

# Electrochemistry and spectroelectrochemistry of bismanganese biscorroles dyads

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**ABSTRACT:** Three manganese biscorrole dyads were synthesized, physicochemically characterized and investigated as to their electrochemistry and spectroelectrochemistry in nonaqueous media. Each dyad contained the same two corroles linked in a face-to-face arrangement *via* one of the three different linking groups, 9,9-dimethylxanthene, anthracene or diphenylether, the exact nature of which determined the distance and possible interaction between the two metallomacrocycles. The initial compounds contained Mn(III) in their air stable form and were shown to exhibit two major redox processes, one being a Mn(III)/Mn(IV) conversion and the other being either Mn(III)/Mn(II) or reduction at the conjugated macrocycle to give a Mn(III) corrole  $\pi$ -anion radical when the solvent was pyridine. The potentials and reversibility of each electron transfer reaction were shown to depend upon the solvent (pyridine, CH<sub>2</sub>Cl<sub>2</sub>, or PhCN), type of spacer separating the two macrocycles and/or the presence or absence of axial ligation. The site of each electron transfer was assigned on the basis of spectroscopic and electrochemical data and by comparison with reactions and properties of the monocorrole (Mes<sub>2</sub>PhCor)Mn which was characterized in a previous publication and also examined in the current study under the same solution conditions as the newly investigated dyads. Some electrode reactions of the dyads were followed by coupled chemical reactions and these were also elucidated in the present study.

**KEYWORDS:** biscorroles, manganese, electrochemistry, ligand binding.

## **INTRODUCTION**

Bis-metalloporphyrins linked in a face-to-face (cofacial) arrangement by a "rigid" or "flexible" bridge have been used as catalysts for many oxidation reactions [1-10]. These dyads may encapsulate guest molecules inside the bismacrocycle pocket, with the exact stoichiometry depending upon the specific combination of metal ions, solvent and shape or length of the bridging spacer [11-16]. Changes in the bridge structure have been used to control the distance between the two porphyrin units as well as the degree of opening and closing which is directly related to changes in the extent of  $\pi$ - $\pi$  interaction between the two macrocycles and the overall properties of the compound [17–21].

Our own interest in this area has focused in large part on homobimetallic and heterobimetallic biscorroles [1, 15, 21] and porphyrin-corrole [16, 22, 23] dyads containing cobalt, manganese or iron as a central metal, each of which can exist in both high and low oxidation states under the application of a specific oxidizing or reducing potential.

We recently reported how anion and solvent binding can affect redox potentials and axial ligation of monomeric Mn(III) corroles [24] and bimetallic Mn(III) porphyrin-corrole dyads [25] and now turn our attention to the electrochemistry, spectroelectrochemistry and UV-visible properties of three manganese biscorrole dyads where the two metallomacrocycles are linked in a

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#### 1: (Mes<sub>2</sub>PhCor)Mn

**Biscorrole Dyads** 



2: (BMes<sub>2</sub>CX)Mn<sub>2</sub>; 3: (BMes<sub>2</sub>CA)Mn<sub>2</sub>; 4: (BMes<sub>2</sub>COx)Mn<sub>2</sub> Chart 1. Structures of investigated bis-manganese complexes

face-to-face arrangement with one of the following three spacers: 9,9-dimethylxanthene (X), anthracenyl (A) or diphenylether (Ox). Structures of the investigated compounds are shown in Chart 1 where Mes = a mesityl substituent and the dyads are represented by  $(BMes_2CX)$  Mn<sub>2</sub> (2),  $(BMes_2CA)Mn_2$  (3) or  $(BMes_2COx)Mn_2$  (4) where X, A or Ox are one of the three named spacer above.

Previous studies of bis-cobalt(III) corrole dyads having different macrocyclic substituents but the same or similar spacers have shown that the two macrocycles exhibit an interaction upon electrooxidation in PhCN [15, 21]. This differs from what is seen in the current study under the same solution conditions but an interaction is observed in  $CH_2Cl_2$  as described on the following pages.

# EXPERIMENTAL

#### Instrumentation

Cyclic voltammetry was carried out with an EG & G model 173 potentiostat/galvanostat. A homemade threeelectrode electrochemistry cell was used and consisted of a platinum button or glassy carbon working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE.

UV-visible spectroelectrochemical experiments were performed with an optically transparent platinum thinlayer electrode of the type described in the literature [26]. Potentials were applied with an EG & G Model 173 potentiostat/galvanostat. Time-resolved UV-visible spectra were recorded with a Hewlett Packard Model 8453 diode array rapid-scanning spectrophotometer. Mass spectra were obtained either with a Bruker Ultraflex II instrument in MALDI-TOF reflectron mode using dithranol (1,8-dihydroxy-9[10H]-anthracene) as a matrix. UV-visible spectra of the synthesized complexes were recorded in  $CH_2Cl_2$  on a Varian Cary 50 Scan spectrophotometer.

#### Chemicals and reagents

Pyridine (py, 99.8%) was obtained from Sigma-Aldrich Chemical Co. and used without further purification. Benzonitrile (PhCN) was purchased from Aldrich Chemical Co. and distilled over P2O5 under vacuum prior to use. Absolute dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, 99.8%) was received from EMD Chemicals Inc. and used without further purification. Tetra-*n*-butylammonium perchlorate (TBAP, ≥99%) and tetrabutylammonium acetate (TBAOAc, ≥99%) were purchased from Fluka Chemical Co. and used as received. Neutral alumina (Merck; usually Brockmann Grade III, i.e. deactivated with 6% water) or Silica gel (Merck : 70–120 µm) was used for column chromatography. Analytical thin layer chromatography was performed using Merck 60 F254 neutral aluminum oxide gel (precoated sheets, 0.2 mm thick) or Merck 60 F254 silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin layer chromatography and spectrophotometry.

The free-base biscorroles (BMes<sub>2</sub>CX)H<sub>6</sub>, (BMes<sub>2</sub>CA)H<sub>6</sub> and (BMes<sub>2</sub>CO)H<sub>6</sub> were prepared as previously reported in the literature [15]. Synthesis of the monocorrole (Mes<sub>2</sub>PhCor)Mn (**1**) was carried out as recently reported [24].

4,5-Bis-[manganese-(5,15-dimesitylcorrol-10-yl)]-9,9-dimethylxanthene (BMes<sub>2</sub>CX)Mn<sub>2</sub> (2). Under nitrogen, a mixture of 286 mg of (BMes<sub>2</sub>CX)H<sub>6</sub> (0.22 mmol, 1 equiv.) and 215 mg of  $Mn(OAc)_2 \cdot 4H_2O$  (0.88 mmol, 4 equiv.) in 200 mL of 1,2-dichloroethane/methanol/ ethanol (15/2/3) was heated at 85 °C for 24 h in the presence of sodium acetate (10 equiv.). The reaction mixture was then allowed to cool to room temperature and washed with water ( $3 \times 75$  mL), dried over MgSO<sub>4</sub>, and then evaporated. The remaining residue was chromatographed on silica (CH<sub>2</sub>Cl<sub>2</sub>/methanol 95/5 as eluent) and the last fraction was collected to give the title biscorrole bismanganese complex (2) in 55% (170 mg, 0.12 mmol). HR-MS (MALDI-TOF): m/z 1378.4514 [M]+\*, 1378.4590 calcd. for  $C_{89}H_{72}Mn_2N_8O$ . UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm ( $\epsilon \times$ 10<sup>3</sup>, M<sup>-1</sup>.cm<sup>-1</sup>) 324 (32), 403 (54), 634 (3.5).

**1,8-Bis-[manganese-(5,15-dimesitylcorrol-10-yl)]anthracene** (**BMes<sub>2</sub>CA**)**Mn<sub>2</sub>** (**3**). This compound was prepared in 58% yield (141 mg, 0.10 mmol), as described for (BMes<sub>2</sub>CX)Mn<sub>2</sub>, starting from (BMes<sub>2</sub>CA)H<sub>6</sub> (225 mg, 0.18 mmol, 1 equiv.) and Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (177 mg, 0.72 mmol, 4 equiv.). HR-MS (MALDI-TOF): m/z1346.4343 [M]<sup>++</sup>, 1346.4328 calcd. for C<sub>88</sub>H<sub>68</sub>Mn<sub>2</sub>N<sub>8</sub>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm (ε × 10<sup>3</sup>, M<sup>-1</sup>.cm<sup>-1</sup>) 312 (27), 405 (42), 634 (5). **2,2'-Bis-[manganese-(5,15-dimesitylcorrol-10-yl)]diphenylether (BMes<sub>2</sub>COx)Mn<sub>2</sub>(4).** This compound was prepared in 62% yield (207 mg, 0.15 mmol), as described for (BMes<sub>2</sub>CX)Mn<sub>2</sub>, starting from (BMes<sub>2</sub>COx)H<sub>6</sub> (308 mg, 0.25 mmol, 1 equiv.) and Mn(OAc)<sub>2</sub>·4H<sub>2</sub>O (245 mg, 1.00 mmol, 4 equiv.). HR-MS (MALDI-TOF): *m/z* 1338.4279 [M]<sup>++</sup>, 1338.4277 calcd. for C<sub>86</sub>H<sub>68</sub>Mn<sub>2</sub>N<sub>8</sub>O. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm ( $\epsilon \times 10^{-3}$ , M<sup>-1</sup>.cm<sup>-1</sup>) 312 (31), 401 (55), 635 (4).

# **RESULTS AND DISCUSSION**

Structures of the investigated bis-manganese and mono-manganese derivatives are given in Chart 1. Each manganese complex was prepared in good yield starting from the corresponding free-base biscorrole dyads [15].

#### UV-visible and mass spectrometry

UV-visible absorption maxima and molar absorptivities of dyads 2-4 in CH<sub>2</sub>Cl<sub>2</sub> are summarized in the Experimental section. Both the monocorrole 1 [24] and biscorroles 2-4 have a split Soret band centered at 400–405 and 427–430 nm along with a broad Q-band at 586–645 nm. Those spectral features in CH<sub>2</sub>Cl<sub>2</sub> are all similar to those of d-type hyperporphyrins [16, 24].

In MALDI/TOF MS, the main ionic pattern corresponded to the molecular ion and this data agrees well with the proposed structural arrangement, *i.e.* the bimetallic nature of each compound. Moreover, the high resolution and mass accuracy of the instrument along with a good fit between experimental and calculated ionic patterns allowed for an unambiguous assignment of the dyads' structure.

#### Electrochemistry and spectroelectrochemistry

Each biscorrole was examined as to its electrochemical and UV-vis properties after oxidation or reduction in PhCN, pyridine or  $CH_2Cl_2$  containing 0.1 M TBAP. The reduced forms of **2–4** in the non-binding solvent  $CH_2Cl_2$ were not stable and the current-voltage curves obtained in this solvent were ill-defined or show several side reactions. In contrast, most reductions of the investigated dyads were reversible in pyridine and PhCN, indicating a stabilization of the electroreduced species in these two higher donor solvents.

Cyclic voltammograms of the bismanganese biscorroles 2–4 in PhCN and pyridine are presented in Fig. 1 and exhibit electrochemical properties extremely close to those of the monocorrole 1 which is also shown in Fig. 1 and was recently described in the literature [24]. For example, in the weakly coordinating PhCN solvent the monocorrole exhibits two oxidations associated with the conversion of Mn(III) to Mn(IV), at  $E_{1/2} = 0.12$  to 0.45 V, and two reductions associated with the conversion of

(a) In PhCN (b) In pyridine (Mes,PhCor)Mn 1 (Mes,PhCor)Mn 1 -1.64 -1.36 0.12 0.45 (BMes<sub>2</sub>CX)Mn, 2 (BMes,CX)Mn, 2 0.09 1.40 0.10 0.44  $1.0^{\circ}$ (BMes,CA)Mn, 3 (BMes,CA)Mn, 3 -1.36 0.13 0.12 0.40 (BMes<sub>2</sub>COx)Mn<sub>2</sub> 4 (BMes,COx)Mn, 4 -1.64 -1.50 0.07 0.45 1.10 1.6 1.2 0.8 0.4 0.0 -0.4 -0.8 -2.0 0.8 0.4 0.0 -0.4 -0.8 -1.2 -1.6 -2.0 -1.2 -1.6 Potential, V vs. SCE Potential, V vs. SCE

**Fig. 1.** Cyclic voltammograms of monomanganese corrole 1 and bismanganese biscorroles 2–4 in (a) PhCN and (b) pyridine containing 0.1 M TBAP at a scan rate of 0.1 V/s. Some small reduction peaks marked by asterisks is due to trace impurities or side reactions

Mn(III) to Mn(II), the first process occurring at  $E_{1/2} =$  -1.36 and the second at  $E_{1/2} =$  -1.64 V. Almost the same behavior is seen for the biscorroles **2–4** as illustrated in Fig. 1a, the only major difference between cyclic voltammograms of the monocorrole and the dyads being the relative intensities of the individual oxidation or reduction peak currents for the related metal-centered oxidation or reduction processes in this solvent.

As indicated in Fig. 1, the first oxidation of dyads in PhCN is split into two processes, the first ranging in potential from  $E_{1/2} = 0.07$  (compound 4) to 0.12 V (compound 3) and the second from  $E_{1/2} = 0.40$  (compound 3) to 0.45 V (compound 4). These two sets of electrode reactions were assigned in the case of 1 to two different forms of axially ligated Mn(IV) under the given solution conditions, [(Cor)Mn<sup>IV</sup>(PhCN)]<sup>+</sup> in one case and (Cor)Mn<sup>IV</sup>X in the other, where X was an unknown anion, probably ClO<sub>4</sub><sup>-</sup>, from the supporting electrolyte [24].

We have previously shown that a single pyridine axial ligand strongly coordinates to the Mn(III) center of the neutral monomeric corrole in pyridine, 0.1 M TBAP [24] and the same seems to occur for compounds **2** and **3**, each of which exhibits reversible one-electron reductions at  $E_{1/2} = -1.47$  to -1.49 V in this solvent. The compounds **1**–4 also show reversible one-electron oxidations at  $E_{1/2} = 0.42$  to 0.48 V in pyridine and, in case of the dyads **2–4** there is an additional re-oxidation on the return scan at  $E_p = 0.09$  to 0.14 V (see Fig. 1b).

The oxidation of compounds 1–3 in pyridine gives the Mn(IV) corrole at  $E_{1/2} = 0.42$  to 0.47 V while reduction of the same three compounds at  $E_{1/2} = -1.46$  to -1.49 V

gives what has been earlier assigned as a Mn(III) corrole  $\pi$ -anion radical in the case of the monomacrocycle [24, 27]. A slightly different current-voltage curve is seen for the biscorrole **4**, which has the most flexible "Ox" spacer. The cyclic voltammogram for this dyad in pyridine resembles in part that of the dyads **2** and **3** and in part that of the monocorrole **1** in PhCN, which also has a reduction at  $E_{1/2} = -1.64$  V.

Two Mn<sup>IV</sup>/Mn<sup>III</sup> re-reduction peaks are also observed for dyads **2–4** in pyridine (Fig. 1b) and these are here assigned to electrode reactions involving the reduction of [(Cor)Mn<sup>IV</sup>(py)]<sup>+</sup> and [(Cor)Mn<sup>IV</sup>(py)<sub>2</sub>]<sup>+</sup> which were characterized by thin-layer spectroelectrochemistry as described in the discussion below. Although the cavity of dyads **2–4** is probably not large enough for two pyridine molecules to both easily fit inside, the overall oxidation and re-reduction sequence of steps for **2–4** (at least for one metallomacrocycle of the dyads) is then proposed to occur in pyridine as shown in Equations 1a and 1b for oxidation and Equation 1c for re-reduction.

$$(Cor)Mn^{III}(py) \rightleftharpoons [(Cor)Mn^{IV}(py)]^{+} + e^{-}$$
$$E_{1/2} = 0.46 \text{ to } 0.48 \text{ V} \quad (1a)$$

$$[(Cor)Mn^{IV}(py)]^{+} + py \rightleftharpoons [(Cor)Mn^{IV}(py)_2]^{+}$$
(1b)

$$[(Cor)Mn^{IV}(py)_2]^+ + e \rightleftharpoons [(Cor)Mn^{III}(py)] + py$$
  
$$E_p = 0.09 \text{ to } 0.14 \text{ V} \qquad (1c)$$

An example of the two step UV-visible changes which occur during oxidation of the dyad **4** and monocorrole **1** in pyridine is shown in Fig. 2 while similar spectral changes involving a two step process are illustrated in



Fig. 2. UV-visible spectral changes of (a) 4 and (b) 1 during the oxidation processes in pyridine, 0.1 M TBAP



Fig. 3. UV-visible spectral changes of 2 and 3 during the oxidation processes in pyridine, 0.1 M TBAP

Fig. 3 for **2** and **3**. In each case, the spectral changes with time involve a two-step process during the first oxidation which is assigned to the electrochemical-chemical (EC) mechanism given in Equations 1a and 1b.

Although the mono and bis-pyridine adducts of **1–4** are spectrally observed as products of the electrooxidation in pyridine, a peak for oxidation or re-reduction of the bis-pyridine adduct is not detected in the cyclic voltammogram of the monocorrole **1**, suggesting conversion of  $[(Cor)Mn^{IV}(py)_2]^+(E_{1/2} = 0.12 \text{ V})$  to the more easily reducible  $[(Cor)Mn^{IV}(py)]^+(E_{1/2} = 0.45 \text{ V})$  under the application of a positive potential.

A further ring-centered oxidation of the biscorroles 2–4 is located at  $E_{1/2} = 1.07$  to 1.10 V in PhCN (see Fig. 1) and this potential may be compared to an  $E_{1/2} = 1.10$  V for the oxidation of 1 under the same solution conditions. The UV-visible spectral changes during this electrooxidation are consistent with the abstraction of one electron from the conjugated  $\pi$ -ring system of the macrocycle to give a Mn<sup>IV</sup> corrole  $\pi$  cation radical which exhibits a broad band at 550–750 nm as shown in Fig. 4 for the case of compound 4.

The spectral changes obtained during controlled potential reduction of **2–4** in a thin-layer cell was also parallel to what was described earlier in the literature for the monocorrole **1**. The prevailing electron transfer mechanism of the dyads also parallels what has been reported in the literature for the monocorrole **1** and depends mainly on the solvent (py or PhCN) and only to a small extent on the structure of the investigated compound and the bridge linking the two metallomacrocycles.



**Fig. 4.** UV-visible spectral changes of (BMes<sub>2</sub>COx)Mn<sub>2</sub> **4** during the first and second oxidations in PhCN, 0.1 M TBAP



Fig. 5. UV-visible spectral changes of 2 and 1 during the reduction processes in pyridine, 0.1 M TBAP

The one-electron reduction of **1–3** in pyridine at  $E_{1/2} = -1.46$  to -1.49 V generates in each case an almost identical UV-visible spectrum which is assigned as a Mn(III)  $\pi$ -anion radical (see examples of spectra in Fig. 5). The two reductions of the biscorroles **2–4** in PhCN at ~-1.36 and ~ -1.65 V are each assigned as a Mn(III)/Mn(II) process, the first of which is followed by a fast chemical reaction (an EC mechanism). The initial reduction gives the bis-manganese(II) corrole which reacts with

trace water in PhCN to regenerate a bis-manganese(III) corrole having two axially coordinated hydroxide ligands (as determined in the case of the monocorrole by spectroscopic titrations of the monomer with TBAOH) [24]. The homogeneously generated bis-Mn(III) corrole dyad is then reduced to a bis-Mn(II) dyad at a more negative potential of -1.65 V. These reactions are given in Equations 2–4 and an example of the two-step spectral changes is shown in Fig. 6a where the two reductions occur



Fig. 6. UV-visible spectral changes of (a) 4 upon controlled potential reduction at -1.90 V and 1 during a stepwise reduction at applied potentials of (b) -1.50 V and (c) -1.80 V in PhCN, 0.1 M TBAP

sequentially when the applied potential in the thin-layer cell is set at -1.90 V.

$$\begin{aligned} \text{bis-(Cor)} \text{Mn}^{\text{II}} + 2e \rightleftharpoons [\text{bis-(Cor)} \text{Mn}^{\text{II}}]^{2-} \\ & E_{1/2} = \sim -1.36 \text{ V} \qquad (2) \\ \text{bis-(Cor)} \text{Mn}^{\text{II}}]^{2-} + 4\text{H}_2\text{O} \rightleftharpoons [\text{bis-(Cor)} \text{Mn}^{\text{II}}(\text{OH})_2]^{4-} \\ & + 2\text{H}^+ + \text{H}_2 \qquad (3) \\ [\text{bis-(Cor)} \text{Mn}^{\text{II}}(\text{OH})_2]^{2-} + 2e \rightleftharpoons [\text{bis-(Cor)} \text{Mn}^{\text{II}}(\text{OH})_4]^{6-} \\ & E_{1/2} = \sim -1.65 \text{ V} \qquad (4) \end{aligned}$$

The first set of spectral changes during controlled potential reduction occurs from 0 to 80 s and generates a species with intense Soret and visible bands at 483 nm and 658 nm, respectively. The second set of spectral changes, from 81 to 574 s, gives a spectrum with a Soret band at 483 nm and a more intense visible band at 672 nm. Almost identical spectral changes are seen during controlled potential reduction of **1** (Figs 6b and 6c when the applied potential is first set at -1.50 V and then switched to -1.80 V). It can therefore be concluded that the biscorroles **2–4** and monocorrole **1** undergo similar electroreduction mechanisms.

The effect of adding acetate ion to solutions of the dyad **2–4** in PhCN is similar to what was reported for **1** under the same experimental conditions [24]. A comparison of cyclic voltammograms for **1** and **3** is shown in Fig. 7. The quite similar electrooxidation behavior for **1** and **3** suggests that oxidizing one  $[(Cor)Mn^{II}(OAc)]^{-1}$  macrocycle of the dyad **3** generates  $(Cor)Mn^{IV}(OAc)$  and this is followed by addition of a second axial ligand to the Mn(IV) metal center to give  $[(Cor)Mn^{IV}(OAc)_2]^{-1}$ . The relevant electron transfer mechanism is shown in the right hand side of Scheme 1 where the listed potentials of the Mn<sup>III</sup>/Mn<sup>IV</sup> process are given for **3** and listed as  $E_{1/2} = 0.23$  for the oxidation and  $E_{pc} = -0.20$  V for the re-reduction. As described earlier for the case of pyridine binding to the oxidized dyads, one or both corrole parts



**Fig. 7.** Cyclic voltammograms of monomanganese corrole **1** and bismanganese biscorroles **3** in PhCN containing 0.1 M TBAOAc at a scan rate of 0.1 V/s

of the dyad form bis-acetate adducts upon the first oxidation, the exact stoichiometry depending on the cavity space inside of the dyad.

Finally, it should be noticed that different oxidation behavior is seen for the dyads 2 and 4 when CH<sub>2</sub>Cl<sub>2</sub> is used as a solvent in place of PhCN or pyridine. As shown in Fig. 8, the cyclic voltammograms of 1 and 3 are similar to each other in shape and the first two oxidations are due to different coordination of Mn(IV) as described in the text. This contrasts with the first two oxidations of 2 and 4 where there is a "splitting" of the first or first and second oxidation processes as is often observed for the case of equivalent interacting redox centers [15, 21, 28]. As seen in the figure, the first of the two Mn(III)/Mn(IV) processes of the monomer 1 which occurs at  $E_{1/2} = 0.03$  V is split into peaks at  $E_{1/2} = -0.13$  and 0.01 V for the dyad **4** or  $E_{1/2} = -0.12$  and 0.01 V for the dyad **2**. The second Mn(III)/Mn(IV) process located at  $E_{1/2} = 0.32$  V for the monomer **1** is also split into two processes at  $E_{1/2} = 0.20$ 



Fig. 8. Cyclic voltammograms of monomanganese corrole 1 and bismanganese biscorroles 2-4 in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP at a scan rate of 0.1 V/s

Solvent PhCN	Compound (Mes <sub>2</sub> PhCor)Mn <sup>a</sup>	#	Oxidation			Reduction	
			Cor ring 1.07	(Cor)Mn <sup>III</sup> /Mn <sup>IV</sup>		(Cor) Mn <sup>III</sup> /Mn <sup>II</sup>	
				0.45	0.12	-1.36	-1.64
	(BMes <sub>2</sub> CX)Mn <sub>2</sub>	2	1.07	0.44	0.10	-1.44 <sup>b</sup>	-1.67
	(BMes <sub>2</sub> CA)Mn <sub>2</sub>	3	1.08	0.40	0.12	-1.36 <sup>b</sup>	-1.65
	(BMes <sub>2</sub> COx)Mn <sub>2</sub>	4	1.10	0.45	0.07	-1.36	-1.65
pyridine	(Mes <sub>2</sub> PhCor)Mn <sup>a</sup>	1		0.42		-1.46	
	(BMes <sub>2</sub> CX)Mn <sub>2</sub>	2		0.46	0.09 Epc	-1.49	
	(BMes <sub>2</sub> CA)Mn <sub>2</sub>	3		0.47	$0.13^{Epc}$	-1.47	
	(BMes <sub>2</sub> COx)Mn <sub>2</sub>	4		0.48	$0.14^{\text{Epc}}$	-1.50	-1.64
CH <sub>2</sub> Cl <sub>2</sub>	(Mes <sub>2</sub> PhCor)Mn	1	1.00	0.32	0.03	-1.45 <sup>b,c</sup>	
	(BMes <sub>2</sub> CX)Mn <sub>2</sub>	2	1.11 <sup>b</sup> , 0.99	0.33, 0.20	0.01, -0.12	not observed <sup>c</sup>	
	(BMes <sub>2</sub> CA)Mn <sub>2</sub>	3	1.17 <sup>b</sup> , 0.99	0.29	0.08	not observed <sup>c</sup>	
	(BMes <sub>2</sub> COx)Mn <sub>2</sub>	4	1.15 <sup>b</sup> , 1.02	0.25	0.01, -0.13	-1.50 <sup>b,c</sup>	

**Table 1.** Half-wave and peak potentials (V vs. SCE) of mono-manganese and bis-manganese complexes in different solvents containing 0.1 M TBAP. The major reactions of the dyads are marked by the red box

<sup>a</sup> Data taken from Reference 24. <sup>b</sup> Peak potential at a scan rate of 0.1 V/s. <sup>c</sup> Some small reduction peaks due to trace impurities or side reactions were observed at  $E_p = -0.49$  to -1.10 V at a scan rate of 0.1 V/s.

$$[(Cor)Mn^{IV}(py)_{2}]^{+} = [(Cor)Mn^{IV}(py)]^{+} = [(Cor)Mn^{IV}(PhCN)]^{+} = [(Cor)Mn^{IV}(OAc)] = [(Cor)Mn^{IV}(OAc)_{2}]^{+}$$

$$-0.13 V (E_{p})^{e} - e^{\oint} 0.47 V - e^{\oint} 0.40 V - e^{\oint} 0.23 V e^{-} -0.20 V (E_{p})$$

$$[(Cor)Mn^{II}(py)] = [(Cor)Mn^{II}(PhCN)] = [(Cor)Mn^{II}(OAc)]^{-}$$

$$e^{\oint} -1.47 V e^{\oint} -1.36 V (E_{p}) e^{\oint} -1.50 V$$

$$[(Cor)Mn^{II}(py)]^{-} = [(Cor)Mn^{II}]^{-} = [(Cor)Mn^{II}(OAc)]^{2-}$$

$$+2H_{2}O_{f} H_{2}$$

$$[(Cor)Mn^{III}(OH)_{2}]^{2-}$$

$$e^{\oint} -1.65 V$$

$$[(Cor)Mn^{II}(OH)_{2}]^{3-}$$

Scheme 1. Redox reactions of monocorrole 1 or one of the two corroles in the dyad 2–4 under different solution conditions (listed potentials are for compound 3 at scan rate of 0.1 V/s)

and 0.33 V in the case of **2**. Surprisingly, no splitting is seen for the dyad **3** containing the A bridge where the first two oxidations are located at similar  $E_{1/2}$  values as for the monocorrole **1** (see top of Fig. 8). The global second one-electron oxidation of the three dyads occurs at the  $E_{1/2} = 0.99$  to 1.02 V for compounds **2**, **3** and **4** and these potentials are similar to the  $E_{1/2} = 1.00$  V measured for oxidation of the monocorrole **1**.

A summary of half wave and peak potentials in PhCN, pyridine and  $CH_2Cl_2$  is given in Table 1. Electrochemical properties of the monocorrole **1** and each metallomacrocycle of the dyad **2–4** are summarized in Scheme 1 which

includes results from the earlier report [24] combined with data from additional experiments described in the present study.

## CONCLUSION

We have reported electrochemical and spectroelectrochemical properties of three newly synthesized manganese biscorrole dyads in PhCN, pyridine and CH<sub>2</sub>Cl<sub>2</sub>. Their electron transfer properties in PhCN and pyridine and the electron transfer site was evaluated as a function of the specific reaction conditions. An interaction between two macrocycles of some investigated biscorrole dyads is observed during their electrooxidation in the non-binding solvent  $CH_2Cl_2$ . It is anticipated that results obtained for the currently examined compounds might provide a basis for applications involving the need to encapsulate guest molecules inside the bismacrocycle pocket.

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