.92062$, calcd. for $C_{43}H_6F_{20}N_4O_2Pd$ $[M+H]^+$: 1095.92159.

[5,10,15,20- Tetra(pentafluorophenyl)porpholactone]platinum(II) (20): Following the general procedure with heating at 80 °C for 4 h, addition of 0.08 mmol Oxone® and 0.08 mmol NaOH. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.77$–8.65 (m, 6H); ^{19}F NMR (282 MHz, $CDCl_3$): $\delta = -136.50$–−137.70 (m, 6F), −138.66 (dd, $J = 23.6$, 9.5 Hz, 2F), −150.29–−150.99 (m, 3F), −151.29 (t, $J = 20.7$ Hz, 1F), −160.64–−161.29 (m, 6F), −161.44–−161.89 (m, 2F); UV-vis (CH_2Cl_2): λ_{max} (log ε) = 392 (5.32), 533 (4.21), 547 (4.17), 573 nm (4.88); fluorescence (CH_2Cl_2, degassed): $\lambda_{max} =$ 741 nm; IR: ν = 768, 899, 930, 948, 964, 993, 1027, 1069, 1085, 1326, 1339, 1365, 1436, 1462, 1496, 1520, 1567, 1770 (C=O), 1780 cm^{-1} (C=O); ESI-MS: $m/z = 1184.98478$, calcd. for $C_{43}H_6F_{20}N_4O_2Pt$ $[M+H]^+$: 1184.98170.

Acknowledgements

This project was supported by the National Scientific Foundation of China (grant no.20971007) and National Key Basic Research Support Foundation of China (NKBRSFC) (2010CB912302). Y. H. thanks National Funding for Fostering Talents of Basic Sciences (J0630421).

References

[1] a) J. L. Sessler, A. Gebauer, S. J. Weghorn, in: *The Porphyrin Handbook*, Vol. 2, (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, pp 55–124; b) T. D. Lash, in: *The Porphyrin Handbook*, Vol. 2, (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, pp 125–200; c) J. Mack, M. J. Stillman, N. Kobayashi, *Coord. Chem. Rev.* **2007**, *251*, 429–453; d) H. J. Xu, J. Mack, A. B. Descalzo, Z. Shen, N. Kobayashi, X. Z. You, K. Rurack, *Chem. Eur. J.* **2011**, *17*, 8965–8983.

[2] a) M. V. Martinez-Diaz, M. Quintiliani, T. Torres, *Synlett* **2008**, 1–20; b) H. Shinokubo, A. Osuka, *Chem. Commun.* **2009**, 1011–1021.

[3] a) M. Gouterman, R. J. Hall, G. E. Khalil, P. C. Martin, E. G. Shankland, R. L. Cerny, *J. Am. Chem. Soc.* **1989**, *111*, 3702–3707; b) K. Jayaraj, A. Gold, R. N. Austin, L. M. Ball, J. Terner, D. Mandon, R. Weiss, J. Fischer, A. DeCian, E. Bill, M. Muther, V. Schunemann, A. X. Trautwein, *Inorg. Chem.* **1997**, *36*, 4555–4566.

[4] a) B. Zelelow, G. E. Khalil, G. Phelan, B. Carlson, M. Gouterman, J. B. Callis, L. R. Dalton, *Sensor Actuat. B: Chem.* **2003**, *96*, 304–314; b) G. E. Khalil, C. Costin, J. Crafton, G. Jones, S. Grenoble, M. Gouterman, J. B. Callis, L. R. Dalton, *Sensor Actuat. B: Chem.* **2004**, *97*, 13–21; c) M. Gouterman, J. Callis, L. Dalton, G. Khalil, Y. Mebarki, K. R. Cooper, M. Grenier, *Meas. Sci. Technol.* **2004**, *15*, 1986–1994; d) M. J. M. Perez Jr, C. Brückner, R. Weissleder, *Nano. Lett.* **2005**, *5*, 2552–2556; e) A. Cetin, C. J. Ziegler, *Dalton Trans.* **2005**, 25–26; f) W. Waskitoaji, T. Hyakutake, J. Kato, M. Watanabe, H. Nishide, *Chem. Lett.* **2009**, *38*, 1164–1165; g) R. Rahimi, A. A. Tehrani, M. A. Fard, B. M. M. Sadegh, H. R. Khavasi, *Catal. Commun.* **2009**, *11*, 232–235; h) G. E. Khalil, P. Daddario, K. S. F. Lau, S. Imtiaz, M. King, M. Gouterman, A. Sidelev, N. Puran, M. Ghandehari, C. Brückner, *Analyst* **2010**, *135*, 2125–2131; i) J. Akhigbe, J. Haskoor, M. Zeller, C. Brückner, *Chem. Commun.* **2011**, *47*, 8599–8601; j) J. Ogikubo, C. Brückner, *Org. Lett.* **2011**, *13*, 2380–2383; k) L. Liang, H. B. Lv, Y. Yu, P. Wang, J. L. Zhang, *Dalton Trans.* **2012**, *41*, 1457–1460; l) J. Ogikubo, E. Meehan, J. T. Engle, C. J. Ziegler, C. Brückner, *J. Org. Chem.* **2012**, *77*, 6199–6207.

[5] M. J. Crossley, L. G. King, *J. Chem. Soc. Chem. Commun.* **1984**, 920–922.

[6] J. R. McCarthy, H. A. Jenkins, C. Brückner, *Org. Lett.* **2003**, *5*, 19–22.

[7] H. B. Lv, B. Y. Yang, J. Jing, Y. Yu, J. Zhang, J. L. Zhang, *Dalton Trans.* **2012**, *41*, 3116–3118.

[8] J. Akhigbe, C. Ryppa, M. Zeller, C. Brückner, *J. Org. Chem.* **2009**, *74*, 4927–4933.

[9] M. Costas, A. K. Tipton, K. Chen, D. H. Jo, L. Que, *J. Am. Chem. Soc.* **2001**, *123*, 6722–6723.

[10] D. Yang, C. Zhang, *J. Org. Chem.* **2001**, *66*, 4814–4818.

[11] a) W. P. Yip, W. Y. Yu, N. Y. Zhu, C. M. Che, *J. Am. Chem. Soc.* **2005**, *127*, 14239–14249; b) C. M. H. W. P. Yip, N. Y. Zhu, T. C. Lau, C. M. Che, *Chem. Asian J.* **2008**, *3*, 70–77; c) T. W. S. Chow, E. L. M. Wong, Z. Guo, Y. G. Liu, J. S. Huang, C. M. Che, *J. Am. Chem. Soc.* **2010**, *132*, 13229–13239; d) G. Q. Chen, Z. J. Xu, C. Y. Zhou, C. M. Che, *Chem. Commun.* **2011**, *47*, 10963–10965.

[12] T. K. M. Shing, E. K. W. Tam, V. W. F. Tai, I. H. F. Chung, Q. Jiang, *Chem. Eur. J.* **1996**, *2*, 50–57.

[13] W. P. Griffith, *Chem. Soc. Rev.* **1992**, *21*, 179–185.

