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Synthesis and Raman, Electrochemical, Fluorescence Studies of Free-Base and Transition Metal Porphyrin-Nicacid Dyads With Different Substituent Groups

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A series of free-base porphyrin-nicacid dyads with different meso-substituents and some transition metal complexes were synthesized and characterized by means of UV–vis, IR, and ¹H NMR spectroscopies, and elemental analysis. The properties of nicacid linked with porphyrin dyads were studied as a new intramolecular electron transfer system. The effects of different metal ions and different substituent groups on the properties of the porphyrinnicacid dyads have been investigated. The studies on the electrochemical and fluorescence spectra, and Raman spectra, showed that different substituents and metal ions affect the properties of the compounds in different ways.

Keywords cyclic voltammetry, fluorescence, porphyrin-nicacid dyad, resonance Raman spectra, transition metal complex

INTRODUCTION

The syntheses and application of porphyrins and metalloporphyrins, especially the binary, ternary, and multiple porphyrins linked with bioactive substances, have been studied extensively because of their distinctive structures and predominant physical, chemical, and optical properties, which are valuable in potential applications in biological science, biochemistry, and medical chemistry. Some porphyrins can accumulate selectively, induce damage in DNA or tumor tissue,^[1,2] and have been used as a tumor-targeting agent in photodynamic therapy (PDT).^[3,4] Nicotinic acid (nicacid) is one of the most extensively studied pyridine derivatives and it has a wide-ranging ability to reduce lipid levels.^[5] Based on its well-known plasma lipid-lowering effect, nicacid and its derivative have been used clinically in the treatment for hyperlipidemia. The synthesis of a series of novel porphyrin-nicacid dyads offers an opportunity to investigate the combination of porphyrin and nicacid as DNA structural probes and mediators of DNA cleavage reactions.

In addition, porphyrin dyads which have electron acceptor and donor have been the topic subject of research because they are very useful to understand the process of photosynthesis.^[6] Many porphyrin dyads, for example porphyrin-quinones,^[7] porphyrin-C60,^[8] and porphyrin-cyclodextrin,^[9] have been reported to mimic electron transfer and energy transfer processes observed in nature.

Electrochemistry is an important experimental method to study porphyrin compounds and a great number of experimental results have been reported over the past four decades concerning the electrochemistry of metalloporphyrins. The Resonance Raman (RR) spectroscopy is an excellent technique to study the molecular and electronic structure of porphyrins and the wavenumbers of RR bands are affected by the structural changes induced by the electron transfer. In this study, we synthesized a series of free-base porphyrinnicacid dyads: 5-(4-Nicotinicoxylpropyloxy)phenyl-10,15,20triphenylporphyrin (NPPTPP), 5-(4-Nicotinicoxylpropyloxy) phenyl-10,15,20-tri(4-methoxyphenyl)porphyrin (NPPTMPP), 5-(4-Nicotinicoxylpropyloxy)phenyl-10,15,20-tri(4-chlorophe nyl) porphyrin (NPPTCPP), and transition metal complexes of the type M(NPPTPP), where M = Mn(III), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) (the structures are shown in Figure 1) and the fluorescence, Raman spectra, and electrochemical behavior of these compounds were investigated. All of these studies may provide useful information for the research of their bioactivities, which can be used for drug screening.

EXPERIMENTAL

Materials and Physical Measurements

All reagents and solvents were of the commercial reagent grade and were used without further purification except dimethyl formamide (DMF), which was predried over activated 4 Å molecular sieve and vacuum distilled from calcium hydride

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$$R = H$$
, OCH₃, Cl
M= 2H, Mn(Cl), Fe(Cl), Co, Ni, Cu, Zn

FIG. 1. The structures of free-base porphyrin-nicacid dyads and their metal complexes.

 (CaH_2) prior to use. The dry CH₃CN was obtained by redistillation from CaH₂.

Raman spectra were recorded with a Renishaw RM1000 Raman spectrophotometer (Gloucestershire, United Kingdom) equipped with an integral microscopy. Radiation of 514.5 nm was obtained from an Ar⁺ laser. Redox potentials of the compounds (10⁻³ mol/dm⁻³) in dried DMF containing 0.1 mol/dm⁻³ TBAP as supporting electrolyte were determined at room temperature by cyclic voltammetry with a CHI 660A electrochemical work station (Shanghai CH Instruments Co., China) 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 an Ag/Ag+ reference electrode (0.01 mol/dm⁻³ AgNO₃ in acetonitrile (CH₃CN) solution). Fluorescence spectra were recorded with a SPEX Fluorolog-2T2 spectrofluorometer (Spex Industries Inc., Edison, NJ, USA, 450-W xenon lamp as the excitation source). The quantum yields of porphyrins were estimated from the emission and absorption spectra by a comparative method^[10] using the following equation:

$$\Phi_{\text{sample}} = \Phi_{\text{TPPZn}}(F_{\text{sample}}/F_{\text{TPPZn}})(A_{\text{TPPZn}}/A_{\text{sample}}) \quad [1]$$

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 absorbance of the sample and the reference. Φ_{sample} and Φ_{TPPZn} ($\Phi_{TPPZn} = 0.033$)^[11] are the quantum yields of the sample and the reference TPPZn at same excitation wavelength.

Preparation of Free-Base and Transition Metal Porphyrin-Nicacid Dyads

Synthesis of NPPTPP

NPPTPP was prepared by the reaction of the 5-(4-(3brmopropyloxy)phenyl)-10,15,20-tri-(4-phenyl)porphyrin (100 mg, 0.133 mmol) which was synthesized in our laboratory according to the literature^[12] with sodium nicotinic (40 mg, 0.276 mmol) 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. When the reaction was completed, 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 neural alumina column with CHCl₃ as eluant. The second red band was collected and condensed. The precipitated product was obtained as purple crystal.

Synthesis of NPPTPPZn

The complex NPPTPPZn was prepared according to the standard method.^[13] NPPTPP (80 mg, 0.101 mmol) and ZnCl₂ (200 mg, 1.47 mmol) was stirred in 20 mL DMF under the protection of nitrogen stream. 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 completed, 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 CHCl₃ as eluant.

The preparation methods and results of NPPTMPP, NPPTCPP, and the other metal complexes of NPPTPP are similar to those mentioned above.

RESULTS AND DISCUSSION

Characterization

NPPTPP

Yield: 90.5%. ¹H NMR (CDCl₃, 500Hz δ / ppm): -2.76(s, 2H, NH), 2.46–2.50(2H, *m*, CH₂), 4.42–4.45(2H, *t*, OCOCH₂), 4.74–4.76(2H, *t*, OCH₂), 7.27–7.29(2H, *d*, ArO-3,5-H), 7.42–7.44(1H, *m*, Py-5-H), 7.73–7.78(9H, *m*, Ar-3,4,5-H), 8.11–8.22(8H, *d*, Ar-2,6-H), 8.38–8.60(2H, *d*, Py-4,6-H), 8.81–8.87(8H, *d*, β -H), 9.33(1H, *s*, Py-2-H); UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 420.0(44.80), 515.0(3.16) 550.0(1.78), 590.0(1.32) 650.0(1.19); IR (KBr, cm⁻¹): 3323(υ_{N-H}), 2918, 2848(υ_{CH2}), 1720($\upsilon_{C=0}$), 1244(υ_{C-O-C}), 966(δ_{N-H}); Elemental analysis: Anal. Calcd. for C₅₃H₃₉N₅O₃: 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).

NPPTMPP

Yield: 84.0%. ¹H NMR (CDCl₃, 500Hz δ / ppm): -2.76(2H, *s*, NH), 2.47–2.53(2H, *m*, CH₂), 4.10(6H, *s*, CH₃), 4.16(3H, *s*, CH₃), 4.43–4.46(2H, *t*, CO₂CH₂), 4.74–4.77(2H, *t*, OCH₂), 7.28–7.30(8H, *d*, Ar-3,5-H), 7.44–7.46(1H, *m*, Py-5-H), 8.12–8.13(8H, *d*, Ar-2,6-H), 8.39–8.52(2H, *d*, Py-4,6-H), 8.82–8.86(8H, *d*, β -H), 9.34(1H, *s*, Py-2-H); UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 425.0(42.80), 520.0(2.53) 555.0(1. 86), 595.0(1.12) 650.0(1.32); IR (KBr, cm⁻¹): 3323(υ_{N-H}), 2922, 2852(υ_{CH2}), 1720($\upsilon_{C=0}$), 1242(υ_{C-O-C}), 966(δ_{N-H}); Elemental analysis: Anal. Calcd. for C₅₆H₄₅N₅O₆: C 76.09, H 5.13, N 7.92; Found: C 75.78, H 5.16, N 7.89. FAB-MS m/z 884.5 (M + 1).

NPPTCPP

Yield: 87.0%. ¹H NMR (CDCl₃, 500Hz δ / ppm): -2.84(2H, *s*, NH), 2.47–2.55(2H, *m*, CH₂), 4.44–4.46(2H, *t*, CO₂CH₂), 4.74–4.77(2H, *t*, OCH₂), 7.30–7.31(2H, *d*, ArO-3,5-H), 7.44–7.46(1H, *d*, Py-5-H), 7.74–7.76(6H, *d*, Ar-3, 5-H), 8.10–8.14(8H, *d*, Ar-2,6-H), 8.39–8.55(2H, *d*, Py-4,6-H), 8.81–8.90(8H, *d*, β -H), 9.34(1H, *s*, Py-2-H); UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 420.0(54.20), 515.0(2.90) 550.0(1.64), 590.0(1.22) 645.0(1.04); IR (KBr, cm⁻¹): 3319(υ_{N-H}), 2922, 2852(υ_{CH2}), 1724($\upsilon_{C=0}$), 1242(υ_{C-0-C}), 966(δ_{N-H}); Elemental analysis: Anal. Calcd. for C₅₃H₃₆Cl₃N₅O₃: C 70.95, H 4.04, N 7.81; Found: C 70.66, H 4.07, N 7.77. FAB-MS m/z 897.6 (M + 1).

NPPTPPZn

Yield: 87.5%. ¹H NMR (CDCl₃, 500Hz δ / ppm): 2.14–2.16(2H, *m*, CH₂), 4.12–4.14(2H, *t*, OCOCH₂), 4.31–4.34(2H, *t*, OCH₂), 7.12–7.14(1H, *d*, Py-5-H), 7.28(2H, *s*, ArO-3,5-H), 7.71–7.74(9H, *m*, Ar-3,4,5-H), 8.21–8.22(8H, *d*, Ar-2,6-H), 8.89–8.99(8H, *m*, β-H); UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 425.1(43.85), 555.0(2.04) 595.0(0.72); IR (KBr, cm⁻¹): 2925, 2858(υ_{CH2}), 1730($\upsilon_{C=0}$), 1242(υ_{C-O-C}), 997(π P); Elemental analysis: Anal. Calcd. for C₅₃H₃₇N₅O₃Zn: C 74.25, H 4.35, N 8.17; Found: C 74.10, H 4.36, N 8.15.

NPPTPPMnCl

Yield: 82.3%. UV–Vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 380.1(7.59), 405.3(6.70), 479.9(14.07),585.0(2.86), 620.1(3.16); IR (KBr, cm⁻¹): 2923, 2854(υ_{CH2}), 1724($\upsilon_{C=0}$), 1244(υ_{C-O-C}), 1010(π P); Elemental analysis: Anal. Calcd. for C₅₃H₃₇N₅O₃MnCl: C 72.15, H 4.23, N 7.94; Found: C 72.01, H 4.24, N 7.92.

NPPTPPFeCl

Yield: 77.5%. UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 379.9(7.76), 420.0(14.00), 510.1(2.29), 575.0(1.04), 655.0(0.91); IR (KBr, cm⁻¹): 2922, 2852(υ_{CH2}), 1724($\upsilon_{C=0}$), 1242(υ_{C-O-C}), 999(π P); Elemental analysis: Anal. Calcd. for C₅₃H₃₇N₅O₃FeCl: C 72.08, H 4.22, N 7.93; Found: C 71.93, H 4.24, N 7.91.

NPPTPPCo

Yield: 84.5%. UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 409.9(26.00), 530.0(2.23); IR (KBr, cm⁻¹): 2922, 2852(ν_{CH2}), 1724($\nu_{C=0}$), 1244(ν_{C-O-C}), 1001(π P); Elemental analysis: Anal. Calcd. for C₅₃H₃₇N₅O₃Co: C 74.82, H 4.38, N 8.23; Found: C 74.66, H 4.40, N 8.21.

NPPTPPNi

Yield: 83.8%. UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 415.0(34.90), 530.0(2.96); IR (KBr, cm⁻¹): 2922, 2852(ν_{CH2}), 1724($\nu_{C=0}$), 1242(ν_{C-0-C}), 1005(π P); Elemental analysis: Anal. Calcd. for C₅₃H₃₇N₅O₃Ni: C 74.84, H 4.38, N 8.23; Found: C 74.68, H 4.40, N 8.22.

NPPTPPCu

Yield: 87.4%. UV–vis (CHCl₃) (λ_{max} / nm ($\varepsilon \times 10^{-4}$ L mol⁻¹ cm⁻¹)) 420.0(47.40), 539.9(3.41); IR (KBr, cm⁻¹): 2924, 2852(ν_{CH2}), 1722($\nu_{C=O}$), 1242(ν_{C-O-C}), 999(π P); Elemental analysis: Anal. Calcd. for C₅₃H₃₇N₅O₃Cu: C 74.41, H 4.36, N 8.19; Found: C 74.26, H 4.37, N 8.17.

RR Spectra

Effect of the central metal ion

Figure 2 displays the RR spectra of NPPTPP and its transition metal complexes excited at 514.5 nm. The observed Raman frequencies and their assignments are listed in Table 1. The RR spectra of tetraphenylporphyrin ligands and their metal derivatives have been studied extensively.^[14–16] Using these spectra and the published data of similar compounds, we have made detailed vibrational assignments. Besides, we have paid more attention on those bands that are the most obvious and persistent from compound to compound. The wavenumber positions of vibration bands in the high-frequency region $(1300-1600 \text{ cm}^{-1})$ are sensitive to the core size, axial ligation, and electron density of the central metal ion. In this region, the bands near 1550, 1460, and 1360 cm⁻¹ of NPPTPP and its complexes are assigned to $\nu(C_{\beta}-C_{\beta})$ stretch ν_2 , $\nu(C_{\alpha}-C_m)$ stretch ν_3 , and $\nu(C_{\alpha}-N/2)$ $C_{\alpha}-C_{\beta}$) stretch ν_4 , respectively, by analogy to the previous works on M(TPP) complexes.^[17] These three bands are metal sensitive. According to the crystal field theory of coordination



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 TABLE 1

 Raman spectra data and assignment of NPPTMPP, NPPTCPP, NPPTPP, and its six metal complexes

| Assigned* | Mn | Zn | Cu | Ni | Co | Fe | NPPTPP | NPPTCPP | NPPTMPP |
|---|--------|--------|--------|--------|--------|--------|--------|---------|---------|
| Phenyl/Py | 1579vs | 1598w | 1594w | 1593w | 1595w | 1589w | 1590w | 1599w | 1572w |
| $v_2, v(\mathbf{C}_{\beta}\mathbf{C}_{\beta})$ | 1566s | 1547m | 1556vs | 1566vs | 1562vs | 1551vs | 1551vs | 1550vs | 1548vs |
| ν_{11} , $\nu(C_{\beta}C_{\beta})/\nu(C_{\alpha}C_{m})$ | 1496s | 1492w | 1500s | 1508m | 1500vs | 1496m | 1496m | 1494m | 1493m |
| v_{3} , $v(\mathbf{C}_{\alpha}\mathbf{C}_{\mathrm{m}})$ | 1458w | 1443m | 1456w | 1472m | 1462m | 1454m | 1456m | 1457m | 1454m |
| v_4 , $v(C_{\alpha}-N)/v(C_{\alpha}C_{\beta})$ | 1372m | 1350vs | 1361vs | 1373vs | 1363vs | 1360m | 1363w | 1360w | 1361w |
| v_{20} , v (pyrrole quarter-ring) | 1267m | 1269w | 1304 | 1342m | 1338m | 1335m | 1329w | 1327w | 1329m |
| $v_1, v(C_m-Ph)$ | 1232m | 1230w | 1232m | 1228m | 1228w | 1232w | 1240m | 1240m | 1240m |
| N-H bend + ν (C _{α} -N) _{asym} | | | | | | | 1136w | 1132w | 1134w |
| $\nu_{34}, \nu_{asym}(C_{\alpha}-H) + \nu_{asym}(C_{\alpha}-C_{\beta})$ | 1188w | 1176m | 1182w | 1188m | 1188w | 1184w | | | |
| $v_{17}, \delta(C_{\beta}-H)$ | 1084w | 1066m | 1078w | 1082w | 1079w | 1080w | 1082w | 1078w | 1080w |
| Φ_7 , Phenyl | 1025w | 1021w | 1025w | 1031w | 1022w | 1016w | 1038w | 1039w | 1040w |
| v_{15} , v (pyrrole breath) + Phenyl | 1007m | 998m | 1003m | 1003s | 1003m | 1003w | 1001w | 999w | 1001w |
| v_6 , v (pyrrole breath) | | | | | | | 962w | 962w | 962w |
| Phenyl/Py | 872w | 875w | 887w | 887w | 887w | 887w | 885w | 885w | 886w |
| v_8 , v (pyrrole translation) | | | | | | | 337w | 328w | 324w |
| ν (M-N) | 393w | 422w | 390m | 391s | 387m | 390m | | | |
| ν (M-Cl) | 328w | | | | | 368w | | | |

^avs = very strong; s = strong; m = medium; w = weak.

chemistry, the electron structure of the metal ions are: Co^{2+} , $Ni^{2+}-d_{x^2-y^2}^0$, $Cu^{2+}-d_{x^2-y^2}^1$, $Zn^{2+}-d_{x^2-y^2}^2$. When the $d_{x^2-y^2}$ orbit is filled with electrons, the distance of metal-nitrogen is increased and the porphyrin core expanded. As we know, the diameter of Co^{2+} is bigger than Ni^{2+} , so the core expansion of NPPTPPCo is larger than NPPTPPNi. With increasing metal-nitrogen distance or core size on going through Ni, Co, Cu, Zn complexes results in significantly downshifted frequencies as shown in Figure 3. The result is same with tetraarylmetalloporphyrins^[18] and octaethylporphyrins.^[19]

Effects of the substituent groups

From Table 1 we can see that the v_2 , v_3 , and v_4 frequencies of NPPTPP, NPPTCPP, and NPPTMPP are almost identical, and they appeared to be relatively insensitive to the electronic ef-



Electrochemistry

Effect of the central metal ion

The cyclic voltammograms of the metal complexes of NPPTPP in DMF containing 0.1 mol/dm⁻³ TBAP as supporting electrolyte are shown in Figure 4 and a summary of the half-wave potentials is listed in Table 2.

All cycle voltammograms of NPPTPPNi, NPPTPPCu, and NPPTPPZn are similar in shape. Each compound undergoes one

1550 1500 1450 1450 1450 1450 1350 H₂ Mn Fe Ni Co Cu Zn

FIG. 3. Positions of bands sensitive to metal complexes.

TABLE 2 Half-wave electrochemical redox data (vs. Ag/Ag⁺) of metal complexes in DMF

| ₹1 F | 82 |
|----------|--|
| .722 –2. | 297 |
| .380 | |
| | |
| .577 –2. | 152 |
| .583 –2. | 096 |
| .738 –2. | 138 |
| | .380 .577 –2. .583 –2. .738 –2. |

Scan rate = 0.1 V/s. O1 is the half-wave potential of the first oxidation; R1, R2 are the half wave potentials of the first and second reduction, respectively.



FIG. 4. The cyclic voltammograms of the metal complexes of NPPTPP in DMF containing 0.1 mol/dm⁻³ TBAP as supporting electrolyte. Scan rate 100 mV/s.

one-electron oxidation and two one-electron reductions with the potential range of the solvent. The first reduction potentials of NPPTPPNi, NPPTPPCu and NPPTPPZn are at -1.582, -1.583, and -1.738 V, respectively, and they are quasireversible. But for the second reduction, at $E_{1/2} = -2.149$, -2.081, and -2.133 V,

respectively, are not completely reversible and gives rise to a new reoxidation peak at $E_{pa} = -0.714$, -0.726, -0.848 V. These irreversible processes are probably due to the formation of isoporphyrin. Only one oxidation is seen from Figure 4, at $E_{1/2} = 0.587$, 0.590, and 0.433 V for NPPTPPNi, NPPTPPCu, and

NPPTPPZn, respectively, and they are not completely reversible. From Table 2, we can see that the first reduction of NPPTPPZn is more difficult than NPPTPPNi and NPPTPPCu. On the contrary, the oxidation of NPPTPPZn is easier than NPPTPPNi and NPPTPPCu. This shows that the redox of porphyrin ring is correlated to the electron density of the conjugated system. Increasing the electron density of the porphyrin ring makes the reduction potentials negative shift.

Three reductions of NPPTPPMnCl are observed. The first, at $E_{1/2} = -0.636$ V is not reversible ($|E_{pa} - E_{pc}| = 395$ mV), which corresponds to the reaction Mn (III)/Mn (II). The second occurs at -1.722 V and can be assigned to the formation of the anion radical. The third, at $E_{pc} = -2.411$ V, is coupled with an oxidation peak at $E_{pa} = -2.182$ V, and the ratio of i_{pa}/i_{pc} is much lower than 1.0, suggesting an EC mechanism.

The cyclic voltammogram of NPPTPPFeCl is shown in Figure 4. The reduction of $E_{1/2} = -1.380$ V corresponds to the formation of the anion radical and the oxidation of $E_{1/2} = 0.832$ V corresponds to the formation of the cation radical. Figure 4 also shows cyclic voltammogram obtained for the Fe(III)/Fe(II) couple of NPPTPPFeCl. On the negative potential sweep, one broad anodic process ($E_{pc} = -0.650$ V) and two cathodic peaks ($E_{pa} = -0.137$, -0.485 V) are observed. The existence of NPPTPPFeCl in DMF containing TBAP as supporting electrolyte is very complicated because Cl⁻, ClO₄⁻, and DMF may coordinate to Fe atom.

In the solvent DMF, NPPTPPCo exhibits a somewhat unusual wave for the Co(III)/Co(II) reduction. Although the waves corresponding to Co(III)/Co(II) redox process are well defined, those due to Co(III)/Co(II) are not. As we can see from the figure, the cathodic wave and anodic wave are ill defined, the height of the wave is small and the separation of the cathodic and anodic wave is broad. This phenomenon might be caused by the axis coordination of the metallporphyrin.^[20] The complex of NPPTPPCo may coordinate with electrolyte anion or DMF to form an ion pair. The removal of ClO_4^- or DMF during reduction should result in a lower rate constant, because the activation energy needed to separate coordination anion from cobalt atom increased.

Effects of the substituent groups

The cyclic voltammetry spectra of free-base porphyrins with different substituent groups are shown in Figure 5 and a summary of the half-wave potentials is listed in Table 3. We can see that NPPTPP undergoes two quasi-reversible oxidation and two quasi-reversible reductions for a scan rate of 0.1 V/S and the compounds of NPPTCPP and NPPTMPP undergo one irreversible oxidation, one quasireversible oxidation, and two quasi-reversible reductions in the range of the solvent. The differences in $E_{1/2}$'s between the first ring oxidation yielding π anion radicals are 2.164, 2.237, and 2.251 V for NPPTMPP, NPPTPP, and NPPTCPP, respectively, which are in good agreement with $E_{1/2}^{\text{ox}}(1) - E_{1/2}^{\text{red}}(1) = 2.25 \pm 0.15$ V obtained by Zerner and



FIG. 5. The cyclic voltammograms of free-base porphyrin-nicacid dyads with different substituent groups.

Gouterman.^[21] The differences between the first and second ring reduction are 0.322, 0.347, and 0.316 V for NPPTMPP, NPPTPP, and NPPTCPP, respectively, and the values are very close to that of the TPP (0.35 V).^[22]

Compared to NPPTPP, the redox potentials of NPPTMPP shifted to the negative direction while the NPPTCPP shifted positively. This can be explained by the effect of substituents. The attachment of an electron-donating group (–OCH₃) at *para* position on phenyl ring will increase the electron density of porphyrin ring, which makes it easier to oxidized and harder to reduced. On the contrary, the electron-withdraw group (–Cl) will decrease the electron density of porphyrin ring, so it is easier to reduced and harder to oxidize.

Fluorescence Spectra

Effect of the central metal ion

Figure 6 shows the emission spectra of NPPTPP and its complexes in $CHCl_3$ and the excitation wavelength is 420 nm. From Figure 6, we can see that the fluorescence intensities of the ligand and the complex NPPTPPZn are much higher than

TABLE 3 Half-wave electrochemical redox data of free-base porphyrin-nicacid dyads with different substituents (vs.

| Ag/Ag^{-}) III CH_2CI_2 | | | | | | |
|------------------------------|--------------------------------|-------|--------|--------|-------|-------|
| Compound | O2 | 01 | R1 | R2 | 01-R1 | R1-R2 |
| NPPTMPP | 0.806 (0.857 ^a) | 0.638 | -1.526 | -1.858 | 2.164 | 0.322 |
| NPPTPP | 1.030 ^a | 0.778 | -1.509 | -1.856 | 2.237 | 0.347 |
| NPPTCPP | 0.987^{a} | 0.799 | -1.452 | -1.876 | 2.251 | 0.316 |

^aValue given is E_{pa} ; O1 and O2 are the half wave potentials of the first and second oxidation, respectively; R1 and R2 are the half wave potentials of the first and second reduction, respectively.



FIG. 6. The fluorescence spectra of NPPTPP and its metal complexes.

other transition metal complexes. The result is same with the reference^[23] and confirmed that the transition metal on the center of porphyrin ring quenches the fluorescence of porphyrin.

Effects of the substituent groups

Figure 7 shows the emission spectra of free-base porphyrins with different subsituents in CHCl₃ and the emission spectral data are given in Table 4. There are fluorescence of the S₂ (Soret band) and the S₁ (Q band) in porphyrin ligands. The fluorescence of S₂ \rightarrow S₀ is too weak to be observed in this work. Fluorescence spectra of NPPTPP, NPPTMPP and NPPTCPP are similar in shape and consist of two bands, Q (0, 0) and Q (0, 1). The Q (0, 0) fluorescent bands are at 650, 654, and 649 nm and Q (0, 1) fluorescent bands are at 710, 714, and 712 nm for NPPTPP, NPPTMPP, and NPPTCPP, respectively. Compared with the



FIG. 7. The fluorescence spectra of the free-base porphyrin-nicacid dyads with different substituent groups.

TABLE 4 Emission spectral data of free-base porphyrin-nicacid dyads with different substituents

| Compounds | Q _x (0,0) | Q _x (1,0) | $\Phi_{\rm f}$ | |
|-----------|----------------------|----------------------|----------------|--|
| NPPTMPP | 654 | 714 | 0.164 | |
| NPPTPP | 650 | 710 | 0.142 | |
| NPPTCPP | 649 | 712 | 0.074 | |

fluorescent bands of NPPTPP, the Q (0, 0) peaks of NPPTMPP and NPPTCPP have shifted to the red region by 4 nm and to the blue region by 1 nm respectively. As we can see from Figure 7 and Table 4, when attached an electron-donating group ($-OCH_3$) on porphyrin ring, the fluorescence intensity and the quantum yield decreased while the attachment of an electron-withdraw group (-Cl) increase the fluorescence intensity and the quantum yield. This is because the electron-donating group strength the conjugate ability of the porphyrin π system while the electronwithdraw group's effect is contrary. We also noticed that the quantum yield of NPPTCPP has changed a lot compared with NPPTPP whereas that of the NPPTMPP has changed a little, which indicates that the effect of electron-withdrawing group ring is more obvious than electron-donating group.

CONCLUSION

Here we studied the cyclic voltammetry, fluorescence spectra, and RR spectra of the nicacid linked porphyrin dyads and their metal complexes. The RR bands of the compounds are assigned and the study showed that with increasing core size on going through Ni, Co, Cu, Zn complexes results in significantly downshifted frequencies. The cyclic voltammetry of Mn, Fe, and Co complexes are different from the porphyrin ligand and other metal complexes, which show not only the redox of porphyrin ring, but also the redox of metal ion. The attachment of an electron-donating group or an electron-withdraw group has different effect on the redox potentials and fluorescence spectra. The fluorescence intensity of NPPTPPZn is much higher than other transition metal complexes.

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