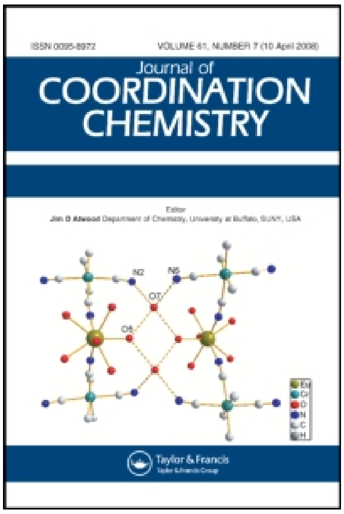

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Synthesis and properties of a series of porphyrin-nicacid dyads and their Mn and Zn complexes

Erjun Sun[ab]; Xiuli Cheng[a]; Dong Wang[a]; Changfu Zhuang[a]; Aiqing Xia[a]; Tongshun Shi[a]
[a] College of Chemistry, Jilin University, Changchun, P.R. China [b] Department of Chemistry, Changchun Normal University, Changchun, P.R. China

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Synthesis and properties of a series of porphyrin-nicacid dyads and their Mn and Zn complexes

ERJUN SUN†‡, XIULI CHENG†, DONG WANG†, CHANGFU ZHUANG†,
AIQING XIA† and TONGSHUN SHI*†

†College of Chemistry, Jilin University, Changchun, P.R. China
‡Department of Chemistry, Changchun Normal University, Changchun, P.R. China

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In this article, a series of porphyrin-nicacid dyads and their Mn and Zn complexes were synthesized and characterized by elemental analysis, UV–Vis, IR, MS, and ^{1}H NMR spectroscopies. Fluorescence studies show that for increasing length of alkoxy chains the fluorescence intensity and quantum yield of the porphyrin ligands is $C_2 > C_3 > C_4 > C_5 > C_6 > C_{10}$. Electrochemical results indicate that the length of side chain has little effect on the redox potential.

Keywords: Porphyrin-nicacid dyads; Cyclic voltammetry; Fluorescence

1. Introduction

Nicotinamide and nicotinic acid (nicacid) are two of the most extensively studied pyridine derivatives. The former is a component of the vitamin B complex and of the vital coenzyme NAD (nicotinamide adenine dinucleotide) [1] and is a typical N-donor ligand system in crystal engineering [2]. Nicacid has wide-ranging ability to reduce lipid levels, but its clinical uses are restricted due to various side effects. Moreover, coordination compounds of nicacid, nicotinamide and their derivatives have antiviral or antibacterial activity [3, 4], and selectively affect tumor tissues [5].

Some porphyrins accumulate selectively, induce damage in DNA or tumor tissue [6, 7], and have been used as tumor-targeting agents in photodynamic therapy (PDT) [8, 9]. Their possible medicinal and biological applications have attracted tremendous interest [10–17]. The synthesis of a series of porphyrin-nicacid dyads offers an opportunity to investigate the combination of porphyrin and nicacid as DNA structural probes and mediators of DNA cleavage reactions.

Many porphyrin dyads, for example porphyrin-quinones, porphyrin-C60 and porphyrin-cyclodextrin, mimic electron transfer and energy transfer processes observed in nature. To our knowledge, there are no reports of investigations made of nicacids linked to porphyrins. Therefore, we synthesized a series of new porphyrin-nicacid dyads

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*Corresponding author. Email: sunerjun1974@hotmail.com

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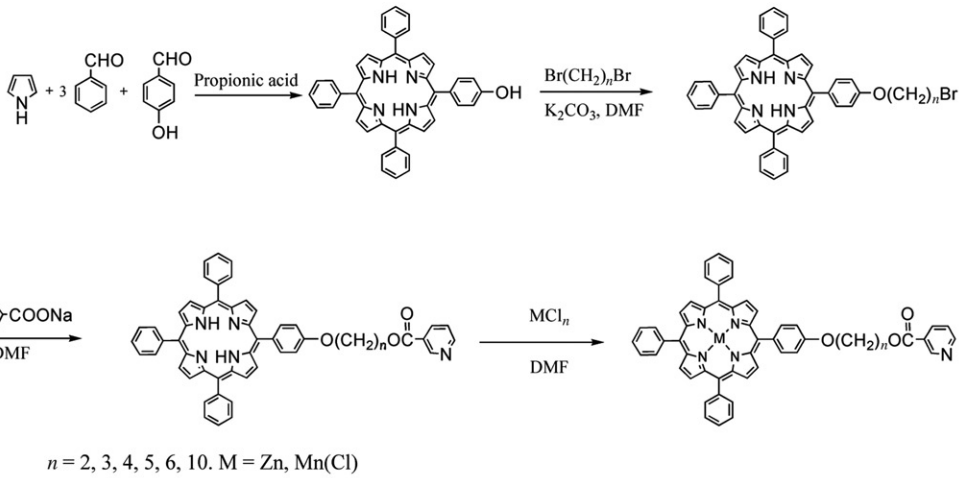

Figure 1. The structures of free-base porphyrin-nicacid dyads and their Mn, Zn complexes. (a) free-base porphyrin-nicacid dyads: $n = 2$, 3, 4, 5, 6, 10 correspond to NEPTPP, NPPTPP, NBPTPP, NAPTPP, NHPTPP, and NDPTPP, respectively; (b) Zn complexes: $n = 2$, 3, 4, 5, 6, 10 correspond to NEPTPPZn, NPPTPPZn, NBPTPPZn, NAPTPPZn, NHPTPPZn, and NDPTPPZn; (c) Mn complexes: $n = 2$, 3, 4, 5, 6, 10 correspond to NEPTPPMnCl, NPPTPPMnCl, NBPTPPMnCl, NAPTPPMnCl, NHPTPPMnCl, and NDPTPPMnCl, respectively.

with different carbon numbers in the alkoxy chain (the synthetic route is shown in figure 1). The dyads synthesized were 5-(4-nicotinicoxylethyloxy)phenyl-10,15,20-triphenylporphyrin (NEPTPP), 5-(4-nicotinicoxylpropyloxy)phenyl-10,15,20-triphenylporphyrin (NPPTPP), 5-(4-nicotinicoxylbutyloxy)phenyl-10,15,20-triphenylporphyrin (NBPTPP), 5-(4-nicotinicoxylamyloxy)phenyl-10,15,20-triphenylporphyrin (NAPTPP), 5-(4-nicotinicoxylhexyloxy)phenyl-10,15,20-triphenylporphyrin (NHPTPP), 5-(4-nicotinicoxyldecyloxy)phenyl-10,15,20-triphenylporphyrin (NDPTPP), and their Zn and Mn complexes. The photophysical and electrochemical properties of these compounds were studied to provide wider ground for choice and application of the porphyrin dyads. The medicinal and biological applications of these compounds are still being studied in our laboratory.

2. Experimental

2.1. *Materials and physical measurements*

All reagents and solvents were of commercial reagent grade and used without purification except DMF, which was pre-dried over activated 4 Å molecular sieves and vacuum distilled from calcium hydride (CaH_2) prior to use. Dry CH_3CN was obtained by distillation from CaH_2.

^1H NMR spectra were recorded on a Varian Unity 500 (MHz) NMR spectrometer. Chemical shifts were reported on the δ-scale relative to tetramethylsilane (TMS). Elemental analyses were measured by a Perkin–Elmer 240 C auto elementary analyzer. UV–Vis spectra were collected on a Shimadzu UV-365 spectrometer. Infrared spectra were recorded on a Nicolet 5PC-FT-IR spectrometer in the region 4000–400 cm^{-1}. Mass spectra were obtained using a VG-Quattro mass spectrometer. Thin layer chromatography was performed on glass micro-plates coated with silica gel G. Redox potentials of the compounds (10^{-3} mol L^{-1}) in dried DMF containing 0.1 mol L^{-1} TBAP as supporting electrolyte were determined at room temperature by cyclic voltammetry with a CHI 660A electrochemical workstation using a three-electrode system under deaerated conditions. Platinum button and platinum wire were used as working and counter electrodes. The reversibility of the electrochemical processes was evaluated by standard procedures and all potentials were recorded against a Ag/Ag^+ reference electrode [0.01 mol L^{-1} $AgNO_3$ in acetonitrile (CH_3CN) solution]. All fluorescence measurements were carried out on a SPEX Fluorolog-2T2 fluorescence spectrometer (450-W xenon lamp as the excitation source) with both excitation and emission slit set at 10 nm.

2.2. *Synthesis of NPPTPP*

5-(4-Nicotinicoxylpropyloxy)phenyl-10,15,20-triphenylporphyrin (NPPTPP) was prepared by reaction of 5-(4-(3-brmopropyloxy)phenyl)-10,15,20-tri-(4-phenyl)porphyrin (100 mg), which was synthesized according to the literature [18] with sodium nicotinic (40 mg) in DMF (25 mL) solution. The reaction mixture was heated to 75°C with stirring and the extent of the reaction was monitored by TLC (R_f: 0.48, $CHCl_3$ as developing solvent, room temperature). When the reaction was complete, the mixture was cooled to room temperature. The crude product was precipitated from the reaction mixture by adding 60 mL of a saturated NaCl solution. The residue was then washed using equal volumes of distilled water and methanol and purified on a neutral alumina column with $CHCl_3$ as eluant. The second red band was collected and condensed. The product was crystallized from chloroform and methanol and obtained as a purple crystal. Yield: 90.5%. ^1H NMR ($CDCl_3$, 500 Hz): δ: -2.76 (s, 2H, NH), 2.46–2.50 (m, 2H, CH_2), 4.42–4.45 (t, 2H, $OCOCH_2$), 4.74–4.76 (t, 2H, OCH_2), 7.27–7.29 (d, 2H, ArO-3, 5-H), 7.42–7.44 (m, 1H, Py-5-H), 7.73–7.78 (m, 9H, Ar-3, 4, 5-H), 8.11–8.22 (d, 8H, Ar-2, 6-H), 8.38–8.60 (d, 2H, Py-4, 6-H), 8.81–8.87 (d, 8H, β-H), 9.33 (s, 1H, Py-2-H); UV–Vis ($CHCl_3$) λ_{max} (10^{-4} $\varepsilon M^{-1} cm^{-1}$) 420.0 (44.80), 515.0 (3.16) 550.0 (1.78), 590.0 (1.32), 650.0 (1.19); IR (υcm^{-1}, KBr) 3323 (υ_{N-H}), 2918, 2848 (υ_{CH_2}), 1720 ($\upsilon_{C=O}$), 1244 (υ_{C-O-C}), 966 (δ_{N-H}); Elemental Anal. Calcd for $C_{53}H_{39}N_5O_3$: C 80.18, H 4.95, N 8.82; Found: C 80.09, H 4.98, N 8.80. FAB-MS m/z 794.5 (M + 1).

2.3. *Synthesis of NPPTPPZn*

The complex NPPTPPZn was prepared according to the standard method [19]. NPPTPP (80 mg) and $ZnCl_2$ (200 mg) were stirred in 20 mL DMF under nitrogen. The mixture was refluxed and the extent of the reaction was monitored by measuring the UV–Vis spectrum of the reaction solution. When the reaction was complete, the mixture was cooled to room temperature. The crude product was precipitated from the reaction mixture by adding 60 mL of a saturated NaCl solution. The residue was then washed using equal volumes of distilled water and methanol and the product was purified on a neutral alumina column using $CHCl_3$ as eluant. Yield: 87.5%.

^{1}H NMR ($CDCl_3$, 500 Hz): δ: 2.14–2.16 (m, 2H, CH_2), 4.12–4.14 (t, 2H, $OCOCH_2$), 4.31–4.34 (t, 2H, OCH_2), 7.12–7.14 (d, 1H, Py-5-H), 7.28 (s, 2H, ArO-3, 5-H), 7.71–7.74 (m, 9H, Ar-3, 4, 5-H), 8.21–8.22 (d, 8H, Ar-2, 6-H), 8.89–8.99 (m, 8H, β-H); UV–Vis ($CHCl_3$) λ_{max} ($10^{-4}\ \varepsilon\,M^{-1}\,cm^{-1}$) 425.1 (43.85), 555.0 (2.04), 595.0 (0.72); IR ($\upsilon\,cm^{-1}$, KBr) 2925, 2858 (υ_{CH_2}), 1730 ($\upsilon_{C=O}$), 1242 ($\upsilon_{C–O–C}$), 997 (πP); Elemental Anal. Calcd for $C_{53}H_{37}N_5O_3Zn$: C 74.25, H 4.35, N 8.17; Found: C 74.10, H 4.36, N 8.15.

2.4. *Synthesis of NPPTPPMnCl*

The preparation of NPPTPPMnCl is similar to NPPTPPZn. Yield: 82.3%. UV–Vis ($CHCl_3$) λ_{max} ($10^{-4}\ \varepsilon\,M^{-1}\,cm^{-1}$) 380.1 (7.59), 405.3 (6.70), 479.9 (14.07), 585.0 (2.86), 620.1 (3.16); IR ($\upsilon\,cm^{-1}$, KBr) 2923, 2854 (υ_{CH_2}), 1724 ($\upsilon_{C=O}$), 1244 ($\upsilon_{C–O–C}$), 1010 (πP); Elemental Anal. Calcd for $C_{53}H_{37}N_5O_3MnCl$: C 72.15, H 4.23, N 7.94; Found: C 72.01, H 4.24, N 7.92.

The preparation methods and results of other ligands and Zn and Mn complexes are similar to those mentioned above and the experimental results are deposited as supplementary information.

3. Results and discussion

3.1. *UV–Vis spectra*

UV–Vis absorption bands of the porphyrins are due to electronic transitions from the ground state (S_0) to the two lowest singlet excited states S_1 (Q state) and S_2 (Soret state) [20]. The $S_0 \rightarrow S_1$ transition gives the weak Q bands in the visible region while $S_0 \rightarrow S_2$ transition produces the strong Soret band in the near UV region. Figure 2 displays the absorption spectra of NPPTPP, NPPTPPZn and NPPTPPMnCl. The absorption bands of NPPTPP appear at 420, 515, 550, 590 and 650 nm. The Q band consists of four absorptions typical of $Q_x(0,0)$, $Q_x(0,1)$, $Q_y(0,0)$, $Q_y(0,1)$ transitions. The relative intensities of these bands are: $420 \gg 515 > 550 > 590 > 650$ nm. These intensities are similar to those observed for TPP [21]. The absorption peaks and relative intensities of porphyrin ligands with different side chain lengths are almost identical, indicating that covalent linking of nicacid groups to TPP has little effect on the π-system of the porphyrin. The position of absorption bands for the Zn complex are also nearly identical to those observed for TPP at 425, 555, 595 nm except NDPTPPZn, which appears at 430, 560, and 600 nm. The absorption patterns of NDPTPPZn are similar to those of five-coordinate zinc porphyrins while the absorption patterns of other Zn porphyrin complexes are similar to those of four-coordinate zinc porphyrins [22]. Because the chain length of NDPTPPZn is much longer than other Zn porphyrin complexes (figure 1), the N atom of nicacid group more easily coordinates Zn causing shift of the absorption spectra. The absorption bands of Mn porphyrin complexes appear at 380, 405, 480, 585, 620 nm with no shift when the length of side chain changed. Decrease in the number of Q bands and the shift in absorption frequencies observed for complexes, relative to the free-base prophyrin–nicacid dyads, is the result of increased molecular symmetry of metal complexes [23].

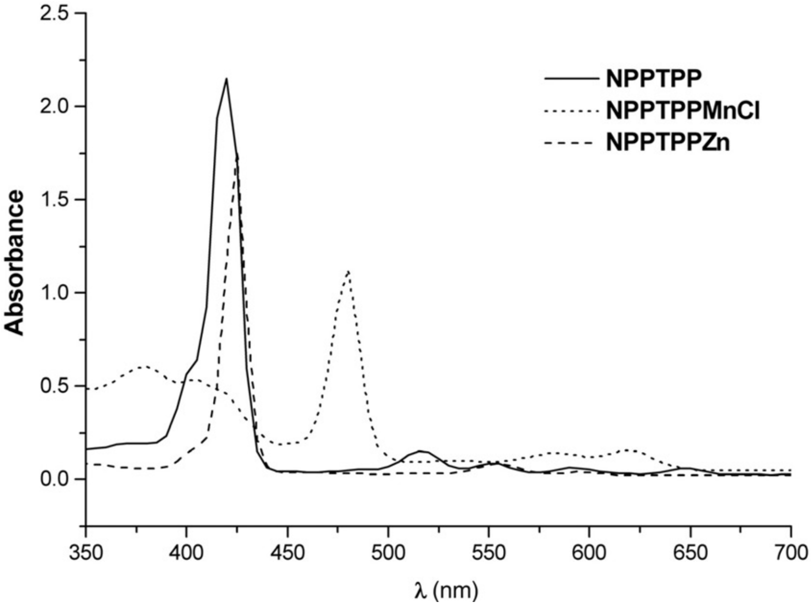

Figure 2. Absorption spectra of NPPTPP, NPPTPPZn, and NPPTPPMnCl in $CHCl_3$ at room temperature.

3.2. *Fluorescence spectra*

Figures 3 and 4 show the emission spectra of porphyrins and Zn porphyrin complexes in $CHCl_3$ (excitation wavelength is 420 nm) and the emission spectral data are given in table 1. The quantum yield of porphyrin ligands and Zn complexes were estimated from the emission and absorption spectra by a comparative method using the following equation:

$$\Phi_{\mathrm{sample}} = \Phi_{\mathrm{TPPZn}}(F_{\mathrm{sample}}/F_{\mathrm{TPPZn}})(A_{\mathrm{TPPZn}}/A_{\mathrm{sample}})$$

where F_{sample} and F_{TPPZn} are measured fluorescence integral areas (under the fluorescence spectra) of the sample and the reference TPPZn, respectively, A_{sample} and A_{TPPZn} are the absorbances of the sample and the reference, Φ_{sample} and Φ_{TPPZn} ($\Phi_{\mathrm{TPPZn}} = 0.033$ [24]) are the quantum yields of the sample and the reference TPPZn at same excitation wavelength.

Fluorescence of the S_2 (Soret band) and the S_1 (Q band) in porphyrin complexes exist. The fluorescence of $S_2 \rightarrow S_0$ is too weak to be observed in this work. Fluorescence spectra of all porphyrin ligands are similar in shape and consist of two bands, Q(0, 0) and Q(0, 1), which are mirror symmetric to the absorption bands $Q_x(0, 0)$ and $Q_x(0, 1)$.

The Q(0, 0) and Q(0, 1) fluorescence bands of porphyrins are in the regions $650 - 651$ and $710 - 714$ nm, respectively. Compared with fluorescence bands at 653 and 715 nm of TPP, the emission peaks of porphyryin ligands shift to the red by $2 - 5$ nm showing that there is energy transfer between the porphyrin ring and nicacid. With increasing the length of side chain (figure 3 and table 1), the fluorescence intensity and the quantum yield decreased. Because the length of the flexible alkyl chain increased, the interaction of the nicacid and the porphyrin ring was weakened.

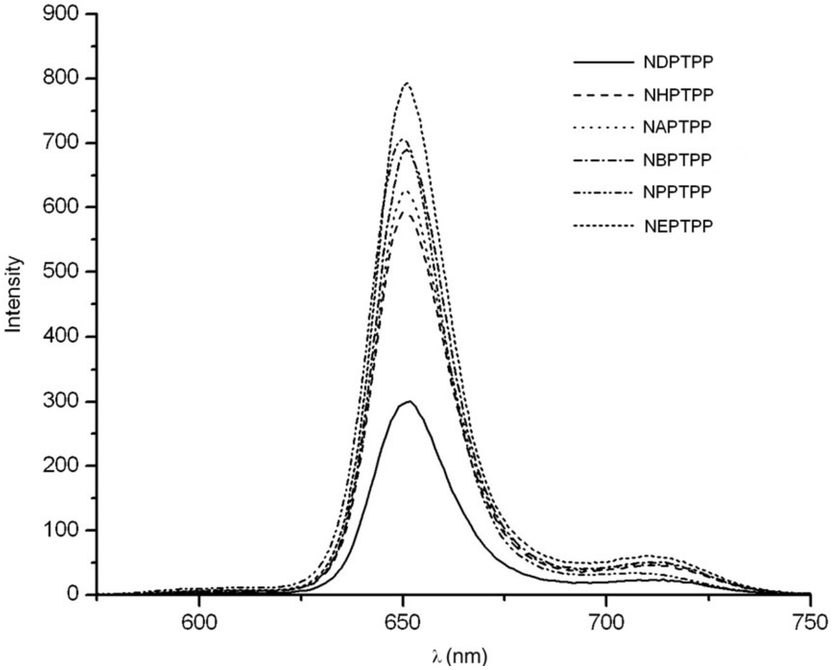

Figure 3. Fluorescence spectra of free-base porphyrin-nicacid dyads in $CHCl_3$ at room temperature. Fluorescence excitation wavelength $\lambda_{ex} = 420$ nm, concentrations of compounds are 1×10^{-5} mol L^{-1}.

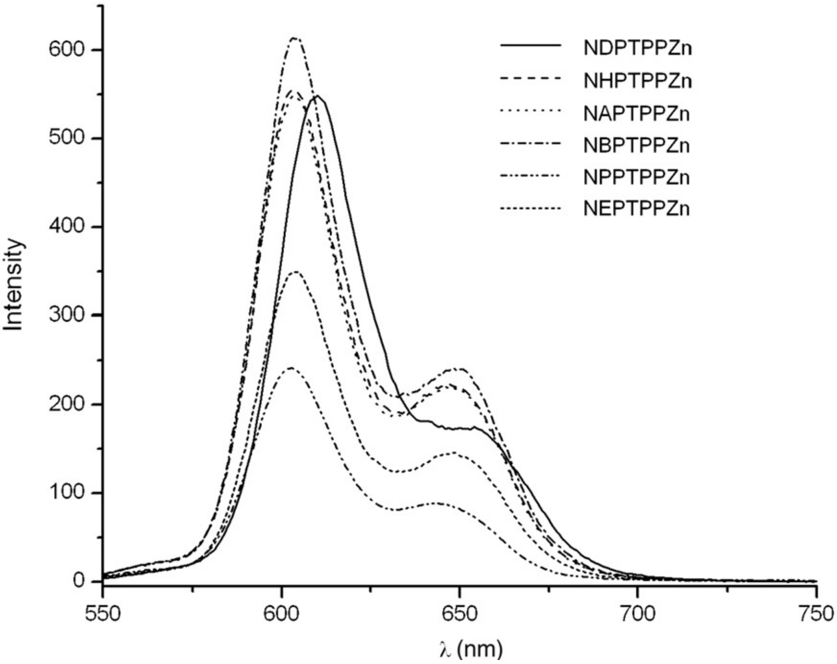

Figure 4. Fluorescence spectra of Zn porphyrin complexes in $CHCl_3$ at room temperature. Fluorescence excitation wavelength $\lambda_{ex} = 420$ nm, concentrations of compounds are 1×10^{-5} mol L^{-1}.

Table 1. Emission spectral data of free-base porphyrin-nicacid dyads and their Zn(II) complexes.

Compounds	Q(0, 0)	Q(0, 1)	Φ_f
NEPTPP	651	710	0.166
NPPTPP	650	710	0.142
NBPTPP	651	714	0.143
NAPTPP	651	712	0.130
NHPTPP	650	712	0.111
NDPTPP	652	714	0.056
NEPTPPZn	604	648	0.013
NPPTPPZn	603	645	0.053
NBPTPPZn	603	648	0.211
NAPTPPZn	603	646	0.188
NHPTPPZn	603	647	0.189
NDPTPPZn	610	654	0.177

Fluorescence bands of Zn complexes are in the regions of 603–604 and 645–648 nm except NDPTPPZn, which shift to the red (610, 654 nm). This red shift may be due to coordination to Zn. The fluorescence intensities of Mn complexes are much weaker than porphyrin ligands and Zn complexes.

3.3. *Electrochemistry*

Cyclic voltammograms of the free-base NPPTPP and its Zn and Mn complexes in DMF containing 0.1 M TBAP are presented in figure 5 and a summary of the redox potentials are listed in table 2.

3.4. *NPPTPP*

Two reductions are observed in DMF. The first at $E_{1/2} = -1.50$ V leads to formation of porphyrin anion radical while the second at $E_{1/2} = -1.83$ V leads to formation of porphyrin dianion. Only one oxidation is seen at $E_{1/2} = 0.71$ V which corresponds to the formation of porphyrin cation radical.

For TPP, four reversible redox processes are observed (not shown). Comparing the data of NPPTPP and TPP, the processes of NPPTPP all shift toward negative potentials. The difference is 220 and 120 mV for the two reductions of NPPTPP in DMF. This can be explained by the attachment of an electron-donating group at *para* position of the phenyl groups.

3.5. *NPPTPPZn*

The spectrum shape of NPPTPPZn is similar to NPPTPP, two reductions and one oxidation are observed with the potential range of the solvent. The first reduction at $E_{1/2} = -1.74$ V is quasi-reversible. The second at $E_{1/2} = -2.14$ V is not completely reversible and gives rise to a reoxidation peak at $E_{pa} = -0.85$ V. The oxidation potential at $E_{1/2} = 0.43$ V is quasi-reversible. Compared to ZnTPP, the potentials of NPPTPPZn shift toward negative values. All the half-wave potentials are negatively shifted to

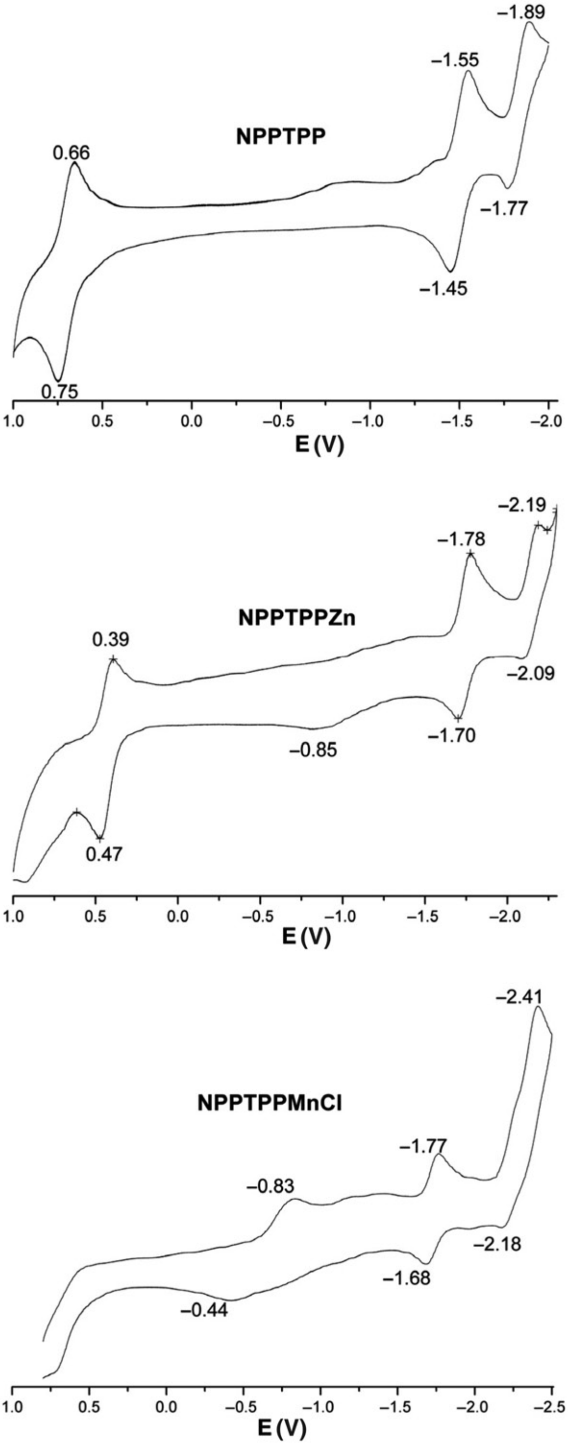

Figure 5. Cyclic voltammograms of NPPTPP and its Zn and Mn complexes.

Table 2. Half-wave potentials for oxidation and reduction of NPPTPP derivatives in DMF containing 0.1 M TBAP.

		Potentials			
Compounds	Solvent	Oxidation	Reduction		
NPPTPP	DMF	0.71	−1.50	−1.83	
NPPTPPZn	DMF	0.43	−1.74	−2.14	
NPPTPPMnCl	DMF		−0.64	−1.73	−2.41[a]

Note: [a]Value given is E_{pc}.

Table 3. Redox potentials of free-base porphyrin-nicacid dyads in CH_2Cl_2 containing 0.1 M TBAP. $E_{1/2}$(V) (*vs.* Ag^+/Ag).

Compounds	2nd oxidation	1st oxidation	1st reduction	2nd reduction	$E_{oxdn} - E_{redn}$
NEPTPP	0.97[a]	0.72	−1.53	−1.88	2.25
NPPTPP	1.03[a]	0.78	−1.51	−1.86	2.29
NBPTPP	0.95[a]	0.71	−1.55	−1.86	2.26
NAPTPP	0.94[a]	0.71	−1.54	−1.90	2.25
NHPTPP	0.94[a]	0.70	−1.54	−1.87	2.24
NDPTPP	1.19	0.71	−1.55	−1.90	2.26

Note: [a]Value given is E_{pa}.

a certain extent as compared to the values for the same redox reactions of free NPPTPP, as expected. The porphyrin ring coordinates with Zn, leading to more difficult reduction as chemical stability increased.

3.6. *NPPTPPMnCl*

Three reductions are observed. First, at $E_{1/2} = -0.64$ V, is not reversible ($E_{pa} - E_{pc}| = 0.39$ V), corresponding to Mn(III)/Mn(II). Second, at $E_{1/2} = -1.73$ V, can be assigned as formation of the anion radical. Third, at $E_{pc} = -2.41$ V, is coupled with an oxidation peak at $E_{pa} = -2.18$ V, and the ratio i_{pa}/i_{pc} is much lower than 1.0, suggesting an EC mechanism. The Mn(III)/Mn(II) redox couple has large peak separation, but both anodic and cathodic peaks are present, perhaps due to coordination of Mn porphyrin.

There are similar results for samples whose central ions are identical. Table 3 shows the redox potential data of free-base porphyrin-nicacid dyads in CH_2Cl_2. As expected, the length of the side chain has little effect on the redox potentials because the substituent constants of the compounds are similar.

4. Conclusion

A series of porphyrin-nicacid dyads and their Mn and Zn complexes were prepared and characterized. Fluorescence studies showed that with increasing length of alkoxy chain, the fluorescence intensity and quantum yield of the free-base porphyrin-nicacid dyads decreased. Electrochemical studies of free-base and metal porphyrin-nicacid dyads indicate that the length of side chain has little effect on the redox potentials.

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