

Molecular and Electronic Structure, and Electrochemical Study of Oxometal(IV) Tetrabenzoporphyrins, [TBPM] (M = VO, TiO)

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Complexes of tetrabenzoporphyrin (TBP) with vanadyl and titanyl were prepared by complexation directly from metal free H₂TBP. They were characterized using spectral and electrochemical methods and peculiarities of their molecular and electronic structure were investigated by DFT calculations. Properties of MTBP complexes were compared with corresponding complexes of meso- and β-substituted porphyrins, porphyrazines and phthalocyanines. It is shown that fusion of benzene rings strongly facilitates the oxidation process which occurs at +0.3 V, what is much easier than in the case of the corresponding porphyrins (by 0.4 - 0.5 V) and phthalocyanines (by 0.5-0.7 V). At the same time the reduction of tetrabenzoporphyrin complexes is observed at similar potentials as in the case of meso-aryl and β-alkyl substituted porphyrins (0.9-1.2 V), and by 0.4-0.6 V more difficult than in the case of phthalocyanine complexes. The obtained data evidence that VO and TiO complexes of tetrabenzoporphyrins can be used as donors in organic electronics.

Keywords: Tetrabenzoporphyrin, cyclic voltammetry, sTDDFT, electronic spectra.

Молекулярное и электронное строение и электрохимическое исследование тетрабензопорфиринато(оксо)металлатов(IV), [TBPM] (M = VO, TiO)

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Комплексы тетрабензопорфирина (ТБР) с ванадилем и титанилом получены комплексообразованием из безметалльного макроцикла H₂TBP. Изучены их спектральные и электрохимические свойства в растворах, а особенности их молекулярной структуры и электронного строения исследованы с помощью квантово-химических расчетов методом DFT. Проведено сравнение свойств полученных комплексов тетрабензопорфирина с аналогичными комплексами мезо- и β-замещенных порфиринов, порфиразинов и фталоцианина. Показано, что аннелирование бензольных колец сильно облегчает процесс окисления, протекающий при +0,3

B, значительно легче, чем в случае соответствующих порфиринов (на 0,4–0,5 В) и фталоцианинов (на 0,5–0,7 В). В то же время восстановление тетрабензопорфириновых комплексов наблюдается при тех же потенциалах, что и в случае мезо-арил- и β-алкиламещенных порфиринов (0,9–1,2 В), и на 0,4–0,6 В труднее, чем в случае фталоцианиновых комплексов. Полученные данные свидетельствуют о возможности использования комплексов тетрабензопорфиринов с VO и TiO в качестве доноров в органической электронике.

Ключевые слова: Тетрабензопорфирин, циклическая вольтамперометрия, sTDDFT, электронные спектры.

Introduction

Porphyrins and phthalocyanines are two main classes of tetrapyrrolic compounds. Porphyrins are widespread in nature, while phthalocyanines (PCs) are obtained exclusively synthetically. The transition link between these compounds are tetrabenzoporphyrins (TBP) (Figure 1). TBP complexes were investigated as donors for thin-film organic electronics,^[1,2] field-effect transistors,^[3–5] fluorescent pH sensors,^[6] IR-luminescent sensors for *in vivo* oxygen content measurement,^[7] and in other fields.^[8]

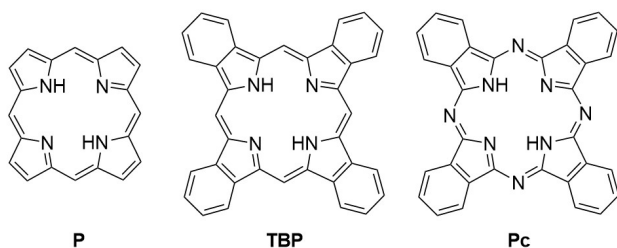


Figure 1. Structural formula of porphyrin (P), tetrabenzoporphyrin (TBP) and phthalocyanine (Pc).

A number of theoretical quantum chemical calculations of tetrabenzoporphyrin (TBP) have been conducted,^[9–12] in which TBP is considered as having intermediate structure between porphyrin and phthalocyanine.^[13] Despite its structural similarity to phthalocyanine, electronic structure of TBP is closer to porphyrins.^[10–11] Overall, only the zinc complex and non-metallic TBP have been extensively studied, while other metal complexes have been subject of limited experimental and theoretical investigations.^[5,7,8,15,17,18] Electrochemistry of substituted TBP complexes with Zn^{II} and Pt^{II} have been studied by Kadish and co-authors.^[14–15] Despite the possible discrepancy between the HOMO-LUMO gap estimated from the TBP redox experiment and the true band gap of the thin layer,^[19] cyclovoltammograms (CVs) are often used to estimate the latter in organic photovoltaics.^[1,19] Previously vanadyl and titanyl TBP complexes were obtained by pyrolysis of corresponding complexes of porphyrin with fused bicyclo-[2.2.2]octadiene units.^[20] This approach is limited by difficult and multistep synthesis of tetra(bicyclo[2.2.2]-octadieno)porphyrin complexes. In our work, we used a more direct and easy approach to the synthesis of vanadyl and titanyl complexes by direct metallation of metal-free tetrabenzoporphyrin. This approach allows the use of more accessible starting reagents, since the starting compound is obtained through the reaction of template synthesis of a

zinc complex ZnTBP from phthalimide and a zinc(II) acetate and its subsequent demetallation.^[19]

In this study, TBP complexes with vanadyl and titanyl were studied using cyclovoltammetry (CV) and their molecular and electronic structure was calculated using density functional theory (DFT) method, and a comparative analysis of the obtained results was conducted. Our work allowed for a more precise understanding of the electronic structure and properties of TBP complexes with different transition metals, which may be useful for further development in thin-film organic electronics and other applications.

Experimental

General

UV–Vis spectra were recorded using a Jasco V-770 UV-Vis spectrophotometer in DMF. Electrochemical studies were performed in a three electrode electrochemical cell with a glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode on a potentiostat Elins P-4. The DMF solution containing 0.1 M tetrabutylammonium perchlorate as supporting electrolyte was deoxygenated with argon. The reference Fc/Fc⁺ couple was observed at +0.53 V vs. Ag/AgCl.

Synthesis

Tetrabenzoporphyrin, H₂TBP, was prepared following the previously reported procedure.^[17] All other chemicals for the syntheses were purchased from certified suppliers (*i.e.*, Sigma-Aldrich, EKOS-1) and used as received.

Titanyl tetrabenzoporphyrinate, TiOTBP. 200 mg (0.4 mmol) of H₂TBP and 100 mg (0.5 mmol) of TiCl₄ were refluxed for 1 hour in quinoline under argon atmosphere. Reaction mixture was poured into EtOH and washed 5 times by 50 mL of solvent. Then resulting black powder was washed by diethylether and dried. Yield: 180 mg (79%). MALDI-TOF (positive) *m/z*: 572.8 [M]⁺ (calcd. for C₃₆H₂₀N₄O₂Ti 572.1). UV-Vis (DMF) λ nm (A/A_{max}): 636(0.41), 436(1).

Vanadyl tetrabenzoporphyrinate, VOTBP, was prepared analogously to TiOTBP from 200 mg (0.4 mmol) of H₂TBP and 80 mg (0.5 mmol) of VCl₃. Yield: 200 mg (86%). MALDI-TOF (CHCA matrix) *m/z*: 575.6 [M]⁺ (calcd. for C₃₆H₂₀N₄OV 575.1). UV-Vis (DMF) λ nm (A/A_{max}): 636(0.49), 444(1).

Computational details

Quantum chemical calculations included the geometry structure optimization of VOTBP and TiOTBP by density functional theory (DFT, functional CAM-B3LYP^[21] combined with def2TZVP basis set^[22] taken from EMSL BSE library^[23–25]). The simplified time-dependent density functional theory (sTDDFT) approach^[26,27] implemented in ORCA 5.0.3 software^[28,29] was employed to simulate the electronic absorption spectra due to it

can deal with the open-shell compounds such as VOTBP. RIJCOSX approximation^[30] was used to accelerate hybrid DFT computations utilizing tighter-than-default DEFGRID3 integration grid. For taking into account the solvent effects, the solvation model based on density (SMD) approach^[31] with the default parameters for the DMF solvent was applied.

Results and Discussion

Synthetic aspects

Our synthetic route (Scheme 1) differs from the one presented in the paper,^[20] where porphyrin with fused bicyclo[2.2.2]octadiene units was metallated and converted into corresponding tetrabenzoporphyrin complex. Although the yields of these two stages are high (90%), the bicyclic porphyrin precursor was obtained in a 5-stage synthesis starting with the Diels–Alder reaction of ((2-nitrovinyl)sulfonyl)benzene with cyclohexadiene-1,3 (yield 80%). The bicyclic pyrrolic precursor was then obtained with ~60% yield and converted to metal free porphyrin with four bicyclic units in 3-steps with 20–30% yield. The overall yield of this multistep procedure is 10–15%. We use another approach starting from direct reaction of phthalimide and Zn^{II} acetate affording ZnTBP, which was then demetallated in concentrated sulfuric acid affording H₂TBP (overall yield 30%). Following complexation with the corresponding metal chloride in quinolone, similarly to the method used for vanadyl complex of tetracrownphthalocyanine,^[32] afforded the target vanadyl and titanyl TBP complexes in three step procedure with overall yield ~24%. MALDI mass-spectra of the obtained VO and TiO complexes contain peaks of molecular ion at 575.6 and 572.8 Da, respectively, and their isotopic distribution pattern corresponds to the theoretical one (see

Figures S2 and S3). UV-Vis spectral data are in agreement with those previously reported.^[20]

Molecular structure

Previously we have studied by DFT method the molecular structure of tetrabenzoporphyrin complexes with Zn^{II} and Fe^{II}.^[33,34] It was established that these complexes have a planar structure of D_{4h} symmetry. According to quantum chemical calculations, the vanadyl and titanyl complexes possess a doming distortion with C_{4v} symmetry since it contains axial oxygen atom and the metal atom is located above the (N_p)₄ plane by 0.504 and 0.553 Å for VOTBP and TiOTBP, respectively (Figure 2). The values of the internuclear distances C–C and C–N for VOTBP and TiOTBP are close to such in ZnTBP and FeTBP (Table 1). The most difference is observed for C_β–C_β bond distance and does not exceed 0.008 Å. Therefore, we can note that the metal nature slightly affects on the geometry of macrocyclic core as was found for some other macrocyclic compounds.^[33,35–37]

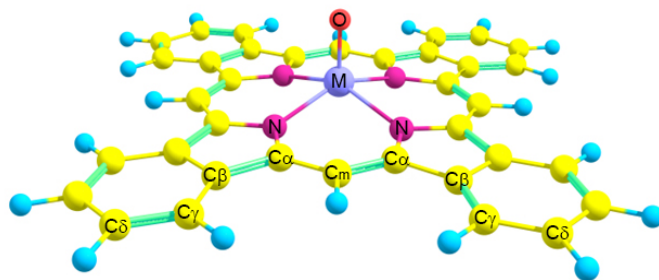
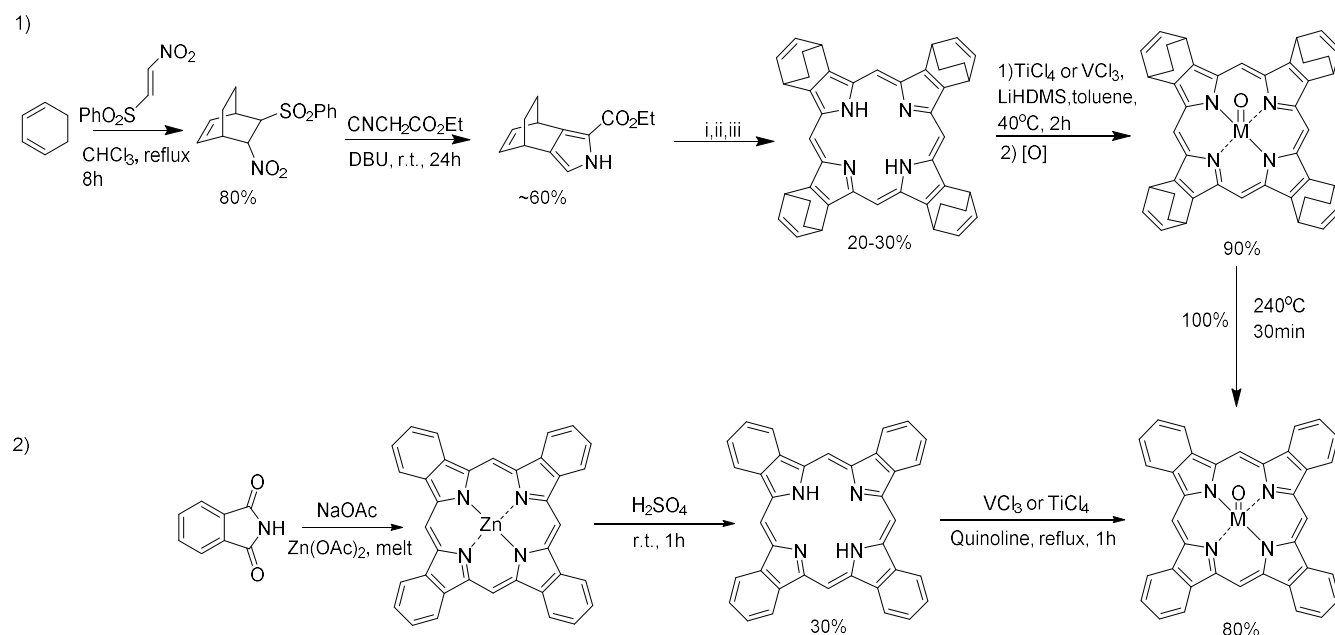


Figure 2. Molecular structure of vanadyl and titanyl tetrabenzoporphyrin calculated at CAM-B3LYP/def2-TZVP level of theory.



Scheme 1. Synthetic rows for MTBP (M = VO, TiO): 1) reported earlier,^[20] reaction conditions: i, LiAlH₄, THF, 0 °C, 3 h; ii, *p*-TsOH, CHCl₃, room temp., 24 h; iii, *p*-chloranil, CHCl₃, room temp., 48 h; 2) Method presented in this work.

Table 1. Selected parameters of TiOTBP and VOTBP calculated at CAM-B3LYP/def2-TZVP level of theory.

Parameter	TiOTBP	VOTBP
Internuclear distances, Å		
r(M–N)	2.135	2.101
r(M–O)	1.598	1.557
r(M–X) ^a	0.553	0.504
r(N–C _α)	1.364	1.365
r(C _α –C _m)	1.380	1.376
r(C _α –C _β)	1.447	1.445
r(C _β –C _β)	1.395	1.393
r(C _β –C _γ)	1.392	1.392
r(C _γ –C _δ)	1.377	1.377
r(C _δ –C _δ)	1.401	1.401
Valence angles, °		
a(M–N–C _α)	124.9	125.3
a(O–M–N)	105.0	103.9
a(N–C _α –C _m)	125.7	125.7
a(N–C _α –C _β)	109.2	109.7
a(C _α –C _m –C _α)	127.3	126.5

^aX is a dummy atom, placed in the center between opposite nitrogen atoms

The distances M–N are 2.101 and 2.135 Å for VOTBP and TiOTBP, respectively, while the values of M=O distances are 1.557 and 1.598 Å. Such elongation in TiOTBP as compared to VOTBP can be explained by a higher ionic radius of titanium.^[41]

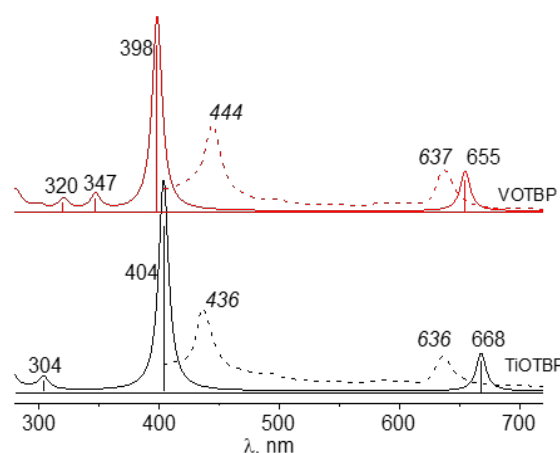
The parameters of the square-pyramidal surrounding of the metal in these TBP complexes obtained by DFT method can be compared with data^[38,40] available for complexes of vanadyl and titanyl with other porphyrins and phthalocyanines.

The larger dimensions of the N₄ coordinating core in tetrabenzoporphyrin macrocycle as compared to phthalocyanines (tetrabenzoporphyrines) leads to smaller withdrawal of metal atoms from the mean N₄ plane (0.504 Å for VOTBP vs 0.591 Å for VOPc^[38] and 0.553 Å for TiOTBP vs 0.649 Å for TiOPc^[40]). At the same time the M...(N)₄ distance in VOTBP is larger and in TiOTBP smaller than in the corresponding β-substituted porphyrins (0.481 Å for VO complex of etioporphyrin III,^[39] and 0.5772 Å for TiO complex of octamethylporphyrin^[40]). This might be explained by different impact of the π-coordination effects in the VO and TiO complexes in β-substituted and β,β-benzo fused porphyrins. The M–O distance in the case of both vanadyl and titanyl TBP complexes is the smallest in comparison with the corresponding complexes of porphyrins and phthalocyanine: VOTBP (1.557 Å) < VOPc (1.574 Å) < VOetioPIII (1.593 Å) and TiOTBP (1.598 Å) < TiOOMP (1.616 Å) ~ TiOPc (1.617 Å). Therefore M=O bond is stronger in TBP complexes.

Electronic absorption spectra

The absorption spectra of VOTBP and TiOTBP show a typical behavior for porphyrin complexes with the most

intense B-band at ~430 nm and Q band at ~630 nm (Figure 3). According to TD DFT calculations (Table 2) the Q-band can be assigned to the transitions from highest occupied molecular orbital (HOMO) to the double-degenerated lowest unoccupied molecular orbital (LUMO) for both VOTBP and TiOTBP. The electron transitions from HOMO-1 to LUMO make a significant contribution to the most intensive peak in the spectra, the Soret band (Table 2). Figure 4 depicts the shapes of the frontier orbitals. The HOMO-1 can be described by combination of atomic orbitals (AO) of the nitrogen and carbon atoms in the *meso*-positions, while HOMO predominantly is localized on the pyrrole rings. This picture is typical for porphyrins and porphyrazines.^[35,43,44]

**Figure 3.** Calculated (solid line) and experimental (dashed line, DMF) electronic absorption spectra of VOTBP and TiOTBP.**Table 2.** Calculated compositions of the selected excited states of TiOTBP and VOTBP, corresponding transition wavelengths and oscillator strengths.

State	λ, nm	f	Composition (%)	λ _{exp} , nm
TiOTBP				
1 ¹ E	668	0.25	HOMO→LUMO (83) HOMO-1→LUMO (15)	636
3 ¹ E	404	1.38	HOMO→LUMO (15) HOMO-1→LUMO (79)	436
10 ¹ E	304	0.08	HOMO→LUMO+5 (79) HOMO-3→LUMO (13)	
VOTBP				
2 ² E	655	0.26	α-HOMO→α-LUMO (43) β-HOMO→β-LUMO (41) α-HOMO-1→α-LUMO (7) β-HOMO-1→β-LUMO (38)	637
4 ² E	398	1.28	α-HOMO-1→α-LUMO (37) α-HOMO→α-LUMO (7)	444
8 ² E	347	0.10	α-HOMO→α-LUMO+4 (90)	

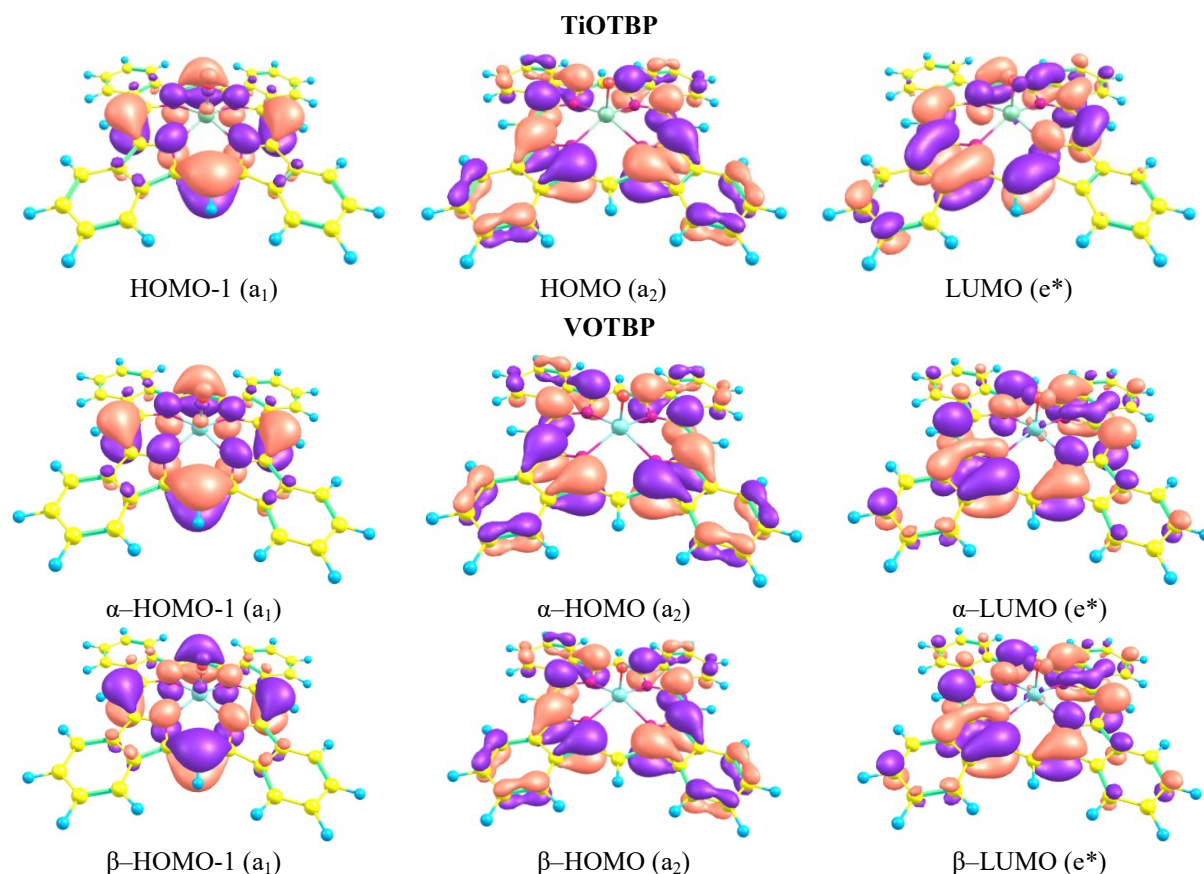


Figure 4. Shapes of the frontier orbitals of TiOTBP and VOTBP.

Electrochemical measurements

Cyclic voltammetry measurements were performed for 1 mM solutions of the VO and TiO tetrabenzoporphyrin complexes in DMF in the potential range from -2 to 1.5 V vs. Ag/AgCl. In the anodic region for two oxidation waves are observed at $E_{\text{ox}}^1 = 0.28 - 0.31$ V and $E_{\text{ox}}^2 = 1.03$ and 1.06 V vs. Ag/AgCl. In the cathodic region we observe irreversible processes at $E_{\text{pc}} = -1.19$ and -1.46 V for VOTBP and at $E_{\text{pc}} = -0.89$ and -1.19 V for TiOTBP (Figure 5).

Vanadyl and titanyl complexes of unsubstituted tetrabenzoporphyrin show typical behavior in anodic region like corresponding complexes of *meso*-tetraphenylporphyrin (TPP),^[44-48] β -octaethylporphyrin (OEP),^[47] and bicyclic porphyrin (BCP)^[20] but oxidation waves are shifted closer to zero (Table 3). When compared with MBCP (M = VO, TiO), it is clear that fusion of benzene rings facilitates oxidation and decreases the first oxidation potential by 0.48 V and 0.41 V for vanadyl and titanyl complexes, respectively. This may be due to an increase in the conjugation length in the molecule due to the appearance of aromatic rings at the periphery. In comparison with MOEP and MTPP, this difference is even more noticeable. For vanadyl complexes, it is 0.68 V and 1.07 V for VOOEP and VOTPP, respectively. However, benzoannulation in TBP does not lead to a significant difference in second oxidation potential compared to porphyrins. Effect of *meso*-azasubstitution which is present in phthalocyanines makes oxidation more difficult and increases the potential of the

first oxidation of MOPc^[51] by 0.65 and 0.54 V as compared to MOTBP, for vanadyl and titanyl complexes respectively.

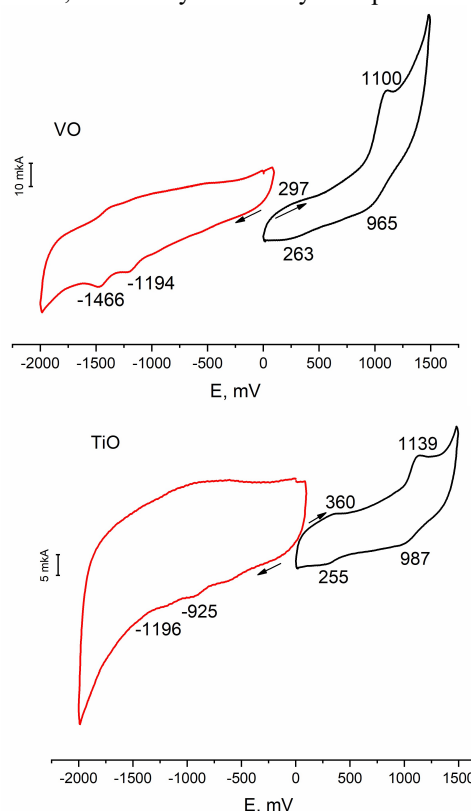


Figure 5. Cyclic voltammograms of TBPM (M = VO, TiO), 0.1 M TBAP. Scan rate 50 mV/s.

Table 3. Half-wave potentials of metal-free, zinc, vanadyl and titanyl complexes of tetrabenzoporphyrin and related compounds.

Compound	Reduction potentials $E_{1/2}$, V			Oxidation potentials $E_{1/2}$, V		RedOx gap, eV	Solvent reference electrode
	1 st	2 nd	3 rd	1 st	2 nd		
H ₂ TBP ^[49]	-1.23	-1.64					DMF SCE
VOTBP	-1.19	-1.42		0.28	1.03	1.47	DMF Ag/Ag ⁺
TiOTBP	-0.89	-1.19		0.31	1.06	1.20	DMF Ag/Ag ⁺
VOOEP ^[47]	-1.25	-1.72		0.96	1.25	2.21	DMF SCE
TiOOEP ^[47]	-1.21	-1.69		1.03	1.32	2.24	DMF SCE
VOBCP ^[20]				0.76	1.08		CH ₂ Cl ₂ Ag/Ag ⁺
TiOBCP ^[20]				0.72	0.97		CH ₂ Cl ₂ Ag/Ag ⁺
H ₂ TPP ^[48]	-1.2	-1.55		1.02	1.26	2.22	CH ₂ Cl ₂ SCE
VOTPP ^[48]	-1.13	-1.51		1.35	1.13	2.48	CH ₂ Cl ₂ SCE
H ₂ OEP ^[47]	-1.46	-1.86		0.81	1.3	2.37	DMF SCE
H ₂ Pc ^[50]	-0.66	-1.06					DMF SCE
VOPc ^[51]	-0.58	-1.08		0.94		1.52	DMF
TiOPc ^[51]	-0.52	-1.02		0.85		1.37	DMF

The behavior of TBP complexes in the cathodic region is similar to the corresponding porphyrin complexes (Table 3) and the first reduction potentials have a close values (−1.1 – −1.2 V for vanadyl complexes of TBP, TPP and OEP). In the corresponding phthalocyanines the presence of electronegative *meso*-nitrogen atoms strongly facilitates the electron uptake and shifts the potential of the first reduction in the less negative region by 0.61 V for VO, and by 0.37 V for titanyl complexes.

It is noteworthy that the gap between first oxidation and reduction potentials for VOTBP and TiOTBP (1.2–1.5) is close to the value typical for the corresponding phthalocyanines (1.4–1.5 V), but much less than for the porphyrin complexes (2.2–2.5 V). Therefore MOTBP similarly to phthalocyanines can be considered as perspective materials for organic electronics, in which they can be used as electron donors.

Conclusions

In this work we investigated vanadyl and titanyl complexes of tetrabenzoporphyrin using DFT, TD DFT and electrochemical methods. It is shown that fusion of benzene rings strongly facilitates the oxidation process which occurs easier than in the case of the corresponding porphyrins (by 0.4 – 0.5 V) and phthalocyanines (by 0.5 – 0.7 V). At the same time the reduction of tetrabenzoporphyrin complexes is observed at similar potentials as in the case of *meso*-aryl and β -alkyl substituted porphyrins, and by 0.4 – 0.6 V more difficult than in the case of phthalocyanine complexes. The obtained data evidence that VO and TiO complexes of tetrabenzoporphyrins can be used as donors in organic photovoltaics, and probably can be combined with corresponding metal phthalocyanines as acceptors.

Supplementary Materials: Cartesian coordinates, estimated molecular orbital diagram and mass spectra can be found in ESI.

Author Contributions: Conceptualization, D.N.F.; Y.A.Z. methodology, A.I.K.; N.E.G.; D.N.F.; investigation, D.N.F.; A.V.E.; A.A.N.; A.S.K.; resources, Y.A.Z.; N.E.G.; data curation, D.N.F.; A.V.E.; writing-original draft preparation, D.N.F.; P.A.S. All authors have read and agreed to the published version of the manuscript.

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