

## Flexible Amide–Bonded Zn(II) Porphyrin Dimer: Electronic Structure Investigation and Its Induced Chirality

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*In this paper, an in-depth electronic structure study of a xanthene-bridged and amide-bonded Zinc(II) porphyrin dimer ( $Zn^{II}$  dimer) by solvent/anion dependent spectroscopy, electrochemistry and spectroelectrochemistry has been described. In addition, the self-assembly behaviors between this  $Zn^{II}$  dimer and chiral (1S,2S)-(+)- and (1R,2R)-(-)-1,2-diaminocyclohexane exhibited distinctive derivative-shaped band morphology of the pseudo-Faraday- $A_1$  terms on the MCD spectra, and the molecular polarization could be modulated by the chirality of guest chiral diamines.*

**Keywords:** Porphyrin dimer, spectroscopy, electrochemistry, spectroelectrochemistry, influenced chirality.

## Подвижный амидосвязанный димер Zn(II)–порфирина: исследование электронной структуры и индуцированная хиральность

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*В работе изучена электронная структура димера цинкового комплекса порфирина ( $Zn^{II}$  димер), связанного через ксантеновый мостик и амидную группу, с использованием растворитель/анион зависимой спектроскопии, электрохимии и спектроскопии электрохимии. Характер самосборки между  $Zn^{II}$  димером и хиральным (1S,2S)-(+)- и (1R,2R)-(-)-1,2-диаминоциклогексаном проявляется в спектрах магнитного кругового дихроизма в виде четкой полосы, соответствующей псевдо-Фарадеевскому  $A_1$ -терму, а молекулярная поляризация зависит от гостевых хиральных диаминов.*

**Ключевые слова:** Порфирин, димер, спектроскопия, электрохимия, спектроскопия электрохимии, индуцированная хиральность.

## Introduction

Porphyrin oligomers containing two or more covalently linked macrocyclic rings have received considerable attention in recent years due to their unique electronic structures and optical properties,<sup>[1]</sup> such as doubly- or triply-fused co-planar porphyrins,<sup>[2]</sup> alkyne-bridged porphyrin strands<sup>[3]</sup> and  $\pi$ -phenylene-bridged twisted/planar porphyrin dimers.<sup>[4]</sup> From this point of view, there has been considerable research interests in the synthesis and properties of cofacial porphyrin dimers,<sup>[5]</sup> since these compounds provide a possible pathway for mimicking the electron transfer properties of the bacteriochlorophyll dimer in photosystem II, which is often referred as the “special pair”.<sup>[6]</sup> On the other hand, supramolecular chirality is a growing multidisciplinary field of modern research and attracts much strong attention from the scientific community because of its vital importance for various natural processes and for its attractive possibilities for new smart technologies.<sup>[7]</sup> Of the vast number of host–guest and self-associated systems, supramolecular assemblies based on porphyrin chromophores are of particular interest for in depth investigation and potential application as a consequence of them having specific and well-suited physicochemical and spectroscopic properties.<sup>[8]</sup> In this paper, the study on the solvent-dependent spectroscopic, electrochemical and spectroelectrochemical properties will be carried out. Also, the electronic structure study of its induced chirality upon addition of (1S,2S)-(+)- and (1R,2R)-(-)-1,2-diaminocyclohexane will be illustrated, since its unique property of producing a stable 1:1 tweezer complex exclusively without any further equilibrium steps as a consequence of its remarkably large association constant.

## Experimental

### Materials and Instruments

All reagents and solvents were of commercial grade and were used without further purification except where noted, and ACS spectral pure grade solvents were used for spectroscopic, electrochemical and spectroelectrochemical measurements. The Zn<sup>II</sup> porphyrin dimer **1** (Scheme 1) was synthesized according to the literature.<sup>[9]</sup> Cyclic voltammetry was performed in a three-electrode cell using a 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. UV-visible spectroelectrochemical measurements were performed with a home-made optically transparent thin-layer cell with Pt mesh as the working electrode. The potential was applied using a Chi-730D electrochemistry station. UV-visible spectra were recorded with a HP 8453A diode array spectrophotometer. All electrochemical and spectroelectrochemical measurements were carried out under a nitrogen atmosphere. Magnetic circular dichroism (MCD) spectra were recorded on a JASCO J-815 spectrodichromometer equipped with a JASCO permanent magnet, which produces magnetic fields of up to 1.6 T (1 T=1.0 tesla) with both parallel and antiparallel fields.

## Results and Discussion

### Optical Spectroscopy and Induced Chirality

To comprehensively understand the effect of the presence or absence of the (1R,2R)-(-)-1,2-diaminocyclohexane guest molecule on the electronic structure of **1** and its optical activity, the magnetic circular dichroism (MCD), circular dichroism (CD) and electronic absorption spectra measurement were carried out (Figure 1). It should be noted that CD and MCD analyses are mutually complementary in aiding the interpretation of the excited states, especially in the case of chiral *bis*- (or *multi*-) porphyrin systems; CD spectroscopy is sensitive to interchromophoric through-space coupling (exciton coupling), whereas MCD spectroscopy is sensitive to intrachromophoric coupling (coupling occurring between electronic transitions within the same chromophoric unit). Since the optical spectroscopy is one of the most useful approaches for characterizing porphyrins and their analogs, due to the presence of the forbidden and allowed Q- and B-bands of Gouterman's 4-orbital model<sup>[10]</sup> in the 500–600 and 400–450 nm regions, respectively. The four spin-allowed  $M_L=\pm 4 \rightarrow \pm 5$  excitations result in two orbitally degenerate  ${}^1E_u$  excited states, due to the  $\Delta M_L=\pm 9$ , and  $\Delta M_L=\pm 1$  transitions. This results in the forbidden and allowed Q- and B-bands of Gouterman's 4-orbital model and Michl's perimeter model<sup>[11]</sup> for porphyrins, since an incident photon can provide only one quantum of orbital angular momentum. In the MCD spectra, the main electronic Q(0,0) and B(0,0) bands can be readily identified due to the presence of intense derivative-shaped Faraday- $A_1$  terms. In the context of lower symmetry compounds, these are replaced by coupled pairs of oppositely-signed Gaussian-shaped Faraday- $B_0$  terms.<sup>[12]</sup> The major UV-visible absorption bands of **1** in CH<sub>2</sub>Cl<sub>2</sub> are similar with the monomeric Zn<sup>II</sup>-*meso*-tetraphenylporphyrin. The B- (or Soret) band lies at 412 nm, and Q(0,1) and Q(0,0) bands observed at 550 and 594 nm.

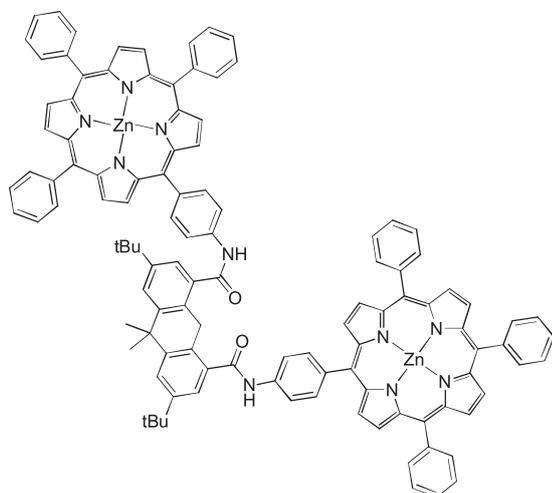
Upon addition of 1.0 eq of (1R,2R)-(+)-1,2-diaminocyclohexane, there is a slight red-shift of the B-band to 414 nm, and a clear red-shift of the Q(0,1) and Q(0,0) bands to 556 and 602 nm is observed at the same time. The MCD spectra of Zn<sup>II</sup> dimer **1** in the presence and absence of 1.0 eq. of (1R,2R)-(+)-1,2-diaminocyclohexane are all similar with the monomeric ZnTPP, since the relative energies of the frontier  $\pi$ -MOs are very similar with each other. Derivative-shaped positive pseudo- $A_1$  terms are observed in the MCD spectra of **1** for the both Q- and B-band region. It is noteworthy that the B-band signals are significantly less symmetrical than those typically observed for Zn<sup>II</sup> tetraphenylporphyrins and the Zn<sup>II</sup> dimer containing archiral guest molecule, such as DABCO. Importantly, the electronic transitions of different polarizations generally exhibit MCD signals of opposite sign and it was found that the two high energy transitions of the same positive CD sign are indeed of different polarization, at 437 and 425 nm with negative to positive sequence. On the other hand, the observed CD signal also indicates the two porphyrin rings were arranged in a clock-wise manner modulated by guest (1R,2R)-(-)-1,2-diaminocyclohexane molecule. When (1S,2S)-(+)-1,2-diaminocyclohexane was used, no changes were observed

in both UV-vis and MCD spectra, too. Also, the opposite sign of CD signals were observed upon addition of (1S,2S)-(+)- and (1R,2R)-(-)-diaminocyclohexane to **1** in CH<sub>2</sub>Cl<sub>2</sub>, and significant difference of the CD intensity could be explained as the modulation of molecular polarization through self-assembly by guest chiral diamines.

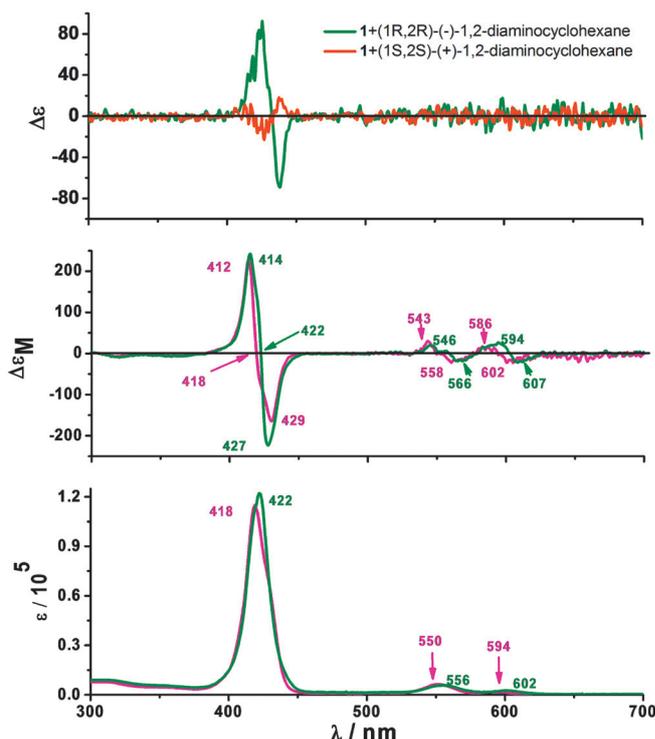
### Solvent and Anion-Dependent Electrochemistry

To gain further insight into the electronic structures of Zn<sup>II</sup> dimer and the effect of solvent polarity on the electronic properties, reductive electrochemical measurements were carried out in *o*-dichlorobenzene (*o*-DCB) as a typical low-polar solvent, and high-polar dimethylformamide (DMF) and PhCN containing 0.1 M various supporting electrolyte [NBu<sub>4</sub>]<sup>+</sup>[ClO<sub>4</sub>]<sup>-</sup> (TBAP), [NBu<sub>4</sub>]<sup>+</sup>[Cl]<sup>-</sup> (TBACl), [NBu<sub>4</sub>]<sup>+</sup>[Br]<sup>-</sup> (TBABr), [NBu<sub>4</sub>]<sup>+</sup>[F]<sup>-</sup> (TBAF) and [NBu<sub>4</sub>]<sup>+</sup>[OAc]<sup>-</sup> (TBAOAc). The redox potentials ( $E_{1/2}$ ) values derived from both CV and DPV measurements (Figure 2). Thus, the influence of solvent polarity and anions of supporting electrolyte could be well illustrated. In DMF, Zn<sup>II</sup> dimer **1** reveals two reversible processes and one quasi-reversible processes in the reduction part at  $E_{1/2} = -0.99, -1.39$  and  $-1.79$  V, and one quasi-reversible process in the oxidation part at  $E_{1/2} = 1.13$  V was also formed when TBAP was used as the supporting electrolyte. It should be mentioned that all reduction values are positively shifted in high-polar solvent DMF compared with the same compound in low-polar *o*-DCB solution containing 0.1 M TBAP. Three reductions appeared at  $E_{1/2} = -0.99, -1.39$  and  $-1.79$  at the reduction part, and at  $E_{1/2} = 1.13$  V for its oxidation in DMF. In addition, all electrochemical redox behaviors are similar with the monomeric Zn<sup>II</sup>-tetraphenylporphyrin.<sup>[13]</sup>

The potentials and reversibility for the electrochemical reductions of Zn<sup>II</sup> dimer **1** depend markedly upon the anions in both high polar DMF and low polar *o*-DCB solutions, and this can be accounted for by differences in the interaction to different anions from supporting electrolyte (Figure 3). In *o*-DCB, the positive shift of the two reversible reduction processes were observed in the case of TBAB; TBAC and TBAF were used as the supporting electrolyte compared with TBAP, and the largest shift was observed



**Scheme 1.** Molecular structure of Zn<sup>II</sup> porphyrin dimer **1**.

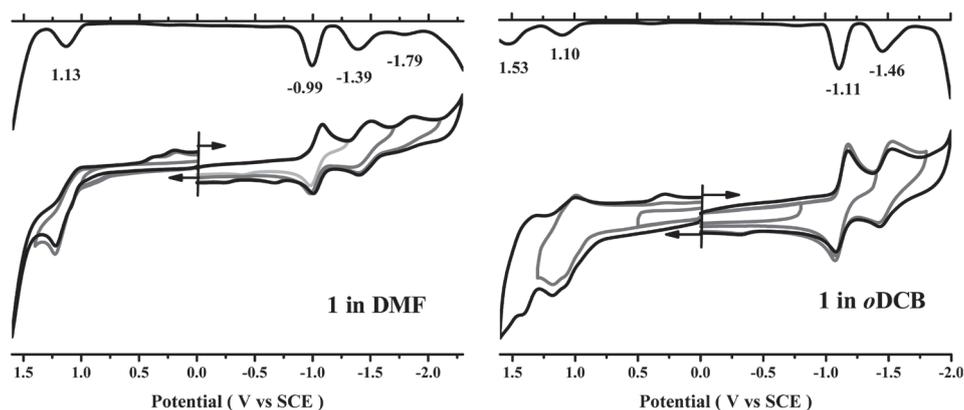


**Figure 1.** Circular dichroism (CD, up), magnetic circular dichroism (MCD, up) and UV-vis (bottom) spectra of **1** in the presence (red) and absence (green) of 1,2-diaminocyclohexane in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

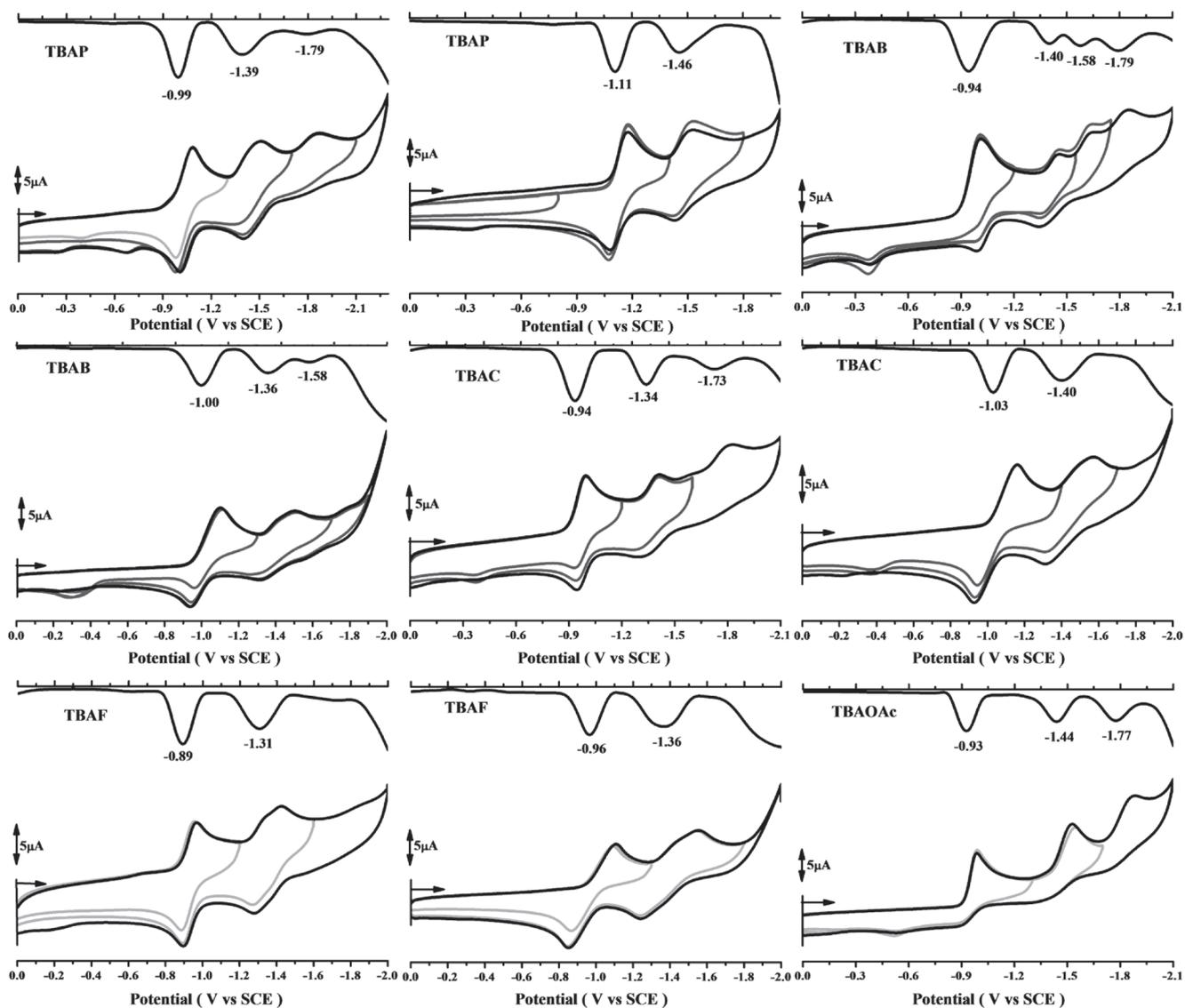
when TBAF was using. It should be pointed out that the flexible porphyrin dimers described in this study have almost same potential values with metallo-porphyrin monomer at their 1<sup>st</sup> oxidation and reduction under same organic solution, probably due to the weak  $\pi$ - $\pi$  interaction between different porphyrin core. The slight change of higher energy region can be explained as the lower molecular symmetry arising from the amide-bonded xanthene bridged porphyrin dimers' molecular structure.

### Solvent and Anion-Dependent Spectroelectrochemistry

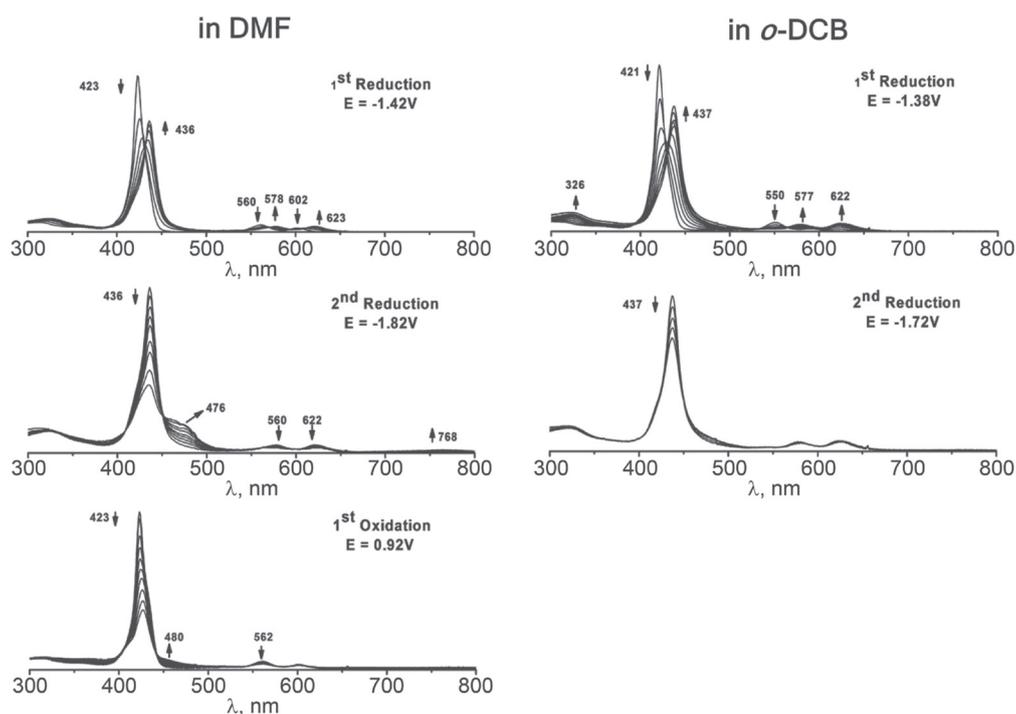
The first reduction step of **1** can be assigned to the reduction of porphyrin ring [Zn<sup>II</sup>Por]/[Zn<sup>I</sup>Por]- process in both low polar *o*-DCB ( $E_{app} = -1.42$  V) and high polar DMF ( $E_{app} = -1.38$  V) solvents, due to the almost identical spectral changes that are observed by thin-layer spectroelectrochemistry (Figure 4). The B-band of the Zn<sup>II</sup> porphyrin dimer lies at 421 nm in *o*-DCB and 423 nm in DMF, which is shifted significantly to the red compared to the spectra that have been reported for Zn<sup>II</sup> porphyrin monomers *at ca.* 436 nm in similar solvents.<sup>[13]</sup> Solvent polarity appears to have a significant effect on the spectral changes of doubly reduced Zn<sup>II</sup>Por dimer **1**. Controlled potential reduction at  $E = -1.82$  V in DMF results in a significantly split B-bands at 436 and 476 nm, while in *o*-DCB a single B-band is observed at 437 nm when a controlled potential value of  $E = -1.72$  V is applied. The spectral changes observed upon the first controlled potential oxidation, at  $E = 0.92$  V, indicate that the Soret band dramatically decreases and broadens in the same



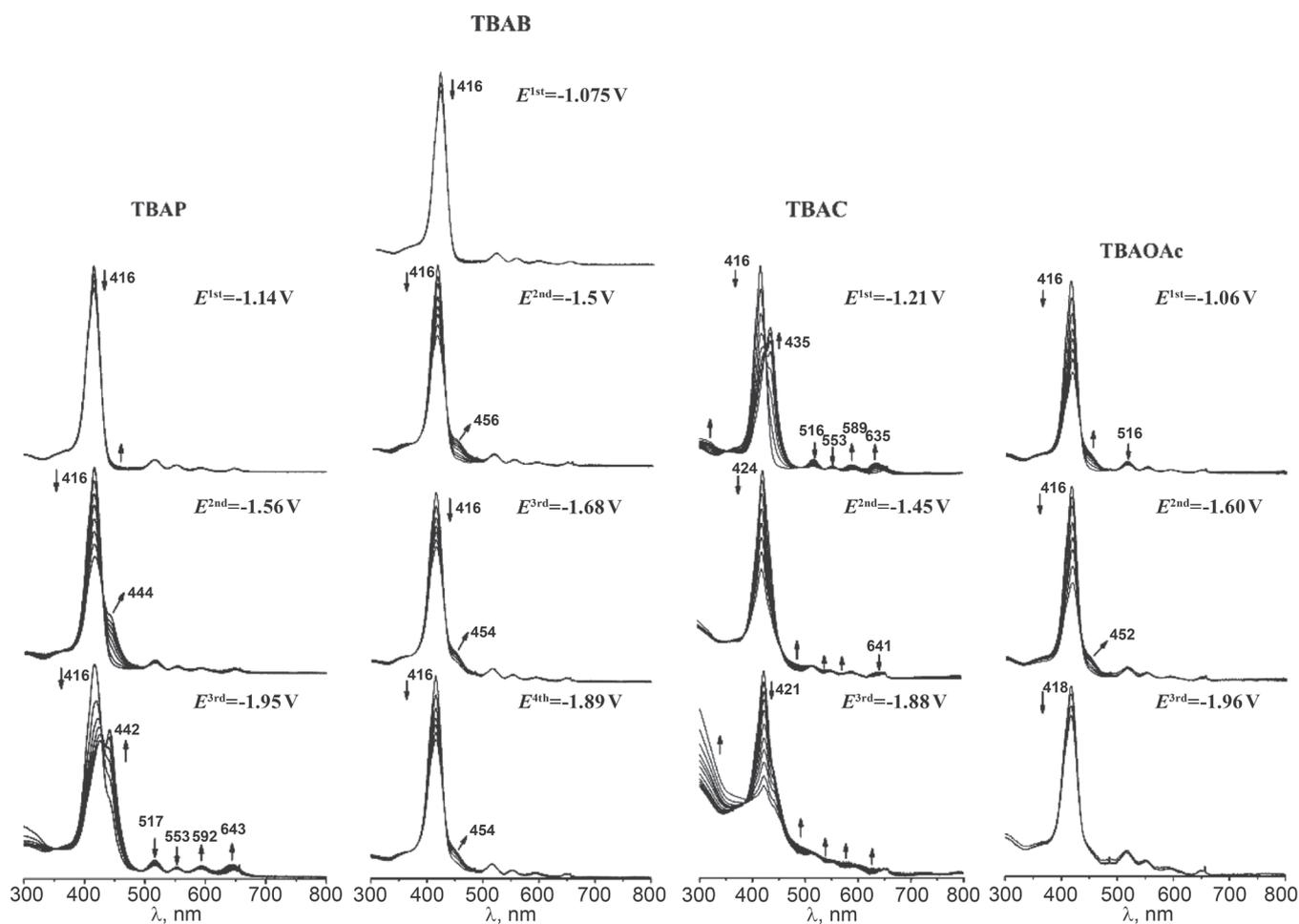
**Figure 2.** CV and DPV measurements of **1** in low polar solvent *o*-DCB and high polar DMF containing 0.1 M TBAP, scan rate 100 mV/s.



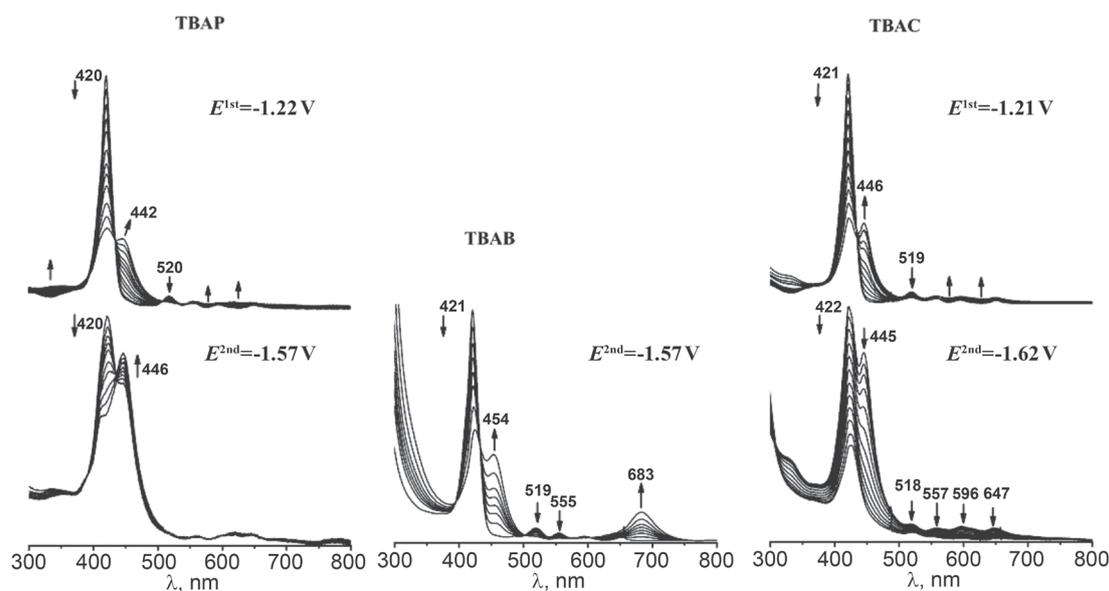
**Figure 3.** Reductive CV and DPV measurements of Zn<sup>II</sup> dimer **1** in *o*-DCB (left) and DMF (right) containing 0.1 M [NBu<sub>4</sub>]<sup>+</sup>[ClO<sub>4</sub>]<sup>-</sup> (TBAP), [NBu<sub>4</sub>]<sup>+</sup>Br<sup>-</sup> (TBAB), [NBu<sub>4</sub>]<sup>+</sup>Cl<sup>-</sup> (TBAC), [NBu<sub>4</sub>]<sup>+</sup>Br<sup>-</sup> (TBAF) and [NBu<sub>4</sub>]<sup>+</sup>OAc<sup>-</sup> (TBAOAc).



**Figure 4.** Spectral changes in the thin-layer UV-visible spectra of Zn<sup>II</sup> dimer complex **1** in DMF (left) and *o*-DCB (right) containing 0.1 M TBAP.



**Figure 5.** Spectral changes in the thin-layer UV-visible spectra of Zn<sup>II</sup> dimer complex **1** in DMF containing 0.1 M [NBu<sub>4</sub>]<sup>+</sup>[ClO<sub>4</sub>]<sup>-</sup> (TBAP), [NBu<sub>4</sub>]<sup>+</sup>Br<sup>-</sup> (TBAB), [NBu<sub>4</sub>]<sup>+</sup>Cl<sup>-</sup> (TBAC) and [NBu<sub>4</sub>]<sup>+</sup>OAc<sup>-</sup> (TBAOAc).



**Figure 6.** Spectral changes in the thin-layer UV-visible spectra of Zn<sup>II</sup> dimer complex **1** in *o*-DCB containing 0.1 M [NBu<sub>4</sub>]<sup>+</sup>[ClO<sub>4</sub>]<sup>-</sup> (TBAP), [NBu<sub>4</sub>]<sup>+</sup>Br<sup>-</sup> (TBAB) and [NBu<sub>4</sub>]<sup>+</sup>Cl<sup>-</sup> (TBAC).

time. No visible band is seen in the spectrum of the doubly oxidized species in Zn<sup>II</sup>Por dimer **1** in DMF. Contrary to what was observed during the first oxidation, the UV-visible spectral modifications are not reversible, and the spectrum of the singly oxidized form can't be recovered when the potential is set back to  $E = +0.7$  V or even lower potential. On the other hand, no spectral changes observed during the oxidation of Zn<sup>II</sup>Por dimer **1** in low polar solvent *o*-DCB. The effect of the counter anion of the supporting electrolyte on the reductive spectroelectrochemical behavior of **1** has also been examined (Figures 5, 6), and was found to have a significant effect on the potentials and reversibility of the electroreductions in both DMF and *o*-DCB.

## Conclusions

In summary, an in-depth study of the electronic structure of a synthetic xanthene-bridged and amide-bonded Zn<sup>II</sup> porphyrin dimer has been carried out, and the solvent/anion dependent optical and redox properties have been analyzed and have been found to be broadly similar to those of the corresponding monomer complexes. In addition, the observed electrochemical and spectroelectrochemical properties indicate that both solvents and anions have a large influence on the electronic structure. Also, the induced chirality of Zn<sup>II</sup> porphyrin dimer upon addition of (1S,2S)-(+)- and (1R,2R)-(-)-1,2-diaminocyclohexane which produced a stable 1:1 tweezer complexes exhibited distinctive derivative-shaped band morphology of the pseudo-Faraday-A<sub>1</sub> terms on the MCD spectra, and the molecular polarization could be modulated by the chirality of guest chiral diamines.

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