RSC Advances

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

Electrochemistry of nonplanar copper(II) tetrabutano- and tetrabenzotetraarylporphyrins in nonaqueous media

Received 00th July 2015,
Accepted 00th July 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

Lina Ye,[a,b] Zhongping Ou,[*,a] Yuanyuan Fang,[a,c] Songlin Xue,[a] Yang Song,[c] Liping Wang,[a] Mengli Wang[a] and Karl M. Kadish[*,c]

Two series of copper tetraarylporphyrins containing β,β'-fused tetrabutano or tetrabenzo groups were synthesized and characterized as to their electrochemistry and spectroelectrochemistry in nonaqueous media. The examined compoun are represented as butano-(T*p*YPP)Cu^{II} and benzo-(T*p*YPP)Cu^{II}, where T*p*YPP is the porphyrin dianion and Y is a CH_3, H or Cl substitutent on the *para*-position of the four *meso*-phenyl rings of the compound. Each neutral porphyrin in the two series is ESR active and shows a typical d^9 Cu(II) signal in frozen CH_2Cl_2 solution. Each Cu(II) porphyrin also undergoes two reversible one-electron reductions and two reversible one-electron oxidations in DMF or CH_2Cl_2 containing 0.1 M tetra-*n*-butylammonium perchlorate to give a π-anion radical and dianion upon reduction and a π-cation radical and dication upon oxidation. A third one-electron oxidation is also observed for butano-(T*p*YPP)Cu (Y = CH_3 and H) and benzo-(TPP)Cu in PhCN and this process is assigned to the Cu^{II}/Cu^{III} transition. The reversible half-wave potential for the first oxidation of each compound in both series is shifted negatively by about 500 mV as compared to $E_{1/2}$ values for oxidation of the related copper tetraarylporphyrin without the four fused benzo or butano rings while smaller positive shifts of 60 and 300 mV are seen for reduction of the tetrabenzotetraarylporphyrins and tetrabutaotetraarylporphyrins, respectively, as compared to the same redox reactions of the related tetraarylporphyrins. The electrochemically measured HOMO-LUMO gap averages 1.76±0.05 V for benzo-(T*p*YPP)Cu^{II}, 2.04±0.06 V for butano-(T*p*YPP)Cu^{II} and 2.33±0.03 for (T*p*YPP)Cu in CH_2Cl_2.

Introduction

It is known that the addition of electron-donating or electron-withdrawing substituents on the *meso*- and/or β-pyrrole positions of a porphyrin macrocycle can significantly affect the spectra and electrochemical properties of the compound.[1,2] The electrochemistry of porphyrins with redox inactive central metals is characterized by two reductions and two oxidations in nonaqueous media, all of which are localized on the macrocyclic π-ring system.[1,2] Additional metal-centered reactions may also be observed for porphyrins with transition metal ions, the most studied of which have been the M^{II}/M^{III} processes involving porphyrins with Fe, Co, Ni or Mn centers.[1,2,3-6] Porphyrins with Ag^{II} and Au^{II} centers can also be oxidized to their +3 oxidation state[7-11] but until recently[12] it was believed that a similar reaction would not occur for Cu^{II} porphyrins which were thought to have a redox inactive central metal ion.[1,2]

A number of *meso* and/or β-substituted copper porphyrins have been synthesized and characterized as to their spectroscopic properties and electrochemistry[1,2,12,13] and these synthetic copper porphyrins have been the subject of numerous investigations.[1,2,13-29] Our recent report of a Cu^{II}/Cu porphyrin oxidation involved highly substituted nonplanar compounds[12] and we wished to know how changing the planarity or π-ring system of the porphyrin macrocycle by addition of four β,β'-fused butano or benzo groups might affect the redox potentials and electron transfer mechanisms of these copper(II) porphyrins.

Tetrazenzoporphyrins have been recognized for their use in the areas of catalysis, medicine and material science.[30] In the present work, two series of copper tetraarylporphyrins containing four fused β,β'-butano or β,β'-benzo rings were synthesized and characterized as to their electrochemistry and spectroelectrochemistry in nonaqueous media. The examined compounds are represented as butano-(T*p*YPP)Cu^{II} and benz (T*p*YPP)Cu^{II}, where T*p*YPP is a dianion of the porphyrin and Y is a CH_3, H or Cl substitutent on the *para*-position of the four meso-phenyl rings. Structures of the examine butanoporphyrins **1b-3b** and benzoporphyrins **1c-3c** are shown in Chart 1 which also includes the (T*p*YPP)Cu^{II} comparison compounds **1a-3a** which are planar and octaethyltetraphenylporphyrin, (OETPP)Cu, and dodecaphenylporphyrin, (DPP)Cu, which are not. Each neutr porphyrin in the three series was characterized b electrochemistry, UV-visible spectroscopy, mass spectromet

---

[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013 P. R. China. E-mail: zpou2003@yahoo.com.
[b] College of Computer, Jilin Normal University, Siping 136000, P. R. China.
[c] Department of Chemistry, University of Houston, Houston, Texas 77204-5003, USA. E-mail: kkadish@uh.edu.

†Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

RSC Advances Accepted Manuscript

and ESR spectroscopy. Each reduced and oxidized form of the neutral porphyrin was also characterized by thin-layer spectroelectrochemistry. The effect of the four fused butano or benzo groups on the spectra and electrochemical properties of the compounds is discussed.

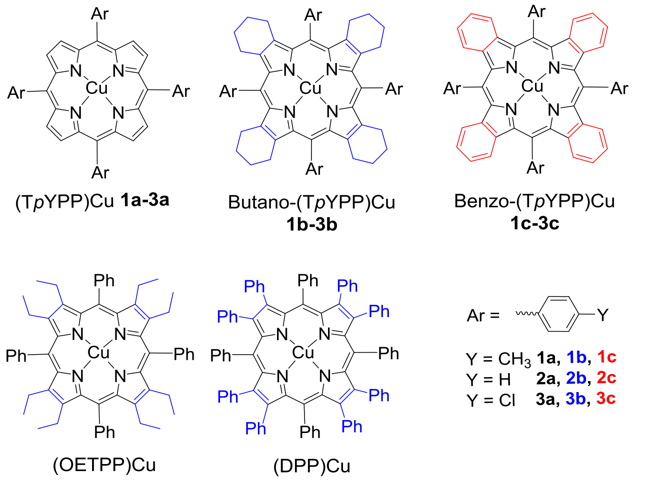
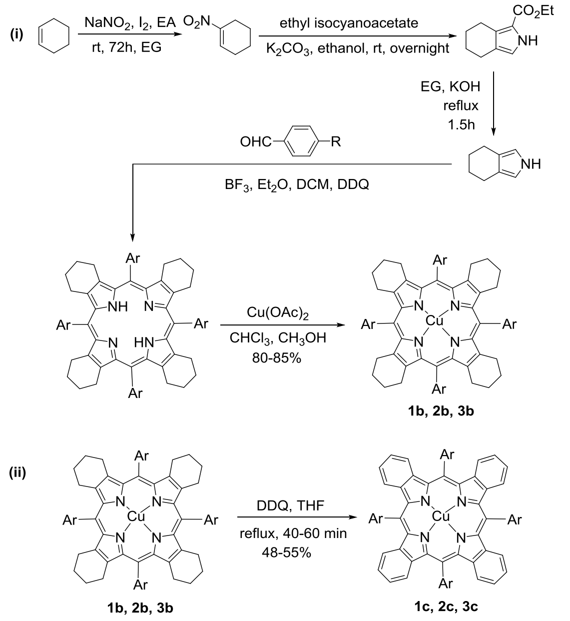


Chart 1. Structures of examined copper porphyrins

Results and discussion

Synthesis and UV-vis spectra

The synthetic routes to obtain butano-(TpYPP)Cu **1b-3b** and benzo-(TpYPP)Cu **1c-3c** are shown in Scheme 1. Cyclohexene was transformed into nitrocyclohexene which was reacted with ethyl isocyanoacetate to give a tetrahydroisoindole ester. 4,5,6,7-Tetrahydroisoindole was obtained from the tetrahydroisoindole ester by refluxing with excess KOH and ethylene glycol (EG) for 1.5h.



Scheme 1. Synthetic routes for tetrabutanotetraarylporphyrins **1b-3b** and tetrabenzotetraarylporphyrins **1c-3c**.

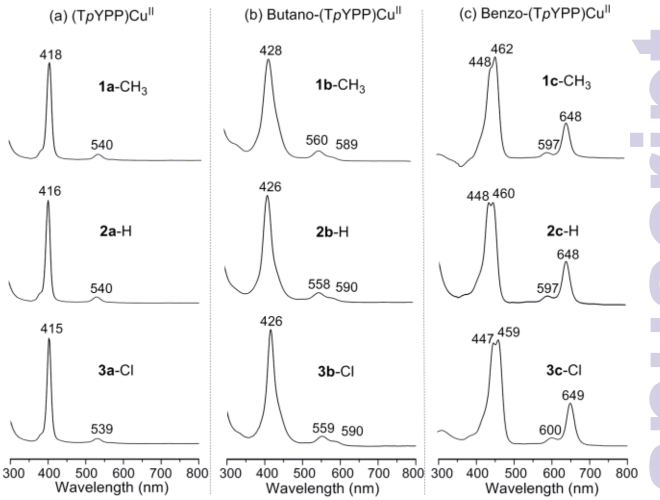


Fig. 1. UV/Vis spectra of (a) (T*p*YPP)Cu^{II} **1a-3a**, (b) butano-(T*p*YPP)Cu^{II} **1b-3b** and (c) benzo-(T*p*YPP)Cu^{II} **1c-3c** in CH$_2$Cl$_2$.

The free-base tetrabutanotetraarylporphyrins were synthesized from tetrahydroisoindole and arylaldehyde using a method reported by Beletskaya, Vinogradov and coworkers.[31] The Cu(II) butanoporphyrins **1b-3b** were then obtained via a reaction between butano-(T*p*YPP)H$_2$ and Cu(OAc)$_2$ in a mixed solvent of CHCl$_3$ and CH$_3$OH (v/v = 4/1) with a yield of 80-85%. After purification by column chromatography, the copper tetrabutanotetraarylporphyrins were oxidized by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in tetrahydrofuran (THF) to give the corresponding copper tetrabenzotetraaryl-porphyrins **1c-3c** with the yield ranging from 48 to 55%.

UV-vis spectra of **1a-3a, 1b-3b** and **1c-3c** in CH$_2$Cl$_2$ are illustrated in Fig. 1. The (T*p*YPP)Cu^{II} compounds **1a-3a** (Fig. 1a) are characterized by a sharp Soret band at 415-418 nm and a low intensity Q band at ~540 nm while the tetrabutanoporphyrins **1b-3b** exhibit red-shifted Soret and Q bands as compared to the (T*p*YPP)Cu^{II} derivatives with the same *meso*-substituents. In addition, the single Q band of the (T*p*YPP)Cu^{II} complexes is replaced by two Q bands for **1b-3b** as seen in the figure. Spectra of the butano-(T*p*YPP)Cu^{II} compounds are similar to the spectrum of (OETPP)Cu which has a Soret band at 430 nm and two Q bands at 568 and 598 nm.[32]

A significant difference is seen in UV-vis spectra of the benzo-(T*p*YPP)Cu^{II} compounds **1c-3c**. These porphyrins, which possess four β,β'-fused ring systems, are characterized in CH$_2$Cl$_2$ by a split Soret band at 447-462 nm, an intense Q band at ~648 nm and a weaker Q band at 597-600 nm (Fig. 1c). The average red shift in the Soret band is about 38 nm as compared to the corresponding tetraarylporphyrins with the same *meso*-substituents while the highest intensity Q band of benzo-(TpYPP)Cu^{II} is shifted by ~110 nm as compared to (T*p*YPP)Cu^{II}. The longest wavelength Q band for the compounds in Fig. 1c has a relatively high intensity due to the increased conjugation between the four fused benzo groups and the macrocycle of the compounds. This result is consistent with what has been reported for benzoporphyrins having different central metal ions.[33-38]

RSC Advances Accepted Manuscript

ESR characterization

ESR spectra for the tetrabutano and tetrabenzo derivatives of Cu(II) at 110 K in CH_2Cl_2 are illustrated in Fig. 2 while the ESR parameters are summarized in Table 1. The spectra of butano-(T*p*YPP)Cu **1b-3b** exhibit features typical of monomeric Cu(II) tetrapyrroles,[39-41] with $g_{//}$ values ranging from 2.193 to 2.204 ($A_{//}$ = 206-210) and $g_\perp$ ranging from 2.053 to 2.054 ($A_\perp$ = 117-130). No nitrogen superhyperfine is seen in the spectra of Fig. 2a, indicating the lack of a strong interaction between the Cu(II) ion and the four nitrogen atoms under the given experimental conditions.

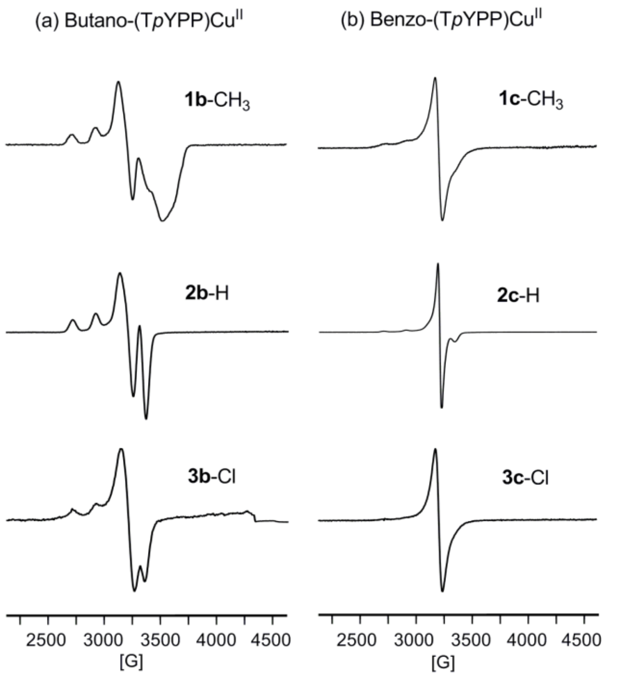


Fig. 2. ESR spectra of copper tetrabutanotetraarylporphyrins **1b-3b** (~10^{-3} M) and tetrabenzotetraarylporphyrins **1c-3c** (~10^{-3} M) in frozen dichloromethane at 110K.

Table 1. ESR Data of (TPP)Cu^{II} **2a**, Butano-(T*p*YPP)Cu^{II} **1b-3b** and Benzo-(T*p*YPP)Cu^{II} **1c-3c** in CH_2Cl_2 at 110 K.

compound	$g_{//}$	$A_{//}$	$g_\perp$	$A_\perp$
(TPP)Cu^{II} **2a**	2.219	222	2.057	218
Butano-(T*p*CH_3PP)Cu **1b**	2.200	210	2.054	130
Butano-(TPP)Cu **2b**	2.193	206	2.054	117
Butano-(T*p*ClPP)Cu **3b**	2.204	206	2.053	117
Benzo-(T*p*CH_3PP)Cu **1c**			2.051	66
Benzo-(TPP)Cu **2c**			2.053	41
Benzo-(T*p*ClPP)Cu **3c**			2.052	66

The ESR spectrum of each Cu(II) tetrabenzotetraarylporphyrin is characterized by a prominent $g_\perp$ value ranging from 2.051 to 2.053 ($A_\perp$ = 41-66 as seen in Table 1), values consistent what was previously reported for other Cu(II) porphyrins.[42-44] It should be pointed out that the Cu(II) hyperfine is ill-defined in spectra of the benzo-(T*p*YPP)Cu derivatives at 110 K in CH_2Cl_2 (Fig. 2b) and this can be accounted for by aggregation of these porphyrins under the given experimental conditions.[39,45-47]

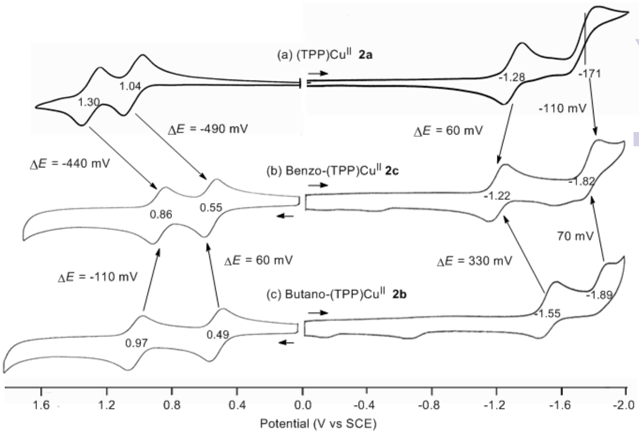


Fig. 3. Cyclic voltammograms of (a) (TPP)Cu^{II} **2a**, (b) benzo-(TPP)Cu^{II} **2c** and (c) butano-(TPP)Cu^{II} **2b** in CH_2Cl_2 containing 0.1 M TBAP.

Electrochemistry

The electrochemistry of butano-(T*p*YPP)Cu **1b-3b** and benzo-(T*p*YPP)Cu **1c-3c** was carried out in CH_2Cl_2, DMF and PhCN containing 0.1 M TBAP. Examples of cyclic voltammograms in CH_2Cl_2 are shown in Fig. 3 and a summary of the measured reduction and oxidation potentials for each porphyrin in the three solvents is given in Table 2, which includes data for several structurally related Cu(II) porphyrins measured under the same solution conditions. A discussion of the data is given below, first for oxidation and then for reduction, each of which is affected differently by the type of β,β'-fused groups.

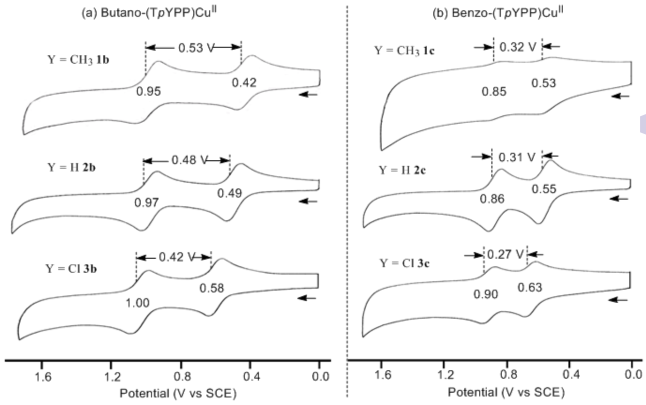


Fig. 4. Cyclic voltammograms showing oxidations of (a) butanoporphyrins **1b-3b** and (b) benzoporphyrins **1c-3c** in CH_2Cl_2 containing 0.1 M TBAP.

Oxidation. The butano-(T*p*YPP)Cu derivatives **1b-3b** exhibit two reversible one-electron oxidations within the positive potential limit of CH_2Cl_2 (~1.8 V) and DMF (~1.4 V). The first oxidation is located at $E_{1/2}$ = 0.42-0.58 V and the second at E = 0.95-1.00 V. The separation in potential between the two reversible one-electron oxidations (listed as $\Delta E_{(2o\text{-}1o)}$ in Table 2) ranges from 0.42 to 0.53 V for the three tetrabutanoar compounds in CH_2Cl_2 (see Fig. 4a). These values are similar t potential separations reported for the nonplanar porphyrin Br_8(TPP)Cu[48] and (DPP)Cu,[49] both of which have a $\Delta E_{(2o\text{-}1o)}$ =

RSC Advances Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

Table 2. Half-Wave Potentials (V vs SCE) of Copper Porphyrins in CH_2Cl_2, DMF and PhCN Containing 0.1 M TBAP.

solvent	compound	oxidation				reduction			ΔE^{d}	ref
		3rd	2nd	1st	$\Delta E_{(2o\text{-}1o)}$	1st	2nd	$\Delta E_{(1r\text{-}2r)}$	(V)	
CH_2Cl_2	(T*p*CH_3PP)Cu **1a**		1.23	0.93	**0.30**	-1.37	-1.83[a]	**0.46**	2.30	48
	(TPP)Cu **2a**		1.30	1.04	**0.26**	-1.28	-1.71	**0.43**	2.32	*tw*
	(T*p*ClPP)Cu **3a**		1.26	1.07	**0.19**	-1.30	-1.75	**0.45**	2.37	48
	Butano-(T*p*CH_3PP)Cu **1b**		0.95	0.42	**0.53**	-1.56	-1.97	**0.41**	1.98	*tw*
	Butano-(TPP)Cu **2b**		0.97	0.49	**0.48**	-1.55	-1.89	**0.34**	2.04	*tw*
	Butano-(T*p*ClPP)Cu **3b**		1.00	0.58	**0.42**	-1.52	-1.82	**0.30**	2.10	*tw*
	Benzo-(T*p*CH_3PP)Cu **1c**		0.85	0.53	**0.32**	-1.23	-1.85	**0.62**	1.71	*tw*
	Benzo-(TPP)Cu **2c**		0.86	0.55	**0.31**	-1.22	-1.82	**0.60**	1.77	*tw*
	Benzo-(T*p*ClPP)Cu **3c**		0.90	0.63	**0.27**	-1.18	-1.75	**0.57**	1.81	*tw*
	Br_8(TPP)Cu		1.41	0.96	**0.45**	-0.87	-1.12	**0.25**	1.83	48
	(DPP)Cu		1.00	0.55	**0.45**	-1.32	-1.60	**0.28**	1.87	49
	(OETPP)Cu		0.97	0.38	**0.59**					52
PhCN[b]	Butano-(T*p*CH_3PP)Cu **1b**	1.99[a]	0.98	0.52	**0.46**	-1.51	-1.94[a]	**0.43**	2.03	*tw*
	Butano-(TPP)Cu **2b**	2.00[a]	0.98	0.54	**0.44**	-1.48	-1.92[a]	**0.44**	2.02	*tw*
	Benzo-(TPP)Cu **2c**	1.88[a]	0.89	0.60	**0.29**	-1.18	-1.78[a]	**0.60**	1.78	*tw*
	(TPP)Cu		1.33	1.03	**0.30**	-1.26	-1.72	**0.46**	2.29	12
	(OETPP)Cu	2.00[a]	0.97	0.46	**0.51**	-1.46	-1.90	**0.44**	1.92	12
	(DPP)Cu	1.88	0.94	0.54	**0.40**	-1.22	-1.61	**0.39**	1.76	12
DMF[c]	(T*p*CH_3PP)Cu **1a**		1.18	0.99	**0.19**	-1.12	-1.77[a]	**0.65**	2.11	*tw*
	(TPP)Cu **2a**		1.19	1.02	**0.17**	-1.15	-1.70	**0.55**	2.17	*tw*
	(T*p*ClPP)Cu **3a**		1.24	1.09	**0.15**	-1.10	-1.60	**0.50**	2.19	*tw*
	Butano-(T*p*CH_3PP)Cu **1b**		0.92	0.56	**0.36**	-1.40	-1.87[a]	**0.47**	1.96	*tw*
	Butano-(TPP)Cu **2b**		0.92	0.59	**0.33**	-1.40	-1.83[a]	**0.43**	1.99	*tw*
	Butano-(T*p*ClPP)Cu **3b**		0.99	0.66	**0.33**	-1.31	-1.74[a]	**0.43**	1.97	*tw*
	Benzo-(TPP)Cu **2c**		0.82	0.61	**0.21**	-1.10	-1.66	**0.56**	1.71	*tw*
	Benzo-(T*p*ClPP)Cu **3c**		0.86	0.67	**0.19**	-1.03	-1.66[a]	**0.63**	1.70	*tw*

[a] Irreversible peak potential at a scan rate of 0.1 V/s. [b] The solubility of cpds **1c, 3b** and **3c** is very low and meaningful data could not be obtained in PhCN. [c] The solubility of cpd **1c** is very low in DMF and no redox processes could be observed. [d] The potential difference between the first oxidation and first reduction (HOMO-LUMO gap).

0.45 V vs SCE under the same experimental conditions. Data for both compounds is given in Table 2.

As compared to the three butano-(T*p*YPP)Cu^{II} derivatives, the first oxidation of the corresponding benzo-(T*p*YPP)Cu^{II} derivatives with the same *meso*-substituents is harder by 50-100 mV while the second oxidation of the benzoporphyrins is easier by 100-110 mV. This is seen in Fig. 3 for compounds **2b** and **2c** in CH_2Cl_2 and also in Fig. 4b where $\Delta E_{1/2}$ between the first two oxidations of **1c-3c** in CH_2Cl_2 ranges from 0.32 V for Y = CH_3 to 0.27 V for Y = Cl. These separations are slightly larger than the $\Delta E_{1/2}$ of the corresponding (T*p*YPP)Cu compounds, as seen in Table 2.

For all of the examined tetrabenzoporphyrins, the separation, $\Delta E_{(2o\text{-}1o)}$ of compounds **1c-3c** is much smaller than that of the tetrabutanoporphyrins **1b-3b**. However, it should be pointed out that the nature of the *para*-substituent on the *meso*-phenyl rings also affects the potential separations of compounds in all three series. The largest values of $\Delta E_{(2o\text{-}1o)}$ are seen for the porphyrins having an electron-donating *para*-CH_3 substituent on the four *meso*-phenyl groups while the smallest $\Delta E_{(2o\text{-}1o)}$ are seen for the porphyrins with an electron-withdrawing Cl group on the phenyl rings of the macrocycle.

RSC Advances Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx

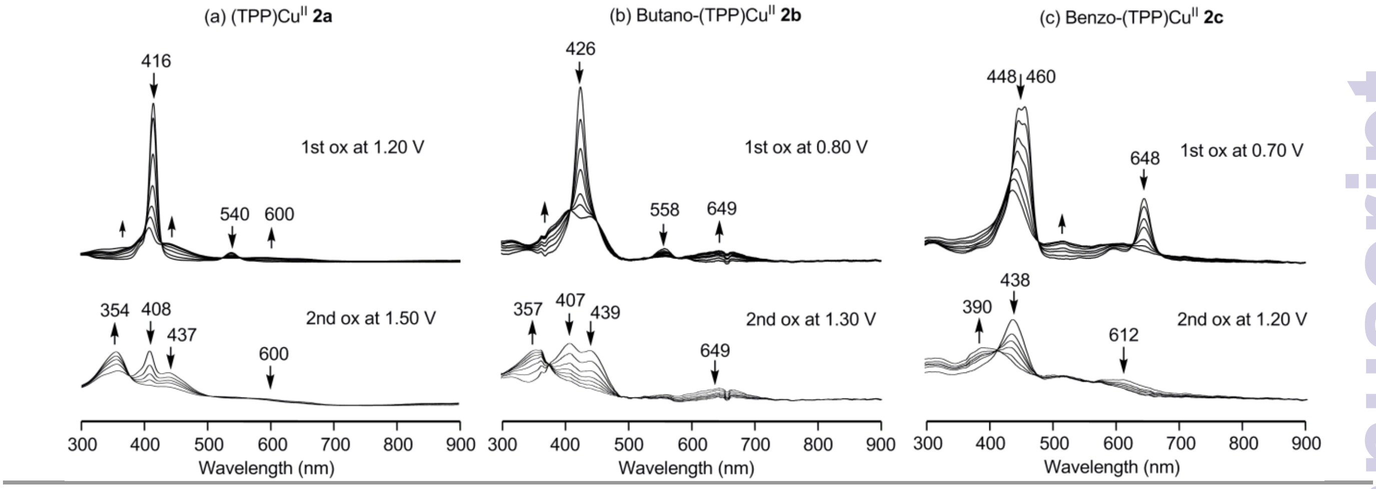


Fig. 5. Thin-layer UV/Vis spectral changes of (a) (TPP)Cu^{II} **2a**, (b) butano-(TPP)Cu^{II} **2b** and (c) benzo-(TPP)Cu^{II} **2c** during the first and second controlled potentia oxidations in CH_2Cl_2, 0.1 M TBAP. Cyclic voltammograms for the compounds are shown in Fig. 4.

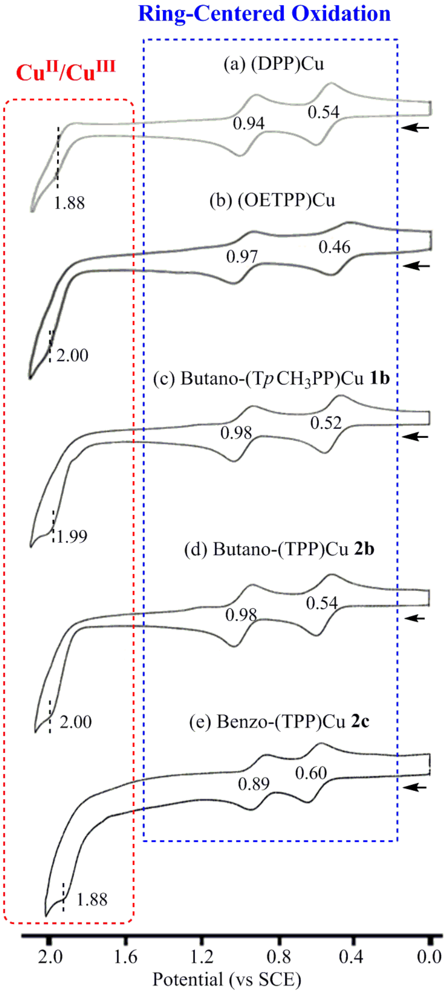


Fig. 6. Cyilc voltammograms of (a) (DPP)Cu, (b) (OETPP)Cu, (c) butano-($TpCH_3PP$)Cu **1b**, (d) butano-(TPP)Cu **2b** and (e) benzo-(TPP)Cu **2c** in PhCN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

Thin-layer UV-visible spectroelectrochemistry was carried out during the two oxidations of each porphyrin in CH_2Cl_2 containing 0.1 M TBAP. Examples of the spectral changes are illustrated in Fig. 5 for compounds **2a**, **2b** and **2c** in CH_2Cl_2. The applied oxidation potentials are indicated in the figure a were in each case sufficiently positive of $E_{1/2}$ for the specific redox couple to guarantee a complete conversion of t neutral porphyrin to its singly or doubly oxidized form.

As seen in the figure, the three porphyrins exhibit similar spectral changes independent of the β,β'-fused groups. The Soret and Q bands both decrease in intensity during the firs oxidation of each compound (see spectra at top of Fig. 5) indicating formation of porphyrin π-cation-radicals under the given solution conditions. The spectral changes during the second oxidation (bottom of Fig. 5) indicate the formation of a porphyrin dication.

It was long thought that Cu(II) porphyrins would undergo only porphyrin macrocycle-centered oxidations in nonaqueous media[1,2] but a metal-centered oxidation to give a Cu(III) porphyrin was recently demonstrated as being possible for t nonplanar copper porphyrins (OETPP)Cu and (DPP)Cu in PhCN containing 0.1 M TBAP.[12] In the case of the currently investigated copper tetrabutanoporphyrins and tetrabenzoporphyrins, a metal-centered oxidation is also observed under the same solution conditions. Examples are given in Fig. 6 for compounds **1b**, **2b** and **2c,** where the Cu^{II}/Cu^{III} process is located at ~2.00 V vs SCE in PhCN. The Cu^{II}/Cu^{III} transitions of (DPP)Cu and (OETPP)Cu are located at similar potentials in this solvent (see Figs 6a and 6b).

Reduction. The tetrabutanoporphyrins **1b**-**3b** and tetrabenzoporphyrins **1c**-**3c** undergo two one-electron reductions in CH_2Cl_2, DMF and PhCN. As seen in Fig. 7, the first reversible reduction is located at similar half-wave potentials of $E_{1/2}$ = -1.56 for **1b**, at -1.55 V for **2b** and at -1.52 V for **3b**. The second quasi-reversible reduction of the same compounds shifts as a function of the electron-donating/electron-withdrawin substituents on the four *meso*-phenyl rings and is located at $E_{1/2}$ values between -1.82 and -1.97 V in CH_2Cl_2. The potential separation between the two reductions ranges from 0.30 t 0.41 V in CH_2Cl_2, values which are similar to the $\Delta E_{1/2}$ betwee the two ring- centered reductions of($TpYPP$)Cu in the sam solvent (see Table 2).

RSC Advances Accepted Manuscript

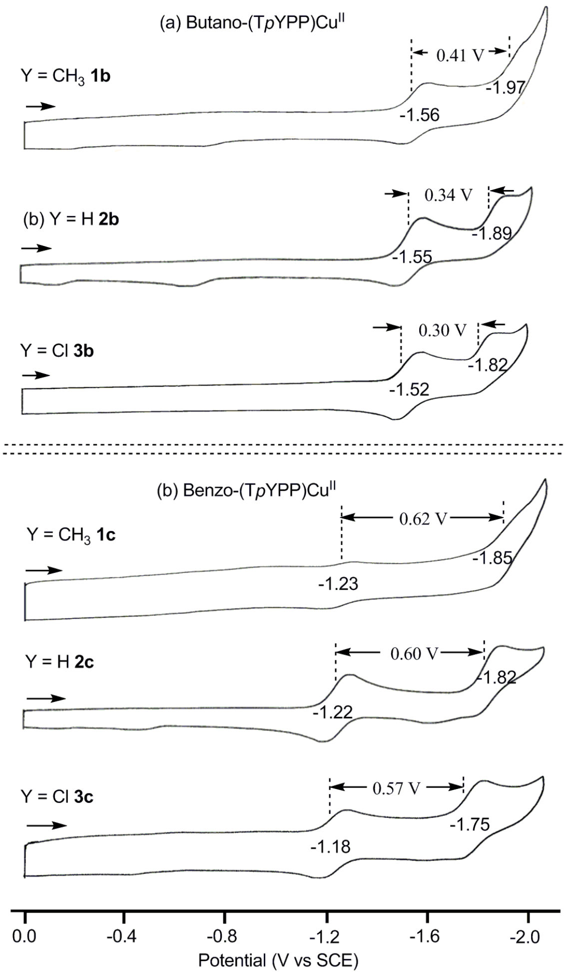


Fig. 7. Cyclic voltammograms showing reductions of the (a) tetrabutanoporphyrins **1b**-**3b** and (b) tetrabenzoporphyrins **1c**-**3c** in CH$_2$Cl$_2$ containing 0.1 M TBAP.

Like the tetrabutanoporphyrins, the copper(II) tetrabenzoporphyrins **1c**-**3c** also undergo two one-electron reductions, but the first reduction is shifted positively by over 300 mV as compared to that of the corresponding tetrabutanoporphyrins **1b**-**3b** (see Figs 3 and 7). This contrasts with the second reduction which occurs at very similar $E_{1/2}$ values of -1.75 and -1.85 V. This difference between the two series of compounds leads to a much larger potential separation (0.57-0.62 V) between the first and second reductions of 1c-3c as compared to **1b**-**3b**.

Fig. 8 illustrates the spectral changes for **2a**, **2b** and **2c** during the first and second one-electron reductions in CH$_2$Cl$_2$, 0.1 M TBAP. As expected, the Soret and Q bands both decrease in intensity upon the stepwise one-electron additions, indicating formation of a π-anion radical and dianion in these processes. Similar spectral changes have been reported for other investigated Cu(II) porphyrins which are converted to their π-anion radical and dianion form in nonaqueous media.[50]

Substituent Effect

It has long been known that modification of a porphyrin structure by addition of electron-withdrawing or electron-donating substituents on the *meso*- and/or β-positions of the macrocycle may have a significant effect on the electrochemical properties.[1,2] This is also the case for the currently investigated β,β'-fused butano- and benzoarylporphyrins.

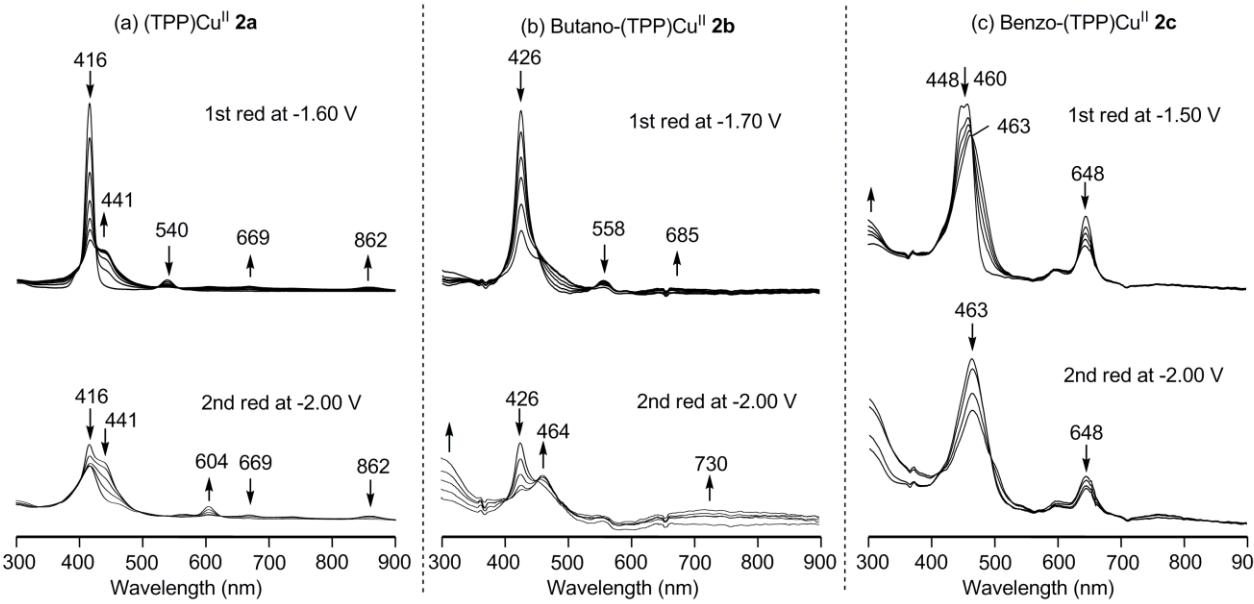


Fig. **8.** Thin-layer UV/Vis spectral changes of (a) (TPP)Cu^{II} **2a**, (b) butano-(TPP)Cu^{II} **2b** and (c) benzo-(TPP)Cu^{II} **2c** during the first and second controlled potential reductions in CH$_2$Cl$_2$, 0.1 M TBAP. Cyclic voltammograms of the compounds are shown in Fig. 7

RSC Advances Accepted Manuscript

Fig. 9 shows how the *meso*-phenyl ring substituents effect redox potentials for reduction and oxidation of the butano-(T*p*YPP)Cu and benzo-(T*p*YPP)Cu compounds in CH_2Cl_2. A linear relationship is observed between the measured $E_{1/2}$ values for electron addition or electron abstraction and the sum of the Hammett substituent constants defined by σ.[51] The magnitude of the substituent effect is given by the slope of the correlation using the relationship $\Delta E_{1/2} = \Sigma\sigma\rho$, where ρ is the reaction constant which measures the magnitude of the substituent effect on the redox potentials.[51]

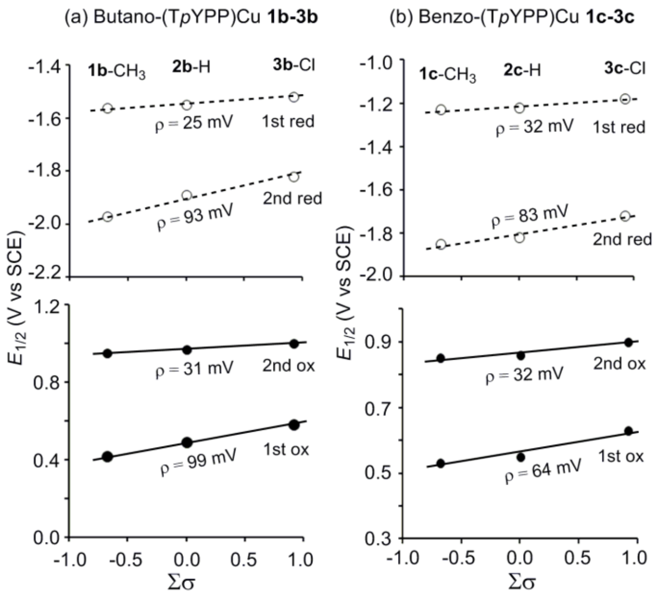


Fig. 9. Plot of reduction and oxidation potentials in CH_2Cl_2 vs the sum of Hammitte constants ($\Sigma\sigma$) of (a) butano-(T*p*YPP)Cu **1b-3b** and (b) benzo-(T*p*YPP)Cu **1c-3c**.

As seen in Fig. 9, the calculated ρ values for the first reduction of **1b-3b** and **1c-3c** are 25 and 32 mV, respectively, and both values are much smaller than the ρ of 93 and 83 mV (the slope of the correlation) for the second reduction of the same compounds. This result indicates that the *meso*-substituents have a larger effect on the second reduction than the first reduction of the compounds. In contract, the first oxidations of compounds in the two series have larger ρ values (99 mV for **1b-3b** and 64 mV for **1c-3c**) than the second oxidations where the slopes (ρ values) are 31 and 32 mV, respectively.

The magnitude of the substituent effect for oxidation of the Cu(II) tetrabenzo- and tetrabutanoporphrins is virtually identical to earlier measured substituent effects for oxidation of Cu(II) tetrarylporphyrins with the same type of *meso*-phenyl substituents.[53] This is significant in that it indicates a similar site of oxidation, independent of the porphyrin ring planarity, the degree of β-pyrrole substitution or the addition of four fused π-ring systems to the macrocycle.

The β,β'-fused tetrabutano and tetrabenzo groups have a significant effect not only on the individual reduction and oxidation potentials but also on the HOMO-LUMO gap of the porphyrins. This is shown by the cyclic voltammograms in Fig. 3 for **2a**, **2b** and **2c** in CH_2Cl_2, 0.1 M TBAP. The first reduction of benzo-(TPP)Cu^{II} **2c** ($E_{1/2}$ = -1.22 V) is easier than the first reduction of **2a** by only 60 mV but the first two oxidations exhibit very large negative shifts (490-440 mV) as compared to the $E_{1/2}$ values for the same two redox reactions of (TPP)Cu^{II} **2a** in CH_2Cl_2. This is due to the effect of the extended π-system and the known distortion of the macrocycle of **2c**.[32] The first oxidation of butano-(TPP)Cu^{II} **2b** is easier than the first oxidation of benzo-(TPP)Cu^{II} **2c**, indicating that a stronger distortion might occur for compound **2b** than for **2c**. The first reduction of **2b** is much more difficult to reduce than **2a**, which is consistent with the electron-donating β,β'-fused butano-substituents on **2b** which lead to a harder reduction at the conjugated π-ring system of the macrocycle.

Finally, it should be pointed out that among the three series of investigated compounds, the tetrabenzotetraaryl-porphyrins have the smallest HOMO-LUMO gap which averages 1.76±0.05 V in CH_2Cl_2, 1.78 V (**2c**) in PhCN and 1.7 ±0.01 V (**2c**, **3c**) in DMF. Similar HOMO-LUMO gaps are also seen for the two nonplanar copper porphyrins, (OETPP)Cu and (DPP)Cu, both of which exhibit a Cu^{II}/Cu^{III} process in PhCN.[12] The HOMO-LUMO gap of the investigated tetrabutanoporphyrins averages 2.04 ± 0.06 V while the average gap of the T(pyPP)Cu derivatives is 2.33±0.03 V in CH_2Cl_2.

Experimental

Chemicals

Dichloromethane (CH_2Cl_2, 99.8%) was purchased from EMD Chemicals Inc. and used as received. *N*,*N*-dimethylformamide (DMF) was purchased from Sigma-Aldrich and used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical or Fluka Chemika Co. and used as received.

Instrumentation

Cyclic voltammetry was carried out at 298 K using an EG&G Princeton Applied Research (PAR) 173 potentiostat/galvanostat. A homemade three-electrode cell was used for cyclic voltammetric measurements. It consisted of a glassy carbon working electrode, a platinum counter electrode, and a homemade 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. UV/Vis spectra were measured using a Hewlett-Packard 8453 diode array spectrophotometer.

Thin-layer UV/Vis spectroelectrochemical experiments were performed with a home-built thin-layer cell which has a light transparent platinum net working electrode. Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat. Time-resolved UV/Vis spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity N_2 was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment. MALDI-TOF mass spectra were carried out on a Bruker BIFLEX

RSC Advances Accepted Manuscript

III ultrahigh resolution. ESR spectra were recorded on a Bruker 300C spectrometer.

Synthesis of (T*p*YPP)Cu 1a-3a

The (T*p*YPP)$_4$Cu derivatives were synthesized and purified according to a published literature procedure.[31]

(T*p*CH_3PP)Cu **1a** (30 mg, 87% yield). UV/Vis (CH_2Cl_2): λ_{max}, 418, 540 nm. MS (MALDI-TOF): *m/z* for $C_{48}H_{36}CuN_4$, calcd, 731.224, found, 730.975.

(TPP)Cu **2a** (38 mg, 90% yield). UV/Vis (CH_2Cl_2): λ_{max}, 416, 540 nm. MS (MALDI-TOF): *m/z* for $C_{44}H_{28}CuN_4$, calcd, 675.161, found, 674.909.

(T*p*ClPP)Cu **3a** (35 mg, 85% yield). UV/Vis (CH_2Cl_2): $\lambda_{max,}$ 415, 539 nm. MS (MALDI-TOF): *m/z* for $C_{44}H_{24}Cl_4CuN_4$, calcd, 811.005, found, 811.004.

Synthesis of copper tetrabutanotetraarylporphyrins 1b-3b

Free-base butano-(TpYPP)H_2 (~100 mg), which was synthesized according to a procedure in the literature,[30,31] was dissolved in 50 mL $CHCl_3$/MeOH (v/v 4:1) containing excess $Cu(OAc)_2•H_2O$ (300 mg). The mixture was stirred at room temperature for half a day and the progress of the reaction was monitored by TLC and UV-vis spectroscopy. After the starting compound was completely consumed, the mixture was evaporated to dryness and then freshly chromatographed with neutral alumina (200-300 mesh) using CH_2Cl_2 as eluent. The brown-red fraction was collected and evaporated to dryness.

Butano-(T*p*CH_3PP)Cu **1b** (86 mg, 80% yield). UV/Vis (CH_2Cl_2): $\lambda_{max,}$ 428, 560 nm. MS (MALDI-TOF): *m/z* for $C_{64}H_{60}CuN_4$, calcd, 947.411, found, 947.410.

Butano-(TPP)Cu **2b** (91 mg, 85% yield). UV/Vis (CH_2Cl_2): λ_{max}, 426, 558 nm. MS (MALDI-TOF): *m/z* for $C_{60}H_{52}CuN_4$, calcd, 891.349, found, 891.347.

Butano-(T*p*ClPP)Cu **3b** (88 mg, 83% yield). UV/Vis (CH_2Cl_2): λ_{max}, 426, 559 nm. MS (MALDI-TOF): *m/z* for $C_{60}H_{48}Cl_4CuN_4$, calcd, 1027.193, found, 1030.239

Synthesis of copper tetrabenzotetraarylporphyrins 1c-3c.[31]

The butano-(T*p*YPP)Cu derivatives (~60 mg) were dissolved in 150 mL distilled dry THF and DDQ was added to the solution which was kept under reflux for 1 h as the color of the solution changed from red to deep green. The reaction mixture was allowed to cool, diluted with CH_2Cl_2 and washed with water and NaCl solution. The solvent was removed under vacuum and the residue was purified on a silica gel column with CH_2Cl_2 as eluent. The first dark-green fraction was collected and evaporated to dryness. The resulting blue-green powder was the pure product.

Benzo-(T*p*CH_3PP)Cu **1c** (28 mg, 48% yield). UV/Vis (CH_2Cl_2): $\lambda_{max,}$ 448, 462, 597, 648 nm. MS (MALDI-TOF): *m/z* for $C_{64}H_{44}CuN_4$, calcd, 931.286, found, 933.289.

Benzo-(TPP)Cu **2c** (32 mg, 55% yield). UV/Vis (CH_2Cl_2): λ_{max}, 448, 460, 597, 648 nm. MS (MALDI-TOF): *m/z* for $C_{60}H_{36}CuN_{4,}$ calcd, 875.224, found, 875.222.

Benzo-(T*p*ClPP)Cu **3c** (26 mg, 45% yield). UV/Vis (CH_2Cl_2): λ_{max}, 447, 459, 600, 649 nm. MS (MALDI-TOF): *m/z* for $C_{60}H_{32}Cl_4CuN_4$, calcd, 1011.068, found, 1016.026.

Conclusions

The four β,β′-fused butano or benzo-rings on the copper porphyrins have a significant effect on UV-vis spectra, reduction-oxidation potentials and the HOMO-LUMO gap of the investigated compounds. A 10-20 nm red-shifted Soret band is seen for the tetrabutanoporphyrins and a 40-110 nm red-shift in the Soret band of the tetrabenzoporphyrins as compared to the related non-β-substituted compounds. A Cu(II)/Cu(III) conversion was observed for the tetrabutano- and tetrabenzo-porphyrins in PhCN, and this is attributed to the nonplanarity of porphyrin macrocycle. As is also the case for the fully β-substitued nonplanar copper porphyrins, (OETPP)Cu and (DPP)Cu, the related β,β′-fused butano- and β,β′-fused benzoporphyrins with Cu(II) metal ions have a HOMO-LUMO gap of 2.04 ± 0.06 V and 1.76 ± 0.05 V, respectively in nonaqueous media.

Acknowledgements

We gratefully acknowledge support from the Natural Science Foundation of China (Grant No. 21071067), Jiangsu University Foundation (Grant No. 05JDG051) and the Robert A. Welch Foundation (K.M.K., E-680).

Notes and references

1 K. M. Kadish, E. Van Caemelbecke and G. Royal, In *The Porphyrin Handbook*, K. M. Kadish, K. M. Smith, R. Guilard, Eds, Academic Press: San Diego 2000, Vol. 8, pp 1−114.
2 K. M. Kadish, *Prog. Inorg. Chem*., 1986, **34**, 435−605.
3 B. Sun, Z. P. Ou, S. B. Yang, D. Y. Meng, G. F. Lu, Y. Y. Fang and K. M. Kadish, *Dalton, Trans.* 2014, **43**, 10809−10815.
4 B. Sun, Z.P. Ou, D. Y. Meng, Y. Y. Fang, Y. Song, W. H. Zhu, P. V. Solntsev, V. N. Nemykin and K. M. Kadish, *Inorg. Chem*., 2014, **53**, 8600−8609.
5 S. B. Yang, B. Sun, Z. P. Ou, D. Y. Meng, G. F. Lu, Y. Y. Fang and K. M. Kadish, *J. Porphyrins Phthalocyanines*, 2013, **17**, 857-869.
6 A. X. Lv, Y. Y. Fang, M. Zhu, S. Huang, Z. P. Ou and K. M. Kadish, *J. Porphyrins Phthalocyanines*, 2012, **16**, 310-315.
7 S. Fukuzumi, K. Ohkubo, W. H. Zhu, M. Sintic, T. Khoury, P. J. Sintic,; W. B. E, Z. P. Ou, M. J. Crossley and K. M. Kadish, *J. Am. Chem. Soc.,* 2008, **130**, 9451-9458.
8 T. D. Lash, D. A. Colby and L. F. Szczepura, *Inorg. Chem*., 2004, **43**, 5258-5267.
9 I. Zilbermann, J. Hayon, E. Maimon, R. Ydgar, E. Korin and A. Bettelheim, *Electrochem. Commu.*, 2002, **4**, 862-865.
10 Z. P. Ou, T. Khoury, Y. Y. Fang, W. H. Zhu, P. J. Sintic, M. J. Crossley and K. M. Kadish, *Inorg. Chem*., 2013, **52**, 2474-2483.
11 Z. P. Ou, W. H. Zhu, Y. Y.Fang, P. J. Sintic, T. Khoury, M. J. Crossley and K. M. Kadish, *Inorg. Chem.*, 2011, **50**, 1280 12809.
12 Y. Y. Fang, M. O. Senge, E. Van Caemelbecke, K. M. Smith, C. J. Medforth, M. Zhang and K. M. Kadish, *Inorg. Chem*., 201 , **53**, 10772-10778.
13 A. A. Sinelshchikova, S. E. Nefedov, Y. Y. Enakieva, Y. G. Gorbunova, A. Y. Tsivadze, K. M. Kadish, P. Chen, Bessmertnykh- Lemeune, C. Stern and R. Guilard, *Inorg. Chem*., 2013, **52**, 999-1008.

RSC Advances Accepted Manuscript

Please do not adjust margins

14 S. Mirra, S. Milione, M. Strianese and C. Pellecchia, *Euro. J. Inorg. Chem*., 2015, 2272-2276.
15 M. M. Yu, C. Wang, J. Li, L. Yuan and W. J. Sun, *Appl. Surf. Sci*., 2015, **342**, 47-54.
16 T. Nguyen, P. Hakansson, R. Edge, D. Collison, B. A. Goodman, J. R. Burns and E. Stulz, *New J. Chem*., 2014, **38**, 5254-5259.
17 M. M. Yu, J. Li, W. J. Sun, M. Jiang and F. X. Zhang, *J. Mat. Sci*., 2014, **49,** 5519-5528.
18 T. I. S. Oliveira, V. N. dos Santos, D. Lomonaco, A. N. Correia, S. E. Mazetto and P. de Lima-Neto, *J. Electrochem. Soc.,* 2013, **160**, B113-B118.
19 Y. Y. Liu, Y. M. Yang, Q. L. Sun, Z. Y. Wang, B. B. Huang, Y. Dai, X. Y. Qin and X. Y. Zhang, *ACS Appl. Mat. & Interf*., 2013, **5**, 7654-7658.
20 P. Hakansson, T. Nguyen, P. B. Nair, R. Edge and E. Stulz, *Phys. Chem. Chem. Phys*., 2013, **15**, 10930-10941.
21 M. H. Ha-Thi, N. Shafizadeh, L. Poisson and B. Soep, *J. Phys. Chem. A*, 2013, **117,** 8111-8118.
22 G. P. Yao, J. Li, Y. Luo and W. J. Sun, *J. Mol. Cat. A: Chem*., 2012, **361-362**, 29-35.
23 G. Q. Liu, A. N. Khlobystov, G. Charalambidis, A. G. Coutsolelos, G. A. D. Briggs and K. Porfyrakis, *J. Am. Chem. Soc*., 2012, **134**, 1938-1941.
24 W. J. Sun, J. Li, G. P. Yao, M. Jiang and F. X. Zhang, *Cat. Comm*., 2011, **16**, 90-93.
25 G. V. Ponomarev, D. V. Yashunsky and D. P. Arnold, *Rec. Res. Develop*. *Pure & Appl. Chem*., 1998, **2**(Pt.1), 199-215.
26 M. S. Asano, K. Okamura, A. Jin-mon, S. Takahashi, Y. Kaizu, *Chem. Phys*., 2013, **419**, 250-260.
27 S. Afzal, W. A. Daoud and S. J. Langford, *ACS Appl. Mat. & Interf*., 2013, **5,** 4753-4759.
28 X. Q. Su, J. Li, Z. Q. Zhang, M. M. Yu and L. Yuan, *J. Alloys Comp*., 2015, **626,** 252-259.
29 W. J. Sun, J. Li, G. Mele, Z. Q. Zhang and F. X. Zhang, *J. Mol. Cat. A: Chem*., 2013, **366,** 84-91.
30 C. M. B. Carvalho, T. J. Brocksom and K. Thiago de Oliveira, *Chem. Soc. Rev.,* 2013, **42**, 3302-3317.
31 O. S. Finikova, A. V. Cheprakov, I. P. Beletskaya, P. J. Carroll and S. A. Vinogradov, *J. Org. Chem*., 2004, **69**, 522-535.
32 L. D. Sparks, C. J. Medforth, M. S. Park, J. R. Chamberlain, M. R.Ondrias, M. O. Senge, K. M. Smith and J. A. Shelnutt, *J. Am. Chem. Soc*., 1993, **115**, 581-592.
33 D. Chumakov, A. Moiseeva, A. Anisimov, B. Uzhinovand A. Khoroshutin, *J. Porphyrins Phthalocyanines,* 2010, **14**, 815-824.
34 M. H. Qi and G. F. Liu, *J. Porphyrins Phthalocyanines,* 2004, **8**, 1187-1195.
35 K. M. Kadish, O. S. Finikova, E. Espinosa, C. P. Gros, G. De Stefano, A. V. Cheprakov, I. P. Beletskaya and R. Guilard, *J. Porphyrins Phthalocyanines,* 2004, **8**, 1062-1066.
36 P. Chen, O. S. Finikova, Z. P. Ou, S. A. Vinogradov and K. M. Kadish, *Inorg. Chem.,* 2012, **51**, 6200-6210.
37 V. V. Rozhkov, M. Khajehpour and S. A. Vinogradov, *Inorg. Chem.,* 2003, **42**, 4253-4255.
38 J. E. Rogers, K. A. Nguyen, D. C. Hufnagle, D. G. McLean, W. J. Su, K. M. Gossett, A. R. Burke, S. A. Vinogradov, R. Pachter and P. A. Fleitz, *J. Phys. Chem. A,* 2003, **107**, 11331-11339.
39 G. Dougherty and R. F. Pasternack, *Inorg. Chim. Acta,* 1992, **195**, 95-100.
40 A. Pezeshk, *J. Phys. Chem.* 1990, **94**, 451-456.
41 C. Mengersen, J. Subramanian and J.-H. Fuhrhop, *Mole. Phys*., 1976, **32**, 893-897.
42 M. Ravikanth, D. Reddy, A. Misra and T. K. Chandrashekar, *J. Chem. Soc., Dalton Trans*., 1993, 1137-1141.
43 L. Banci, *Inorg. Chem*., 1985, **24**, 782-786.
44 S. P. Greiner, D. L. Rowlands and R. W. Kreilick, *J. Phys. Chem*., 1992, **96**, 9132-9139.
45 S. Konishi, M. Hoshino and M. Imamura, *Chem. Phys. Lett*., 1983, **94**, 267-269.
46 J. A. De Bolfo, T. D. Smith, J. F. Boas and J. R. Pilbrow, *J. Chem. Soc., Dalton Trans*., 1975, 1523-1525.
47 P. D. W. Boyd, T. D. Smith, J. H. Price and J. R. Pilbrow, *J. Phys. Chem*., 1972, **56**, 1253-1263.
48 G. Hariprasad, S. Dahal and B. G. Maiya, *J. Chem. Soc., Dalton Trans*., 1996, 3429-3436.
49 J. Takeda and M. Sato, *Chem. Lett*., 1995, 939-940.
50 K. M. Kadish, C. Araullo, G. **B.** Maiya, D. Sazou, J.-M. Barbe, and R. Guilard, *Inorg.* Chem. 1989, **28**, 2528-2533.
51 P. Zuman, In *Substituent Effects in Organic Polarography*, Plenum Press: New York, 1967.
52 M. W. Renner, K. M. Barkigia, Y. Zhang, C. J. Medforth, K. M. Smith and J. Fajer, *J. Am. Chem. Soc*., 1994, **116**, 8582-8592.
53 K. M. Kadish and M. M. Morrison, *Bioinorg. Chem*., 1977, **7**, 107-115.

RSC Advances Accepted Manuscript

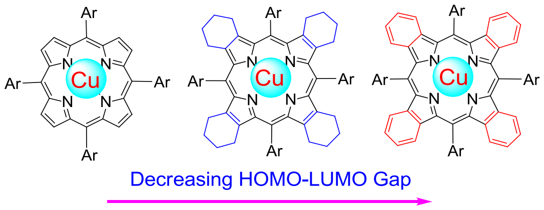
Please do not adjust margins

TOC

Electrochemistry of nonplanar copper(II) tetrabutano and tetrabenzotetraarylporphyrins in nonaqueous media

Lina Ye, Zhongping Ou*, Yuanyuan Fang, Songlin Xue, Liping Wang, Mengli Wang, Yang Song, Karl M. Kadish*

Copper tetrabutano and tetrabenzoporphyrins were synthesized and electrochemically characterized, the substituent effect on spectra, potentials and the HOMO-LUMO gap is discussed.



RSC Advances Accepted Manuscript

This journal is © The Royal Society of Chemistry 20xx