

Effect of Solvent on the Spectroscopic, Electrochemical and Spectroelectrochemical Properties of Near-Infrared Oxovanadium(IV) α,α' -Octapentoxyphthalocyanine

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A near-infrared oxovanadium(IV)- α,α' -octapentoxyphthalocyanine (oxo-V(IV)-Pc) has been synthesized and characterized. Solvent-dependent optically spectroscopic and electrochemical investigations including UV-vis absorption and magnetic circular dichroism (MCD) spectroscopy, cyclic voltammetry (CV), DPV and multi-scan rate CV electrochemistry measurements were carried out to give in-depth understanding of the electronic structure of this oxo-V(IV)-Pc. Both α,α' -substituents and solvent polarities have large influence on the electronic structure of this NIR absorbed oxovanadium(IV)-phthalocyanine.

Keywords: Phthalocyanine, oxovanadium complexes, near infrared absorption, solvent polarity, magnetic circular dichroism, cyclic voltammetry, spectroelectrochemistry.

Влияние растворителя на спектральные, электрохимические и спектроэлектрохимические свойства α,α' -октапентоксифталоцианината оксованадия(IV), поглощающего в ближней ИК области

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В работе получен и охарактеризован оксованадий(IV)- α,α' -октапентоксифталоцианин, поглощающий в ближней ИК области. С помощью спектральных и электрохимических методов, включая спектроскопию электронного поглощения и магнитного кругового дихроизма, циклическую вольтамперометрию, дифференциальную пульсирующую вольтамперометрию, было показано, что природа α,α' -заместителей и полярность растворителя оказывают значительное влияние на электронную структуру полученного комплекса.

Ключевые слова: Фталоцианин, комплексы оксованадия, поглощение в ближней ИК области, полярность растворителя, магнитный круговой дихроизм, циклическая вольтамперометрия, спектроэлектрохимия.

Introduction

Currently, there are increased research interests in phthalocyanines (Pcs) including fundamental theories to industrial applications.^[1] The large π -system of phthalocyanines can lead to strong absorption and emission in the red/near-infrared (NIR) region, and exhibit relatively high molar extinction of the lowest energy $\pi \rightarrow \pi^*$ band (usually referred to as the Q band), which is considerably more intense than the corresponding bands in the spectra of porphyrins and tetraazaporphyrins.^[2] Although the red-shift of the Q bands of phthalocyanine can be achieved to longer wavelength region through fused-ring-expansion with benzene rings to form naphthalocyanine (Nc)^[3] and then anthracocyanine (Ac),^[4] the significant destabilization of HOMO level makes these compounds unstable. Additionally, the absence of peripheral substituents are also issues with solubility. In contrast, Pcs with substituents at both peripheral (β -) and non-peripheral (α -) positions generally exhibit enhanced solubility, especially the α -substituted Pcs revealed more satisfied results due to its deformed molecular structures.^[5] On the other hand, introduction of electron donating substituents at α -positions results in a greater destabilization of the highest occupied molecular orbital (HOMO) state relative to the lowest unoccupied molecular orbital (LUMO) state leading to the red-shift of the Q band absorption in metallophthalocyanines (MPcs) and hence lower first oxidation potentials, since there are large MO coefficients at these positions in the HOMO of the π -system.^[6] NIR phthalocyanines have excellent light, weather and thermal resistances, and these complexes find use in optical recording materials, liquid crystal display devices and IR radiation filters.^[7] Oxovanadium(IV)-phthalocyanines, the high-valence metallo-phthalocyanines have various potential applications such as optical active materials, non-linear optical materials and catalysis,^[8] but solvent dependent spectroscopic and electrochemical investigations have never been described before. In this paper, the solvent-dependent UV-vis, magnetic circular dichroism (MCD) spectra, cyclic voltammetry (CV), DPV and thin-layer spectroelectrochemistry will be described. The solvent-dependent spectroscopic, electrochemical and spectroelectrochemical properties indicate the polarities of the solvents have large effect on the electronic structure of NIR electron-rich, high-valence oxovanadium(IV)phthalocyanine.

Experimental

Chemicals

Analytical pure *N,N*-dimethylmethanamide (DMF) for electrochemical measurements was purchased from the Aladdin Reagent Company of Shanghai, and freshly distilled before use. All other chemicals and solvents were analytical pure grade and were purchased from the Shanghai Guoyao Company. All solvents were dried and distilled prior to use.

Materials and Instruments

¹H NMR spectra were recorded on a Bruker AVANCE 400 spectrometer (operating at 400.13 MHz) using the residual solvent as an internal reference for ¹H ($\delta = 5.32$ ppm for CD₂Cl₂). Cyclic voltammetry was performed in a three-electrode cell using Chi-730D

electrochemistry station. A glassy carbon disk electrode was utilized as the working electrode while a platinum wire and a saturated calomel electrode (SCE) were employed as the counter and reference electrodes, respectively. An "H" type cell with a fritted glass layer to separate the cathodic and anodic sections of the cell was used during bulk electrolysis. The working and counter electrodes were made from platinum mesh and the reference electrode was an SCE. The working and reference electrodes were placed in one compartment while the counter electrode was placed in the other. UV-visible absorption spectra were recorded with a HP 8453A diode array spectrophotometer. All of the electrochemical measurements were carried out under a nitrogen atmosphere. Magnetic circular dichroism (MCD) spectra were measured with a JASCO J-815 equipped with a 1.6 T (tesla) permanent magnet by using both the parallel and anti-parallel fields. The conventions of Piepho and Schatz are used to describe MCD intensity and the Faraday terms.^[9] Spectral pure grade *o*-dichlorobenzene, CH₂Cl₂ and DMF for spectroscopic and electrochemical measurements was purchased from the Aladdin reagent company of Shanghai. Other chemicals and solvents were of analytical pure grade and were obtained from the Shanghai Guoyao Co. which were dried or distilled prior to use.

Syntheses

Synthesis of 3,6-dipentoxyphthalonitrile. 3,6-Dihydroxyphthalonitrile (1.6 g, 10 mmol) was added to 20 mL of a dry acetone solution containing 1-iodopentane (4.4 g, 22 mmol, 2.2 eq.) and K₂CO₃ (5.5 g, 40 mmol, 4.0 eq). The resulting mixture was gradually heated to 60 °C, and the temperature was maintained for 4 h. After removal of the solvent, the reaction mixture was purified by silica gel column chromatography with CHCl₃ as the eluent. Recrystallization from CHCl₃ and MeOH provided 3,6-dipentoxyphthalonitrile as a white solid compound in 88 % yield (2.64 g). ¹H NMR (400 MHz, CDCl₃) δ ppm: 7.15 (s, 2H; β -phenyl), 4.04 (t, $J = 8.0$ Hz, 4H; -OCH₂-), 1.84 (dd, $J_1 = 12.0$ Hz, $J_2 = 8.0$ Hz, 4H; -CH₂-), 1.49-1.35 (m, 8H; -CH₂CH₂-), 0.93 (t, $J = 8.0$ Hz, 6H; -CH₃).

Synthesis of α, α' -*n*-octapentoxyphthalocyanine (*H₂Pc*). Lithium (56 mg, 8.0 mmol) was added to 6 mL of freshly distilled 1-butanol, and the solution was stirred and heated at 150 °C under an N₂ atmosphere until the lithium was completely dissolved. 3,6-Dipentoxyphthalonitrile (300 mg, 1.0 mmol) was then added and the resulting mixture was gradually heated at 160 °C, and the temperature was maintained for 2 h. After removal of the solvent, the reaction mixture was purified by silica gel column chromatography with CHCl₃:MeOH (100:3) as the eluent. Recrystallization from CHCl₃ and MeOH provided the target compound, as a green solid in 63 % yield (2.64 g). MALDI-TOF-MS: $m/z = 1203.78$ (Calcd. for C₇₂H₉₈N₈O₈ [M+H]⁺ = 1203.70). ¹H NMR (500 MHz, CD₂Cl₂) δ ppm: 7.49 (m, 8H; β -phenyl), 4.82 (m, 16H; -OCH₂-), 2.19 (m, 16H; -CH₂-), 1.64-1.48 (m, 32H; -CH₂CH₂-), 1.09-0.85 (m, 24H; -CH₃).

Synthesis of oxo-*V*(IV)- α, α' -octapentoxyphthalocyanine (oxo-*V*(IV)*Pc*, **1).** Following the method reported by Leznoff^[10] and Kasuga^[11] cyclic tetramerization of α, α' -pentoxyphthalonitrile, and a metal insertion reaction with V₂O₅ in molten urea gave oxo-*V*(IV) *Pc* quite easily in a yield 35.6 %, and the structure was confirmed by MALDI-TOF-mass and ¹H NMR spectra (Figure 1). MALDI-TOF-mass: $m/z = 1269.13$ (Calcd. [M+H]⁺ = 1269.52). ¹H NMR (CD₂Cl₂, 298 K) δ ppm: 8.52 (br s, 8H; β, β' -H), 4.94 (br s, 16H; -OCH₂-), 2.29 (br s, 16H; -CH₂-), 1.69~1.52 (br s, 32H; -CH₂-), 1.02 (br s, 24H; -CH₃).

Results and Discussion

Solvent Dependent Spectroscopy

The spectroscopic properties of oxo-*V*(IV)*Pc* in both low-polar solvent CH₂Cl₂ and polar solvent DMF are shown

in Figure 2. The UV-vis spectra of **1** is characteristic sharp of metallo-phthalocyanines, but the Q bands lie at a significantly longer wavelength than those of normal oxo-V(IV)Pcs without substituent groups ($\lambda = 695$ nm in chlorobenzene).^[12] In the low-polar solvent CH_2Cl_2 (Figure 2, left, bottom), the Q-band absorption of oxo-V(IV)Pc exhibits main absorption bands at 788 and 703 nm. The Soret band of **1** appears at 338 nm, and an extra band at 479 nm can be assigned as intramolecular charge-transfer band. In the case of oxo-V(IV)Pc in DMF (Figure 2, right, bottom), the Q-band absorption exhibits a mirror red-shift to 792 nm. Similarly, the Soret band appears at 349 nm and the charge transfer band appears at 473 nm. On the other hand, the magnetic circular dichroism (MCD) spectra of oxo-V(IV)Pc is also typical of metallo-phthalocyanines,^[13] showing a clear Faraday *A*-term type of curve associated with the Q_{00} absorption peak at $\lambda = 788$ nm in CH_2Cl_2 (Figure 2). In the Soret band region, three bands were observed at $\lambda = 336, 358$ and 498 nm, and the additional band at around 490 nm can be plausibly assigned to a transition involving the ether oxygen lone pairs $n-\pi^*$ transition.^[14] Similar shape of the MCD signals of oxo-V(IV)Pc in DMF were observed, but slightly shifted to the longer wavelength region. The assigned Faraday *A*-term type of curve associated with the Q_{00} absorption peak at $\lambda = 792$ nm in DMF was detected (Figure 2), and Soret bands were appeared at $\lambda = 323, 369$ and 410 nm, respectively. Solvent dependent UV-vis measurements (Figure 3) were also carried in various organic solvents containing different solvent polarities, including CH_2Cl_2 , toluene, ethylacetate, DMF and benzonitrile in order to further insight understand the solvent dependent spectroscopic properties of this oxo-V(IV)Pc **1**. It is known that the red-shift of the Q-band absorptions is a function of the solvent's refractive index,^[15] and Table 1 also shows the red-shift of the Q-band absorptions based on the increase of the solvent polarities.

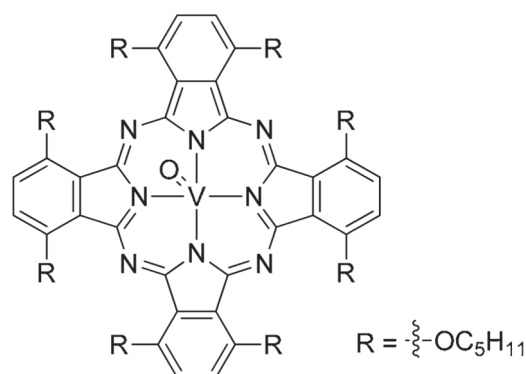
Solvent Dependent Electrochemistry

Electrochemical measurements were performed to give further in-depth understand of the electronic properties of this α, α' -substituted phthalocyanines, since it is well established that the HOMO and LUMO energies of phthalocyanine derivatives correlate well with their first oxidation and reduction potentials. Electrochemical measurements were carried out in low-polar solvent *o*-dichlorobenzene and polar solvent DMF containing 0.1 M TBAP to gain further insight into the electronic properties, and the redox potentials $E_{1/2}$ values derived cyclic and differential pulse voltammetry (CV and DPV) measurements. The voltammograms for oxo-V(IV)Pc in low-polar *o*-dichlorobenzene (Figure 4) contain two reversible one-electron reduction steps at $E_{1/2} = -0.71$ V for $[\text{oxo-V(IV)Pc}]/[\text{oxo-V(III)Pc}]$, and at $E_{1/2} = -1.06$ V for the ring reduction $[\text{oxo-V(III)Pc}]/[\text{oxo-V(III)Pc}]^{2-}$, respectively, under these experimental conditions. One more irreversible reduction at $E_{1/2} = -1.85$ V derived from DPV measurement can be assigned as further ring reduction $[\text{oxo-V(III)Pc}]^{2-}/[\text{oxo-V(III)Pc}]^{3-}$. Additionally, two reversible one-electron oxidation curves are also observed at $E_{1/2} = 0.64$ and 1.03 V assigned as the ring oxidation $[\text{oxo-V(IV)Pc}]/[\text{oxo-V(IV)Pc}]^+$ and $[\text{oxo-V(IV)Pc}]/[\text{oxo-V(IV)Pc}]^{2+}$ for 1st and 2nd oxidation steps, respectively. More interesting, the voltammo-

grams for oxo-V(IV)Pc in polar solvent DMF (Figure 4) exhibit similar shape of the spectra, but the oxo-V(IV)Pc complex is more easily reached the 1st oxidation and 1st reduction processes, at 0.58 V and -0.67 V, respectively. The energy difference between the 1st oxidation and 1st reduction in polar DMF solution is smaller than that in low-polar *o*-DCB during the CV measurements (Scheme 2), that is also reflected in the red-shift of the main absorption band in polar solvents during the optically spectroscopic measurements. Compared with other vanadium phthalocyanines reported previously, this oxo-V(IV)Pc **1** with electron donating substituents introduced at α, α' -positions, is easily oxidized than the complexes without electron donating groups at α, α' -positions (Table 2). The i_p^{Red} and i_p^{Ox} values, determined from CV measurements of **1** made at various scan-rates from 10-500 mV in both low-polar CH_2Cl_2 and polar DMF (Figure 5), provide an insight into the reversibility of the system on an experimental time-scale. The good linear correlations observed for plots of peak current versus $v^{1/2}$ for oxo-V(IV)Pc (Figure 6) confirm that all of the oxidation and reduction processes are diffusion controlled.

Solvent Dependent Spectroelectrochemistry

In order to confirm further the effect of the solvent polarities on the spectroelectrochemistry properties, thin-layer UV-visible spectra during the first and second reduction and/or oxidation of oxo-V(IV)Pc **1** were carried out in both low polar solvent *o*-dichlorobenzene and polar solvent DMF. The comparison of spectral changes at different potential values for reversible processes were shown in Figure 7. During the first reduction process, the electroreduced oxo-V(IV)Pc **1** reveals the significant decrease of the main absorption band (Q-band), but the further increase of the additional bands in the visible region in the DMF solution. In addition to measure the spectral changes of further electroreduced oxo-V(IV)Pc **1**, the changes were only observed in the DMF measurements, and this clearly show that the solvent effects have large influence on the electroreduced spectral changes. The electrooxidized spectral changes were also measured in both *o*-dichlorobenzene and DMF, no significant difference was observed based on the different solvent measurements. Since the 2nd oxidation process of **1** in DMF is irreversible, thus the spectroelectrochemistry was not further proceeded under this experiment conditions.



Scheme 1. Molecular structure of oxo-V(IV)Pc.

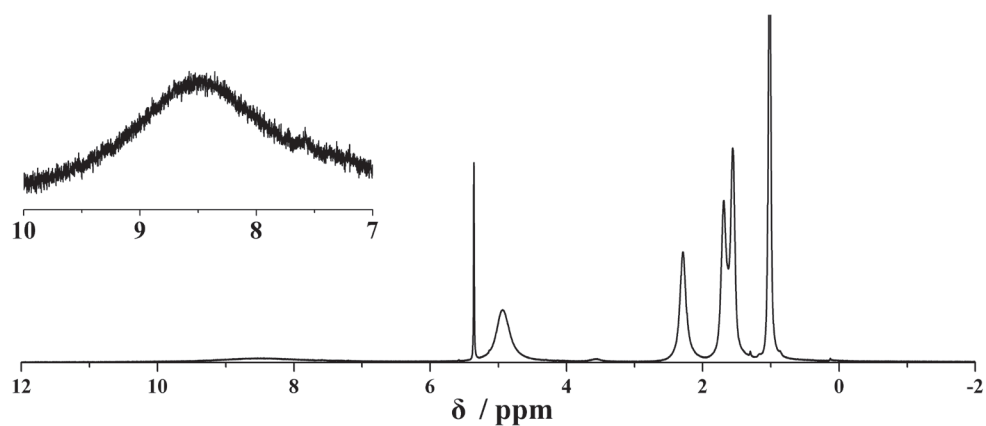


Figure 1. ^1H NMR spectra of **1** in CD_2Cl_2 .

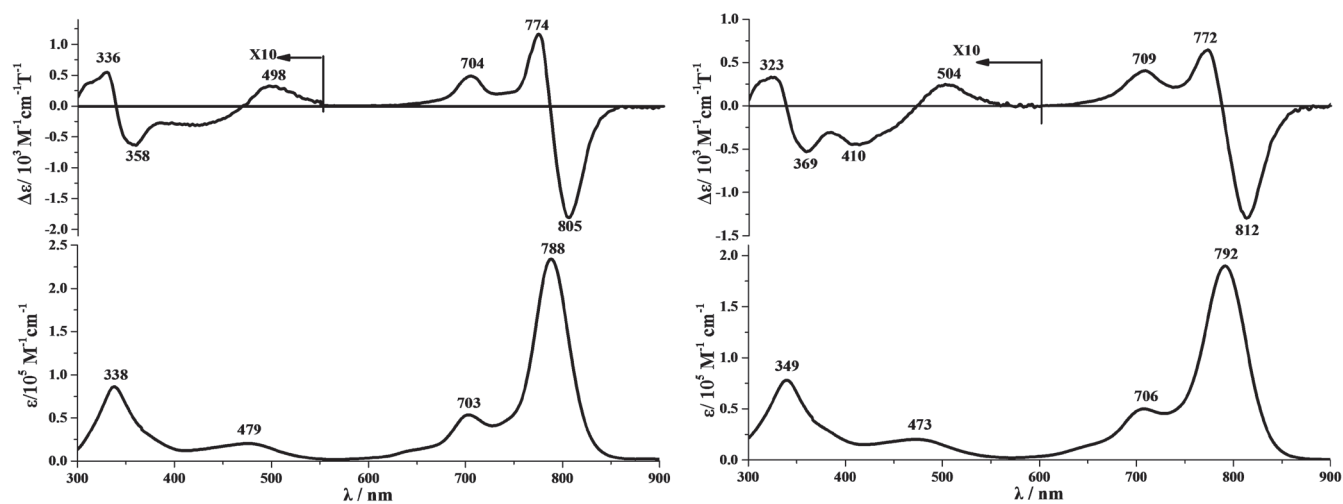
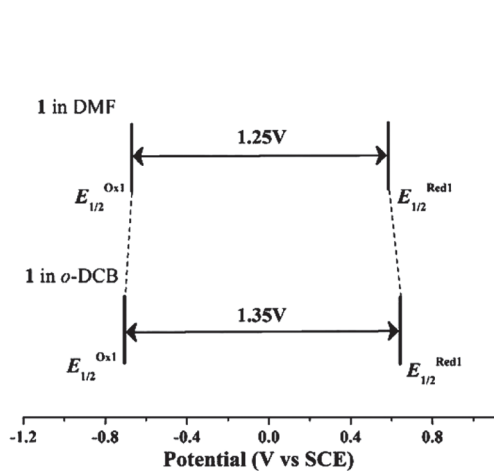


Figure 2. UV-vis absorption and MCD spectra of **1** in CH_2Cl_2 (up) and DMF (bottom).



Scheme 1. Energy difference of electrochemistry measurements in low-polar *o*-DCB and polar DMF of oxo-V(IV)Pc.

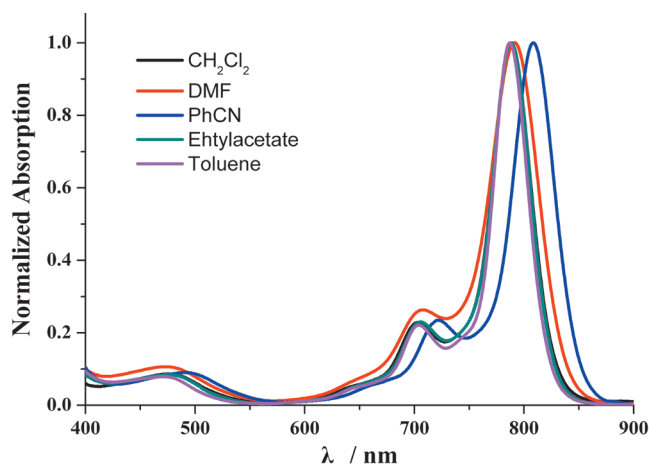


Figure 3. Q-band absorptions of UV-vis spectra of oxo-V(IV)Pc in various organic solvents.

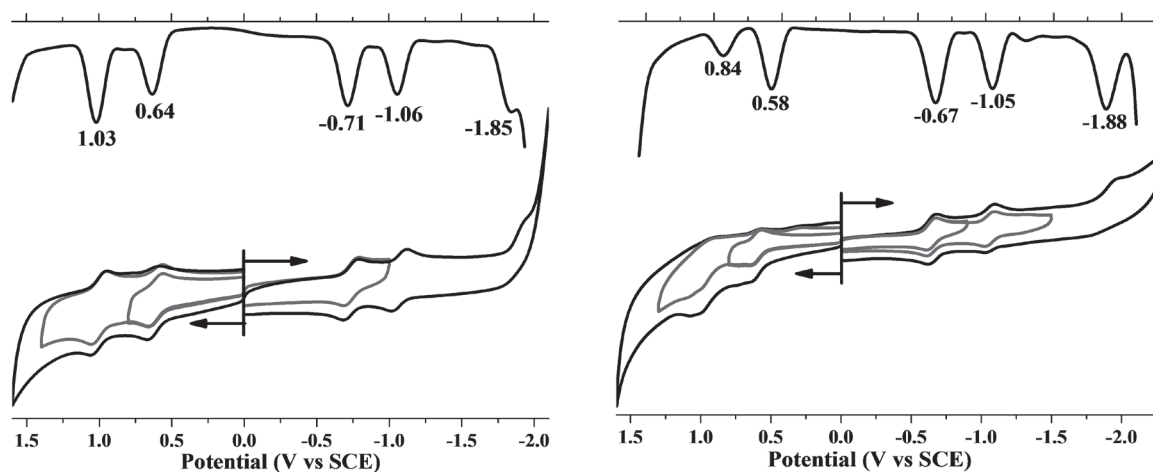


Figure 4. Cyclic voltammetry (CV) and DPV measurements of oxo-V(IV)Pc in *o*-dichlorobenzene (left) and DMF (right).

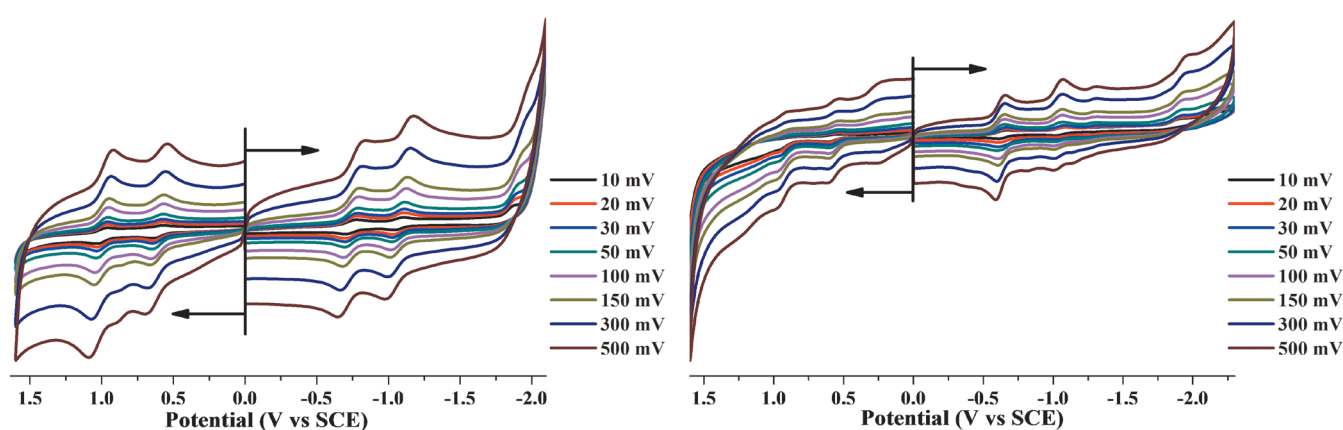


Figure 5. Multi-scan rate of cyclic voltammetry (CV) measurements of oxo-V(IV)Pc in *o*-dichlorobenzene (left) and DMF (right).

Table 1. Values of Q-band UV-vis absorptions of oxo-V(IV)Pc in various solvents.

	CH ₂ Cl ₂	Toluene	Ethylacetate	DMF	PhCN
Oxo-V(IV)Pc 1	788 nm	787 nm	789 nm	792 nm	810 nm

Table 2. Electrochemistry measurements of various oxo-V(IV)Pc derivatives.

Molecular Structure	Solvent	Reduction			Oxidation		Ref.
		V ^{III} Pc ²⁺ /V ^{III} Pc ³⁺	V ^{III} Pc ²⁺ /V ^{III} Pc ³⁺	V ^{III} Pc ³⁺ /V ^{III} Pc ⁴⁺	V ^{III} Pc ³⁺ /V ^{III} Pc ⁴⁺	V ^{III} Pc ³⁺ /V ^{III} Pc ⁴⁺	
Oxo-V(IV)Pc	<i>o</i> -DCB	-1.85	-1.06	-0.71	0.64	1.03	This work
OV[Pc(Bu) ₄]	CH ₂ Cl ₂	-	-1.08	-0.58	0.94	-	[16]
OV(PcF ₁₆)	CH ₂ Cl ₂	-1.41	-0.62	-0.29	0.85 ^a	-	[17]
OV[Pc(SC ₅ H ₁₁) ₈]	CH ₂ Cl ₂	-1.14	-0.89	-0.54	0.68	1.02	[18]
Oxo-V(IV)Pc	DMF	-1.88 ^a	-1.05	-0.67	0.58	0.84	This work
OV[Pc(OC ₆ H ₃ (<i>t</i> -Bu) ₂) ₄]	DMF	-2.07	-1.12	-0.62	0.76	1.21	[19]
OV[Pc(C ₈ H ₁₇) ₄]	DMF	-1.94	-0.97	-0.51	0.94	1.34	[19]

a: irreversible processes

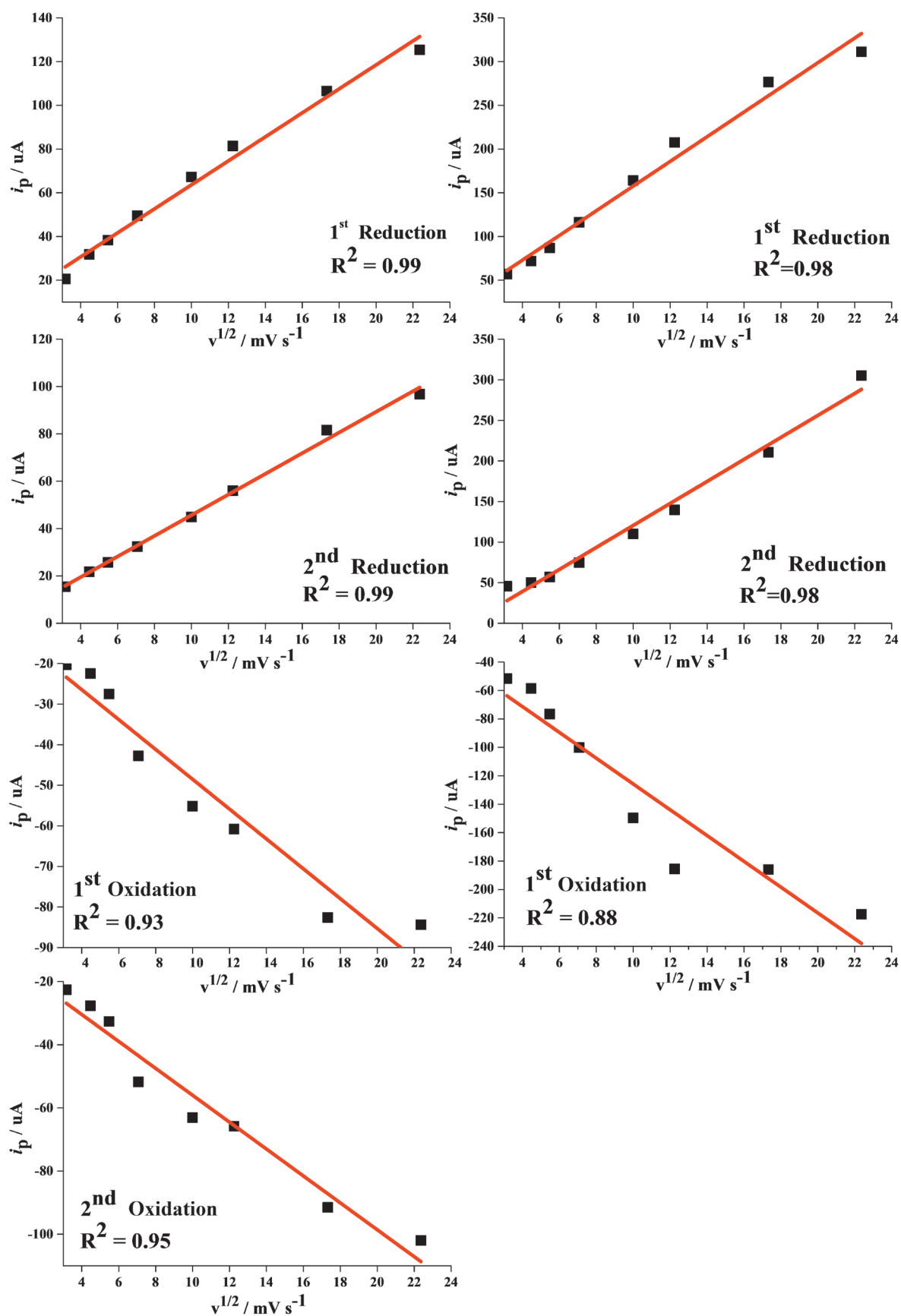


Figure 6. The dependence of square root of the scan-rate ($v^{1/2}$) on the peak current (i_p) for the all oxidations and reductions of oxo-V(IV)Pc in *o*-dichlorobenzene (up) and DMF (bottom) containing 0.1 M TBAP.

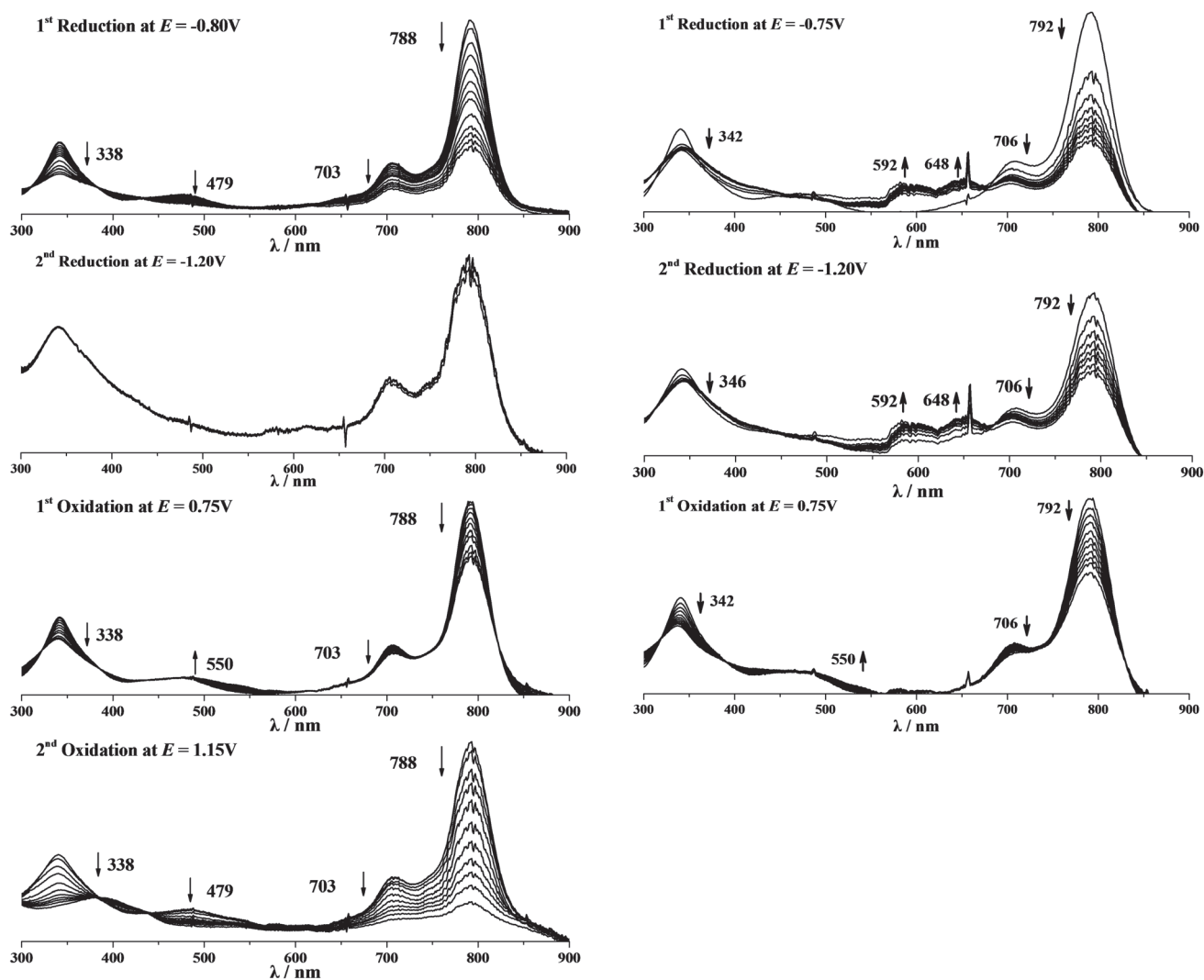


Figure 7. Thin-layer UV-visible spectral changes obtained during the second reduction and/or oxidation of oxo-V(IV)Pc in *o*-dichlorobenzene and DMF.

Conclusions

A oxo-V(IV)Pc having main absorption band at NIR region has been synthesized and characterized. Solvent dependent spectroscopy, electrochemistry and spectroelectrochemistry studies were carried out including UV-vis, magnetic circular dichroism (MCD) spectra, CV, DPV, multi-scan rate CV and thin-layer spectroelectrochemistry to give detailed understanding the effect of the substituents and solvent polarities on the electronic structures of this near-infrared oxo-V(IV)Pc. Considered NIR phthalocyanines have a wide range of potential applications in various high-tech fields, such as NIR optical recording materials and in IR radiation filters. The studies about solvent dependent electronic structure provide useful information for future rational molecular design, characterization, and potential applications.

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References

- Mack J., Kobayashi N. *Chem. Rev.* **2011**, *111*, 281–321;
 - Claessens C.G., Hahn U., Torres T. *Chem. Rec.* **2008**, *8*, 75–97;
 - Jiang Y., Li M.Z., Liang X., Mack J., Wildervanck M., Nyokong T., Qin M.F., Zhu W.H. *Dalton Trans.* **2015**, *44*, 18237–18246;
 - Gao Y., Chen Y., Li R., Bian Y., Li X., Ji-ang J. *Chem. Eur. J.* **2009**, *15*, 13241–13252;
 - Wang R., Li R., Li Y., Zhang X., Zhu P., Lo P., Ng D.K.P., Pan N., Ma C., Kobayashi N., Jiang J. *Chem. Eur. J.* **2006**, *12*, 1475–1485.
 - Liu Q., Li Y., Liu H., Chen Y., Wang X., Zhang Y., Li X., Jiang J. *J. Phys. Chem. C* **2007**, *111*, 7298–7301.
 - Gao Y., Li R., Dong S., Bian Y., Jiang J. *Dalton Trans.* **2010**, *39*, 1321–1327;
 - Wohrle D., Meissner D. *Adv. Mater.* **1991**, *3*, 129–138;
 - Rostalki J., Meissner D. *Sol. Energy Mater. Sol. Cells* **2000**, *63*, 37;
 - Koeppe R., Sariciftci N.S., Troshin P.A., Lyubovskaya R.N. *Appl. Phys. Lett.* **2005**, *87*, 244102;
 - Torre G., Vazquez P., Agullo-Lopez F., Torres T. *Chem. Rev.* **2004**, *104*, 3723–3750.
- Linstead R.P., Whalley M.J. *J. Chem. Soc.* **1952**, 4839–4846;
 - Shimizu S., Haseba Y., Yamazaki M., Kumazawa G., Kobayashi N. *Chem. Eur. J.* **2014**, *20*, 4822–4828;
 - Mack J.,

- Sosa-Vargas L., Coles S.J., Tizzard G.J., Chambrier I., Cammidge A.N., Cook M.J., Kobayashi N. *Inorg. Chem.* **2012**, *51*, 12820–12833; (d) Donzello M.P., Ercolani C., Gaberkorn A.A., Kudrik E.V., Meneghetti M., Marcolongo G., Rizzoli C., Stuzhin P.A. *Chem. Eur. J.* **2003**, *9*, 4009–4024; (e) Ayhan M.M., Özpınar G.A., Durmuş M., Gürek A.G. *Dalton Trans.* **2013**, *42*, 14892–14904; (f) Safonova E.A., Martynov A.G., Nefedov S.E., Kirakosyan G.A., Gorbunova Y.G., Tsivadze A.Y. *Inorg. Chem.* **2016**, *55*, 2450–2459.
3. Bradbrook E.F., Linstead R.P. *J. Chem. Soc.* **1936**, 1739–1744.
 4. Freyer W., Minh L.Q. *Monatsh. Chem.* **1986**, *117*, 475–489.
 5. *The Porphyrin Handbook, Properties and Materials* (Kadish K.M., Smith K.M., Guillard R., Eds.). New York: Academic Press, **2003**, Chapter 17.
 6. Christie R.M. *Dyes Pigm.* **1995**, *27*, 35–43.
 7. (a) Lim B., Bloking J.T., Ponc A., McGehee M.D., Sellinger A. *ACS Appl. Mater. Interfaces* **2014**, *6*, 6905–6913; (b) Sun Y.Q., Liu J., Lv X., Liu Y.L., Zhao Y., Guo W. *Angew. Chem. Int. Ed.* **2012**, *51*, 7634–7636.
 8. Eguchi K., Nakagawa T., Takagi Y., Yokoyama T. *J. Phys. Chem. C* **2015**, *119*, 9805–9815.
 9. (a) Piepho S.B., Schatz P.N. *Group Theory in Spectroscopy with Applications to Magnetic Circular Dichroism*, New York: Wiley, **1983**; (b) Mack J., Stillman M.J., Kobayashi N. *Coord. Chem. Rev.* **2007**, *251*, 429–453.
 10. Leznoff M., Hu C.R., McArthur Y., Qin Y., van Lier J.E. *Can. J. Chem.* **1994**, *72*, 1990–1998.
 11. Kasuga K., Kawashima M., Asano K., Sugimori T., Abe T., Kikkawa K.T., Fujiwara T. *Chem. Lett.* **1996**, 867–868.
 12. Freyer W., Minh L. Q. *J. Prakt. Chem.* **1987**, *329*, 365–373.
 13. (a) Stillman M.J., Nyokong T. In: *Phthalocyanines: Properties and Applications*, Weinheim: VCH, **1989**, Chapter 3; (b) In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Guillard R., Eds.). New York: Academic Press, **2003**, Chapter 103; (c) Michl J. *J. Am. Chem. Soc.* **1978**, *100*, 6801–6811; (d) Michl J. *J. Am. Chem. Soc.* **1978**, *100*, 6812–6818; (e) Ceulemans A., Oldenhof W., Gçriller-Walrand C., Vanquickenborne L.G. *J. Am. Chem. Soc.* **1986**, *108*, 1155–1163.
 14. Guo L., Ellis D.E., Hoffman B.M., Ishikawa Y. *Inorg. Chem.* **1996**, *35*, 5304–5312.
 15. Ogunsipe A.O., Maree M.D., Nyokong T. *J. Mol. Struct.* **2003**, *650*, 131.
 16. Lever A.B.P., Milaeva E.R., Speier G. In: *Phthalocyanines: Properties and Applications*, New York: VCH Publishers, **1993**, Vol. 3.
 17. Handa M., Suzuki A., Shoji S., Kasuga K., Sogobe K. *Inorg. Chem. Acta* **1995**, *230*, 41.
 18. Mbambisa G., Nyokong T. *Polyhedron* **2008**, *27*, 2799–2804.
 19. Jiang Z., Ou Z. P., Chen N., Wang W., Huang J., Shao J., Kadish K.M. *J. Porphyrin Phthalocyanines* **2005**, *9*, 352.

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