

Dalton Transactions

Accepted Manuscript



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. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it 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.

ARTICLE

Polypyrrole-Functionalized Ruthenium Carbene Catalysts as Efficient Heterogeneous Systems for Olefin Epoxidation

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mohamed Dakkach,^{a,b} Xavier Fontrodona,^a Teodor Parella,^c Ahmed Atlamsani,^b Isabel Romero,^{a,*} Montserrat Rodríguez^{a,*}

New Ru complexes containing the bpea-pyr ligand (bpea-pyr stands for N,N-bis(pyridin-2-ylmethyl)-3-(1H-pyrrol-1-yl)propan-1-amine), with formula $[\text{RuCl}_2(\text{bpea-pyr})(\text{dmsO})]$ (isomeric complexes **2a** and **2b**) or $[\text{Ru}(\text{CN-Me})(\text{bpea-pyr})\text{X}]^{\text{nt}}$ (CN-Me = 3-methyl-1-(pyridin-2-yl)-1H-imidazol-3-ium-2-ide; X = Cl, **3**, or X = H₂O, **4**) have been prepared and fully characterized. Complexes **3** and **4** have been anchored onto an electrode surface through electropolymerization of the attached pyrrole group, yielding stable polypyrrole films. The electrochemical behaviour of **4**, which displays a bielectronic Ru(IV/II) redox pair in solution, is dramatically affected by the electropolymerization process leading to the occurrence of two mono-electronic Ru(IV/II) and Ru(III/II) redox pairs in the heterogeneous system. A carbon felt modified electrode containing complex **4** (**C-felt/poly-4**) has been evaluated as heterogeneous catalyst in the epoxidation of various olefin substrates using $\text{PhI}(\text{OAc})_2$ as oxidant, displaying TON values of several thousands in all cases and good selectivity for the epoxide product.

Introduction

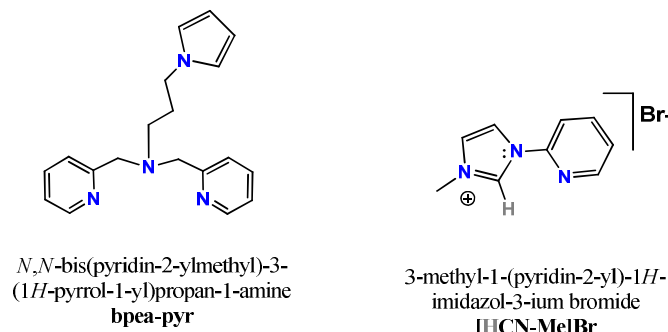
Heterogeneous catalysis is of unquestionable importance in chemical industry since more than 80% of the described procedures involve a heterogeneous catalytic step.¹ One of the remarkable advantages of heterogeneous catalysis is the easy separation of the catalyst from the reaction mixture, thus avoiding the use of purification techniques which might often be arduous and that increase the overall cost of the process. Catalyst self-deactivation pathways are also generally minimized, thus increasing the catalyst performance. In this framework, new strategies towards the heterogenization of classical homogeneous catalysts are being developed.^{2,3}

Although homogeneous catalysts based on transition metals usually display good performance in oxidation reactions, degradation of the complexes takes place to a considerable extent including pathways such as auto-oxidation or oligomerization, in some cases through formation of oxo bridges. To circumvent such drawbacks some authors have described the immobilization of the catalyst within organic polymeric matrices,⁴ a strategy which avoids or minimizes the contact between molecules of the catalyst and consequently leads to a much lower degree of auto-deactivation. Among the different techniques described in the literature, the electropolymerization onto an electrode surface is one of the most developed^{5,6} and involves the inclusion of redox-active functional groups in the catalyst structure which allow, upon oxidation or reduction, the formation of a polymeric film on the surface, leading to a *modified* electrode. A wide diversity of

modified electrodes has been described, which have been used as heterogeneous catalysts for a variety of chemical reactions.⁷⁻¹⁰ Their main advantages, besides the ones mentioned above for heterogeneous systems, are the possibility of carrying out electrocatalysis through the electrode itself and the low amount of catalyst generally used.¹¹

Polypyrrole has become the most studied conducting polymer in the latest decades due to its stability and high electrical conductivity.¹² The use of polypyrrole as organic matrix for catalyst heterogenization usually encompasses the presence of a covalently bonded pyrrole unit in the catalyst structure that, after electrochemical polymerization, allows the anchoring of the catalyst into the polypyrrole backbone at the electrode surface. These heterogeneous systems have been widely used in oxidative catalysis^{6,13} and, in the particular case of olefin epoxidation, most of the polypyrrole-based catalysts contain Mn-porphyrin entities.¹⁴ However, despite that ruthenium complexes have been broadly studied in homogeneous epoxidation catalysis,^{15,16} the polypyrrole-based heterogeneous Ru systems applied to oxidative catalysis deal mainly with alcohol¹⁷ or water¹⁸ oxidation.

In this work we describe the synthesis of a family of Ru complexes containing the bpea-pyr and CN-Me ligands (Scheme 1) together with their anchoring to electrode surfaces through oxidative polymerization of the pendant pyrrole group of the bpea-pyr ligand. One of the Ru-OH₂ complexes synthesized has been tested in olefin epoxidation and constitutes, to the best of our knowledge, the first Ru-polypyrrole system successfully applied to heterogeneous epoxidation catalysis.



Scheme 1. Ligands used in this work.

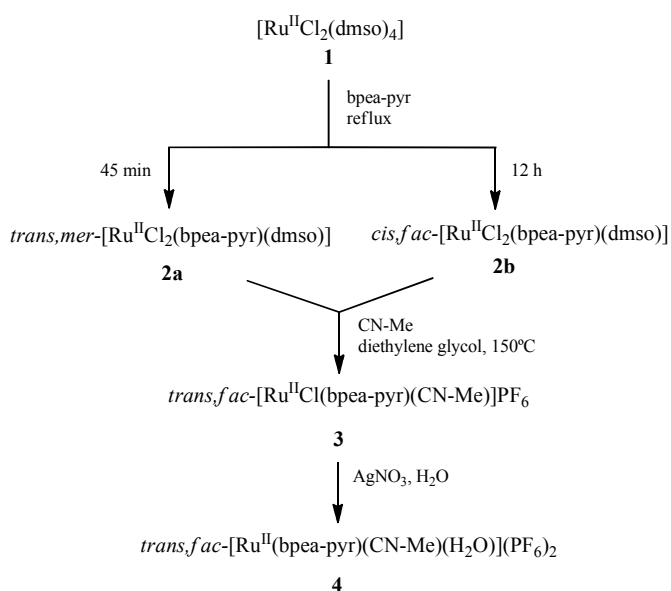
Results and discussion

Synthesis, structure and spectroscopic properties

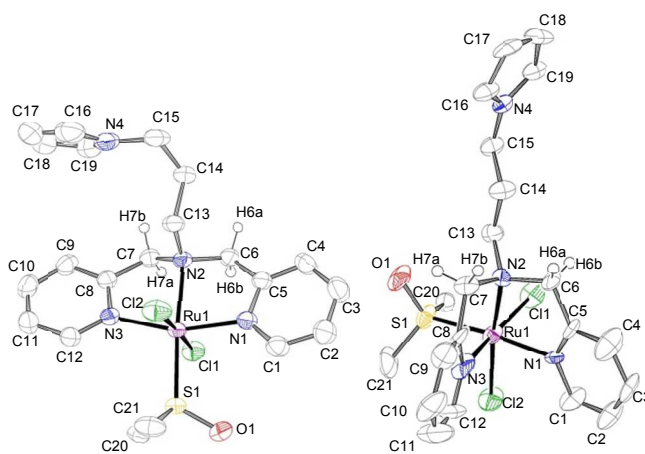
The synthetic strategy followed for the preparation of the complexes is outlined in Scheme 2. The addition of the tridentate bpea-pyr ligand to $[\text{RuCl}_2(\text{dmsO})_4]$ leads to the displacement of three of the four dmsO ligands, giving yield either to complex **2a** or **2b** that can be obtained separately in their respective pure form by simply controlling the extent of the reaction. The *trans* or *cis* notation used refers to the relative position of the two chloro ligands in isomers **2a** and **2b**, and also to the position of the monodentate (Cl^- or H_2O) ligand with regard to the aliphatic N atom of the bpea-pyr ligand in **3** and **4**. On the other hand, *mer* or *fac* indicates the meridional or facial disposition of the tridentate ligand in each case. The flexibility of the bpea-pyr ligand, as is the case of the related ligand bpea,¹⁹ permits its coordination to a metal center either in a *mer* or *fac* fashion, being the former a kinetically stable arrangement of the ligand which is relatively uncommon in octahedral environments.

The X-ray diffraction structure of the two isomeric complexes **2a** and **2b** has been solved and the corresponding ORTEP plots are shown in Fig. 1, whereas the crystallographic data and the main bond distances and angles are gathered in the supporting information. Both complexes present a distorted octahedral geometry with the dmsO ligand coordinated through its S atom. The meridional disposition of the ligand in **2a** does not make any remarkable differences between the structural parameters of the two isomers, which are similar to other Ru complexes containing bpea-type of ligands previously described in the literature.^{19,20}

The addition of the bidentate carbene ligand CN-Me to a solution of either complex **2a** or **2b** leads to the formation of the chloro complex $[\text{Ru}^{\text{II}}\text{Cl}(\text{CN-Me})(\text{bpea-pyr})]^+$, **3**. The coordination of the CN-Me ligand could potentially lead to a set of seven possible isomers including those presenting the bpea-pyr ligand in a *mer* or *fac* fashion (see supporting information for a schematic representation of the different isomers). However, complex **3** is obtained exclusively under the *trans, fac* form, which is probably favoured by the occurrence of H-bonding interactions between the monodentate chloro ligand and the H atoms in the 2-position of the pyridyl rings of the bpea-pyr ligand (H1 and H12, see Fig. 2 for a numbering scheme), as has been already discussed for analogous complexes.^{20a,b} On the other hand, the bpea-pyr ligand adopts a facial disposition in complex **3** even when the CN-Me coordination is carried out using the *mer* isomer **2a** as starting



Scheme 2. Synthesis of complexes 2-4.

Fig. 1 ORTEP plots (ellipsoids at 50% probability) for the structures of complexes **2a** (left) and **2b** (right).

product, again evidencing that *fac* is the thermodynamically preferred coordination geometry.

Finally, the aquo complex **4** is easily obtained by reaction of complex **3** with a silver salt in aqueous media, keeping the former *trans, fac* geometry.

All the complexes have been thoroughly characterized through mono- and bidimensional NMR experiments, allowing to unambiguously assigning all the resonances (see experimental section). Fig. 2 displays the ^1H -NMR spectra of complex **3**, together with the numbering scheme used.

The UV-vis spectra of complexes **3** and **4** registered in dichloromethane are shown in Fig. 3. In the range between 250 and 350 nm the complexes display a set of $\pi\text{-}\pi^*$ intraligand absorptions whereas at higher wavelengths $d\pi\text{-}\pi^*$ MLCT absorptions can be observed (see experimental section).²¹ The replacement of a chloro ligand by aquo in **4** produces an hypsochromic shift of the maximum wavelength originated by

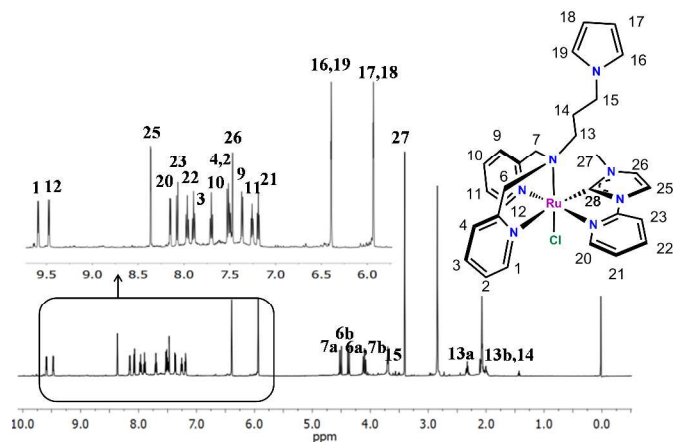


Fig. 2 $^1\text{H-NMR}$ spectrum of complex **3** together with numbering scheme.

the lower π -donor capacity of H_2O when compared to the anionic Cl^- ligand, thus leading to the stabilization of the $d\pi(\text{Ru})$ levels and consequently to higher energy MLCT transitions in the case of the aquocomplex.

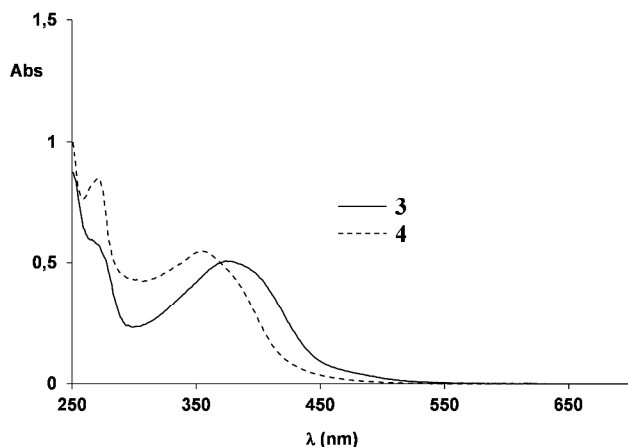
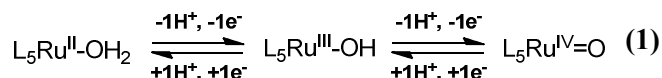


Fig. 3 UV-vis spectra of complexes **3** and **4** in dichloromethane (concentration $1 \cdot 10^{-4}$ M).

Redox properties

All complexes have been characterized electrochemically through CV experiments and display chemically and electrochemically reversible waves. The cyclic voltammetry of chlorocomplex **3** displays a Ru(III/II) redox pair at $E_{1/2} = 0.67$ V vs. SSCE (see supporting information), which is in the range of other Ru chlorocomplexes with N- or C-donor ancillary ligands.^{20a,22}

The redox properties of the aquocomplex **4** have been investigated in dichloromethane and also in aqueous media. The electrochemical behaviour of Ru^{II} -aquocomplexes is generally pH-dependent due to the simultaneous exchange of electrons and protons during the redox processes as indicated in eq. (1):



The reversibility of these redox processes constitutes the basis for the use of this kind of complexes in redox catalysis. In most cases, the two mono-electronic redox processes indicated in eq. (1), corresponding to the Ru(III/II) and Ru(IV/III) redox couples, can be observed in cyclic voltammetry. However, in the case of complex **4** a unique redox wave is displayed throughout a wide pH range in aqueous media (Fig. 4).

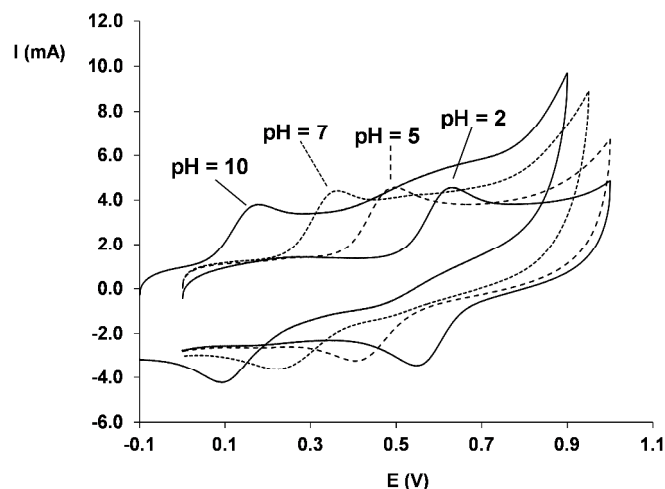
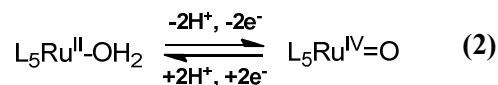


Fig. 4 Cyclic voltammograms of complex **4** at different pH values in aqueous solution (scan rate 100 mV s^{-1}).

The dependence of the $E_{1/2}$ values vs. pH accomplishes the Nernst equation with a slope value of c.a. 58 mV, corresponding to the transfer of an equivalent number of protons and electrons (see supporting information), which would be in accordance with the simultaneous transfer of two protons and two electrons as indicated in eq. (2):



This behaviour is also consistent with the bielectronic wave displayed by the analogous complex $[\text{Ru}(\text{CN-Me})(\text{bpea})(\text{H}_2\text{O})]^{2+}$ (where bpea is $\text{N,N}'$ -bis(2-pyridylmethyl)ethylamine)²³ which contains practically identical ligands and consequently similar electronic effects are expected to be exerted at the metal center. On the basis of the electrochemical properties displayed by other previously reported Ru complexes, carbenic ligands seem to provide a balance between σ -donor and π -acceptor properties that can reduce to a considerable extent the difference between the Ru(III/II) and the Ru(IV/III) $E_{1/2}$ values leading in some cases to bielectronic Ru(IV/II) processes.^{22a,24} This behaviour may play an important role in the selectivity obtained when using these complexes as catalysts in epoxidation reactions as will be discussed later. On the other hand, the cyclic voltammetry of the aquocomplex **4** performed in dichloromethane also displays a single, reversible wave (see supporting information) with a difference between the anodic and cathodic peak potentials ($E_{p,a} - E_{p,c}$) which is a half of that found for the CV of the analogous chlorocomplex **3** registered under the same conditions, a fact indicative of the transfer of two electrons in the case of **4**.

Heterogenization of the complexes

The anchoring of complexes **3** and **4** onto an electrode surface to generate the corresponding modified electrodes **C/poly-3** and **C/poly-4** was first carried out using a glassy carbon electrode (3 mm diameter), through successive scans of potential between 0 and 1.3 V from a 1 mM solution of the corresponding complex in dichloromethane. Fig. 5A displays the voltammograms obtained in the course of the polymerization for the aquocomplex **4**, where the intensity of the metal-centred redox process (found at around 0.95 V) increases continuously, indicating the deposition of the catalyst at the surface (the CV obtained in the analogous experiment performed with the chlorocomplex **3** are gathered in the supporting information).

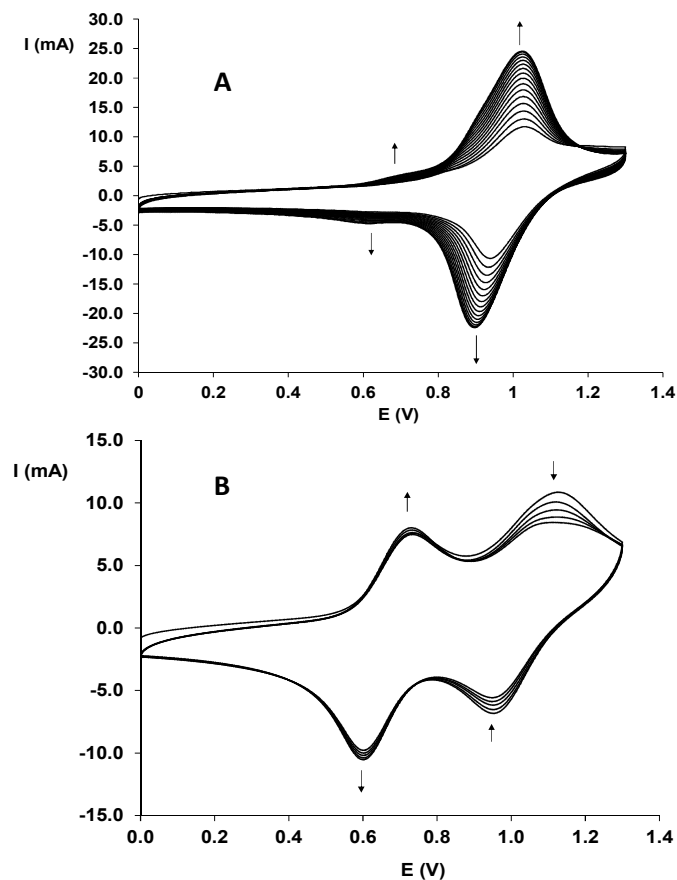


Fig. 5 A) Growth of a **C/poly-4** film during the first 20 consecutive CV cycles on a glassy carbon disk electrode (3 mm diameter) in 1 mM of **4** in 0.1 M TBAH, CH_2Cl_2 ($\nu = 100 \text{ mV}\cdot\text{s}^{-1}$). B) Five voltammetric cycles for the **C/poly-4** film coated electrode upon transferring it to a blank electrolyte solution of 0.1 M TBAH in CH_2Cl_2 ($\nu = 100 \text{ mV}\cdot\text{s}^{-1}$). Final amount of anchored complex = $7.70 \cdot 10^{-10} \text{ mols}\cdot\text{cm}^{-2}$.

During polymerization of **4**, a new wave with low intensity appears at c.a. 0.65-0.70 V that is discussed next. After 20 cycles, the modified **C/poly-4** electrode is transferred to a blank electrolyte solution and five further cycles are registered (Fig. 5B). It is striking to see that, once the complex is anchored at the electrode surface, it displays two clearly differentiated redox processes of equal intensity that can be assigned to the monoelectronic Ru(IV/III) and Ru(III/II) redox pairs, at $E_{1/2}$ values of 1.04 V and 0.66 V respectively. Thus, the polypyrrole environment dramatically affects the redox behavior of the complex avoiding the occurrence of the bielectronic process

observed in homogeneous solution. On the other hand, the polymer generated at the surface of the electrode displays high stability with a good maintenance of the intensity of the signals despite the low level of cross-linking expected for a compound with only one pyrrole group per monomer unit.^{5c,11a,14a}

Catalytic activity

The catalytic performance of the heterogeneous **poly-4** system was tested in the epoxidation of some olefins using iodobenzene diacetate as oxidant in dichloromethane. The heterogeneous catalysts were set following the procedure described above but at a preparative scale using carbon felt (1x1x0.5 cm) as working electrode instead of a glassy carbon disk (the modified electrode is termed in this case **C-felt/poly-4**). The results obtained in the oxidation of the olefin substrates tested are gathered in Table 1, where the amount of supported Ru-catalyst **4** is indicated in each case.

Table 1. Epoxidation of different olefins using the heterogeneous **C-felt/poly-4** system (*Conv.* and *Sel.* stand for conversion and selectivity values respectively). Conditions: substrate ($1.25 \cdot 10^{-4} \text{ mol}$), oxidant $\text{PhI}(\text{OAc})_2$ ($1.25 \cdot 10^{-4} \text{ mol}$), CH_2Cl_2 (5 mL), 25°C, 32h. The amount of supported catalyst is indicated in each case. Conversions and yields are evaluated by GC analysis using biphenyl as internal standard.

	Substrate	Product	Mols of 4	Conv. (%)	Sel. ^a (%)	TON
1			$4.07 \cdot 10^{-9}$	9	16	2683
2			$3.4 \cdot 10^{-9}$	24	92	8823
3			$1.72 \cdot 10^{-9}$	40 ^b	82	29024
4			$2.59 \cdot 10^{-9}$	35	94	16891
5			$5.79 \cdot 10^{-9}$	18	85	3874
6			$2.22 \cdot 10^{-9}$	26	89 ^c	14712

^a Calculated as [epoxide yield/substrate conversion]x100. ^b Epoxide 96% *cis* / 4% *trans*. ^c Epoxidation exclusively at the cyclohexene ring.

As can be observed, the heterogeneous system shows a highly remarkable catalytic activity with turnover numbers of several thousands in all cases. The selectivity for the epoxide product is excellent for either aromatic or aliphatic olefins except for styrene (entry 1), which also displays the lowest conversion degree among the substrates tested. In this case, the occurrence of two monoelectronic redox processes at the anchored Ru-catalyst will probably favour the generation of radical intermediates which can drive the reaction towards substrate polymerization instead of epoxidation. This hypothesis would also explain the formation of a certain amount of *trans* epoxide when oxidizing *cis*-β-methylstyrene (entry 3), as the *cis*→*trans* isomerization prior to epoxide ring

closure must involve a radical intermediate, where the C-C bond rotation is allowed.²⁵ At this point, it is interesting to briefly mention the results obtained in olefin epoxidation using the analogous $[\text{Ru}(\text{CN-Me})(\text{bpea})(\text{H}_2\text{O})]^{2+}$ complex (which displays a Ru(IV/II) bielectronic wave) as homogeneous catalyst under analogous conditions,²³ with a selectivity for the styrene epoxide product higher than 93% and with the *cis*- β -methylstyrene epoxide obtained quantitatively under its *cis* form, though with much lower TON values. Consequently, despite the occurrence of the two monoelectronic processes in the polypyrrole-anchored complex, the overall catalytic activity of the heterogeneous **C-felt/poly-4** system is excellent, with TON values among the highest reported for this type of process either in homogeneous and heterogeneous phase and with remarkably good selectivity values.

Attempts to reuse the **C-felt/poly-4** catalyst in a second run resulted in very low degree of conversion. We considered then the possibility of catalyst leaching from the electrode surface, but no traces of ruthenium were found by ESI-MS and ICP-AES spectrometry carried out on the residual solution after the end of the catalysis. Finally, no epoxidation was detected when using a bare carbon felt electrode (without Ru complex) as heterogeneous catalyst.

Experimental procedures

Synthesis of ligands and complexes

The ligands *N,N*-bis(pyridin-2-ylmethyl)-3-(1H-pyrrol-1-yl)propan-1-amine (bpea-pyr)²⁶ and 3-methyl-1-(pyridin-2-yl)-1H-imidazol-3-ium bromide (HCN-Me),²⁷ as well as the complex $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{dmsO})_4]$, **1**,²⁸ have been prepared following synthetic methods previously described in the literature. All the manipulations have been systematically performed under nitrogen atmosphere using Schlenk techniques.

Synthesis of *trans,mer*- $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{bpea-pyr})(\text{dmsO})]$, **2a.** 0.14 g (0.412 mmol) of bpea-pyr and 0.2 g (0.412 mmol) of $[\text{RuCl}_2(\text{dmsO})_4]$ were dissolved in 20 mL of absolute ethanol. The solution was kept under reflux for 45 min leading to the formation of an orange precipitate. After finishing the reaction the volume of the solution was reduced under reduce pressure and the precipitate was filtered, washed with cold ethanol and diethyl ether and dried in vacuo. Yield: 0.155 g (67.6%). **Elem. Anal.** found (calc.) for $\text{C}_{21}\text{H}_{28}\text{Cl}_2\text{N}_4\text{O}_1\text{Ru}_1\text{S}_1$: C, 45.21 (45.32); N, 10.18 (10.06); H, 5.43 (5.07); S, 5.59 (5.76). **¹H-NMR (600 MHz, CD₂Cl₂)** δ (ppm): 8.76 (d, 2 H, H1, H12, J_{1-2} and J_{12-11} = 6.45 Hz), 7.62 (pt, 2 H, H3, H10, J_{3-2} and J_{10-11} = 6.75 Hz, J_{10-9} and J_{3-4} = 7.45 Hz), 7.24 (pt, 2 H, H2, H11, J_{2-1} and J_{11-12} = 6.45 Hz, J_{2-3} and J_{11-10} = 6.75 Hz), 7.20 (d, 2H, H4, H9, J_{9-10} and J_{4-3} = 7.45 Hz), 6.56 (t, 2 H, H16, H19, $J_{16-17,18}$ and $J_{19-17,18}$ = 2 Hz), 6.05 (t, 2 H, H17, H18, $J_{17-16,19}$ and $J_{18-16,19}$ = 2 Hz), 5.79 (d, 2 H, H6b, H7a, J_{6b-6a} and J_{7a-7b} = 14.3 Hz), 4.28 (d, 2 H, H6a, H7b, J_{6a-6b} and J_{7b-7a} = 14.3 Hz), 3.75 (t, 2 H, H15, J_{15-14} = 6.8 Hz), 3.52 (s, 6 H, H20, H21), 3.06 (m, 2 H, H13), 2.03 (m, 2 H, H14). **¹³C-NMR (151 MHz, CD₂Cl₂, 25°C)** δ (ppm): 165.1 (C5, C8), 156.4 (C1, C12), 135.9 (C3, C10), 123.7 (C2, C11), 121.4 (C4, C9), 120.3 (C16, C19), 108.2 (C17, C18), 63.8 (C6, C7), 56.7 (C213), 47.0 (C15), 45.9 (C20, C21), 27.2 (C14). **NOEs:** H7b-H13 and H14; H7b-H9; H12-H20. For the NMR signal assignment we have used the same numbering scheme described for the X-ray structure shown in . **IR (ν_{max} , cm⁻¹):** 3095 (w), 2944 (w), 1440 (s), 1076 (s), 1004 (m), 892 (m). **$E_{1/2}$ (III/II),** (CH₂Cl₂ + 0.1 M TBAH (tetrabutylammonium hexafluorophosphate)): 0.58 V vs. SSCE. **UV-vis** (CH₂Cl₂): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹) 254 (7775), 362

(2614), 428 (4994). **ESI-MS: m/z (relative intensity, assignment) = 521 (100%, [M - Cl]⁺).**

Synthesis of *cis,fac*- $[\text{Ru}^{\text{II}}\text{Cl}_2(\text{bpea-pyr})(\text{dmsO})]$, **2b.** This compound has been obtained through a procedure analogous to the one described for complex **2a** but prolonging the reflux up to 12 hours. Yield: 0.125 g (54.5%). **Elem. Anal.** found (calc.) for $\text{C}_{21}\text{H}_{28}\text{Cl}_2\text{N}_4\text{O}_1\text{Ru}_1\text{S}_1$: C, 44.86 (45.32); N 9.96 (10.06); H 5.06 (5.07); S 5.71 (5.76). **¹H-NMR (600 MHz, CD₂Cl₂)** δ (ppm): 9.73 (d, 1 H, H1, J_{1-2} = 6.5 Hz), 9.21 (d, 1 H, H12, J_{12-11} = 5.5 Hz), 7.63 (td, 1 H, H3, J_{3-2} and J_{3-4} = 7.8 Hz, J_{3-1} = 1.6 Hz), 7.47 (td, 1 H, H10, J_{10-11} and J_{10-9} = 7.8 Hz, J_{10-12} = 1.5 Hz), 7.26 (pt, 1 H, H2, J_{2-1} = 6.5 Hz, J_{2-3} = 7.8 Hz), 7.22 (d, 1 H, H4, J_{4-3} = 7.8 Hz), 7.08 (d, 1 H, H9, J_{9-10} = 7.8 Hz), 7.06 (pt, 1 H, H11, J_{11-12} = 5.5 Hz, J_{11-10} = 7.8 Hz), 6.75 (t, 2 H, H16, H19, $J_{16-17,18}$ and $J_{19-17,18}$ = 2.1 Hz), 6.15 (t, 2 H, H17, H18, $J_{17-16,19}$ and $J_{18-16,19}$ = 2.1 Hz), 4.52 (d, 1 H, H7a, J_{7a-7b} = 10.5 Hz), 4.49 (d, 1 H, H6b, J_{6b-6a} = 15.9 Hz), 4.15 (m, 1 H, H13a), 4.00 (d, 1 H, H7b, J_{7b-7a} = 10.5 Hz), 3.99 (m, 2 H, H15), 3.98 (m, 1H, H13b), 3.92 (d, 1 H, H6a, J_{6a-6b} = 15.9 Hz), 3.52 (s, 3 H, H20), 3.03 (s, 3 H, H21), 2.23 (m, 2 H, H14). **¹³C-NMR (151 MHz, CD₂Cl₂, 25°C)** δ (ppm): 164.4 (C8), 160.4 (C5), 154.2 (C12), 152.5 (C1), 137.0 (C3), 135.4 (C10), 124.1 (C2), 124.0 (C9), 120.9 (C16, C19), 120.6 (C4), 120.6 (C11), 108.8 (C17, C18), 69.5 (C7), 68.3 (C6), 62.9 (C13), 47.8 (C15), 45.1 (C20), 44.7 (C21), 26.2 (C14). **NOEs:** H12-H21; H18-H19. For the NMR signal assignment we have used the same numbering scheme described for the X-ray structure shown in Fig. 1. **IR (ν_{max} , cm⁻¹):** 3089 (w), 2950 (w), 1477 (m), 1068 (s), 1004 (s), 892 (m), 757 (s). **$E_{1/2}$ (III/II),** (CH₂Cl₂ + 0.1 M TBAH): 0.57 V vs. SSCE. **UV-vis** (CH₂Cl₂): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹) 251 (6770), 371 (4531). **ESI-MS: m/z (relative intensity, assignment) = 521 (100%, [M - Cl]⁺).**

Synthesis of *trans,fac*- $[\text{Ru}^{\text{II}}\text{Cl}(\text{CN-Me})(\text{bpea-pyr})](\text{PF}_6)_3$, **3-0.8 CH₂Cl₂.** A sample of complex **2a** or **2b** (0.050 g, 0.099 mmol) together with LiCl (0.081 g, 1.98 mmol) were dissolved in 20 mL of diethylene glycol and the solution was stirred at room temperature for 30 min. Afterwards the mixture was progressively warmed and, when the temperature reached 60°C, a solution of [HCN-Me]Br pre-ligand (0.016 g, 0.099 mmol) and NEt₃ (0.04 mL, 0.297 mmol) in 2 mL of diethylene glycol was added. The mixture was kept at 150°C overnight. After cooling, 40 mL of H₂O and 2 mL of a saturated aqueous NH₄PF₆ solution were added. A yellowish precipitate was formed which was filtered and recrystallized from CH₂Cl₂: pentane 1:1 (v:v). The final precipitate was filtered, washed with diethylether and pentane and dried in vacuo. Yield: 0.040 mg (54.1%). **Elem. Anal.** found (calc.) for $\text{C}_{28}\text{H}_{31}\text{Cl}_1\text{F}_6\text{N}_7\text{P}_1\text{Ru}_1 \cdot 0.8\text{CH}_2\text{Cl}_2$: C, 42.55 (42.44); N, 11.86 (12.03); H 4.27 (4.03). **¹H-NMR (600 MHz, d₆-acetone, 25°C)** δ (ppm): 9.59 (ddd, 1 H, H1, J_{1-2} = 5.5 Hz, J_{1-3} = 1.4 Hz, J_{1-4} = 0.7 Hz), 9.49 (ddd, 1 H, H12, J_{12-11} = 6.5 Hz, J_{12-10} = 1.4 Hz, J_{12-9} = 0.7 Hz), 8.37 (d, 1 H, H25, J_{25-26} = 2.2 Hz), 8.15 (ddd, 1 H, H20, J_{20-21} = 6.5 Hz, J_{20-22} = 1.4 Hz, J_{20-23} = 0.7 Hz), 8.07 (dt, 1 H, H23, J_{23-22} = 8.2 Hz, J_{23-21} = 1.0 Hz), 7.96 (ddd, 1 H, H22, J_{22-23} = 8.2 Hz, J_{22-21} = 6.5 Hz, J_{22-20} = 1.4 Hz), 7.89 (td, 1 H, H3, J_{3-2} and J_{3-4} = 7.7 Hz, J_{3-1} = 1.4 Hz), 7.70 (td, 1 H, H10, J_{10-11} and J_{10-9} = 7.7 Hz, J_{10-12} = 1.4 Hz), 7.52 (d, 1 H, H4, J_{4-3} = 7.7 Hz), 7.50 (m, 1 H, H2), 7.47 (d, 1 H, H26, J_{26-25} = 2.2 Hz), 7.36 (d, 1H, H9, J_{9-10} = 7.7 Hz), 7.26 (pt, 1 H, H11, J_{11-12} = 6.5 Hz, J_{11-10} = 7.7 Hz), 7.18 (td, 1H, H21, J_{21-22} and J_{21-20} = 6.5 Hz), 6.39 (t, 2 H, H16, H19, $J_{16-17,18}$ and $J_{19-17,18}$ = 2.2 Hz), 5.93 (t, 2 H, H17, H18, $J_{17-16,19}$ and $J_{18-16,19}$ = 2.2 Hz), 4.51 (d, 1 H, H7a, J_{7a-7b} = 16.6 Hz), 4.37 (d, 1 H, H6b, J_{6b-6a} = 16.6 Hz), 4.10 (d, 1 H, H7b, J_{7b-7a} = 16.6 Hz), 4.08 (d, 1 H, H6a, J_{6a-6b} = 16.6 Hz), 3.70

(m, 2 H, H15), 3.40 (s, 3H, H27), 2.32 (m, 1 H, H13a), 2.10 (m, 1 H, H14a), 2.05 (m, 1 H, H14b), 2.00 (m, 1 H, H13b). ¹³C-NMR (151 MHz, d₆-acetone, 25°C) δ (ppm): 203.4 (C28), 161.8 (C8), 159.9 (C5), 155.2 (C24), 152.0 (C12), 151.5 (C20), 149.9 (C1), 137.0 (C22), 136.8 (C3), 135.1 (C10), 125.0 (C26), 124.0 (C2), 123.4 (C11), 121.7 (C4), 121.1 (C21), 120.7 (C9), 120.1 (C16, C19), 116.2 (C26), 110.7 (C25), 108.1 (C17, C18), 68.4 (C7), 66.5 (C6), 65.0 (C13), 46.0 (C15), 35.2 (C27), 24.6 (C14). **NOEs:** H9-H7b; H27-H7a; H6b-H4; H25-H23; H20-H1. For the NMR signal assignment we have used the numbering scheme shown in Fig. 2. **IR** (ν_{max}, cm⁻¹): 1614 (m), 1492 (w), 1093 (m), 836 (s), 738 (m), 555 (m). **E_{1/2}** (III/II) (CH₂Cl₂ + 0.1 M TBAH): 0.67 V vs. SSCE. **UV-vis** (CH₂Cl₂): λ_{max}, nm (ε, M⁻¹ cm⁻¹) 246 (8631), 270 (5809), 373 (5046). **ESI-MS:** m/z (relative intensity, assignment) = 602.1 (100%, [M - PF₆]⁺).

Synthesis of trans-fac-[Ru^{II}(CN-Me)(bpea-pyr)OH₂](PF₆)₂ · 4·6H₂O. To a solution of **3** (0.025 g, 0.033 mmol) in 15 mL of H₂O were added 1.5 equivalents (0.0085 g, 0.05 mmol) of AgNO₃. The solution was kept under reflux for 3 h. After cooling in an ice bath, the precipitated AgCl was filtered through celite and 1 mL of saturated aqueous NH₄PF₆ solution was added to the filtrate. The solution was concentrated under reduced pressure until precipitation. The green solid obtained was filtered, washed with diethylether and pentane and dried in vacuo. Yield: 0.020 g (69.3%). **Elem. Anal.** found (calc.) for C₂₈H₃₃F₁₂N₇O₁P₂Ru₁·6H₂O: C 34.40 (34.22); N 9.83 (9.98); H 3.33 (4.62). **¹H-NMR** (600 MHz, d₆-acetone/10% D₂O, 25°C) δ (ppm): 9.05 (d, 1 H, H1, J₁₋₂ = 5.5 Hz), 8.85 (d, 1 H, H12, J₁₂₋₁₁ = 6.5 Hz), 8.49 (d, 1 H, H25, J₂₅₋₂₆ = 2.2 Hz), 8.35 (d, 1 H, H20, J₂₀₋₂₁ = 5.8 Hz), 8.21 (d, 1 H, H23, J₂₃₋₂₂ = 7.6 Hz), 8.12 (td, 1 H, H22, J₂₂₋₂₁ and 22-23 = 7.6 Hz, J₂₂₋₂₀ = 1.6 Hz), 7.99 (td, 1 H, H3, J₃₋₂ and 3-4 = 7.6 Hz, J₃₋₁ = 1.6 Hz), 7.81 (td, 1 H, H10, J₁₀₋₁₁ and 10-9 = 7.7 Hz, J₁₀₋₁₂ = 1.6 Hz), 7.62 (m, 2 H, H2, H4), 7.59 (d, 1 H, H26, J₂₆₋₂₅ = 2.2 Hz), 7.46 (d, 1 H, H9, J₉₋₁₀ = 7.7 Hz), 7.39 (pt, 1 H, H11, J₁₁₋₁₂ = 6.5 Hz, J₁₁₋₁₀ = 7.7 Hz), 7.26 (pt, 1 H, H21, J₂₁₋₂₂ = 7.6 Hz, J₂₁₋₂₀ = 5.8 Hz), 6.37 (t, 2 H, H16, H19, J_{16-17,18} and 19-17,18 = 2.0 Hz), 5.92 (t, 2 H, H17, H18, J_{17-16,19} and 18-16,19 = 2.0 Hz), 4.54 (d, 1 H, H7a, J_{7a-7b} = 16.6 Hz), 4.42 (d, 1 H, H6b, J_{6b-6a} = 16.6 Hz), 4.11 (d, 1 H, H7b, J_{7b-7a} = 16.6 Hz), 4.09 (d, 1 H, H6a, J_{6a-6b} = 16.6 Hz), 3.67 (m, 2 H, H15), 3.53 (s, 3 H, H27), 2.14 (td, 1 H, H13a, J_{13a-14} = 3.8 Hz, J_{13a-13b} = 11.9 Hz), 2.00 (m, 1 H, H14a), 1.97 (m, 1 H, H14b), 1.90 (td, 1 H, H13b, J_{13b-14} = 4.6 Hz, J_{13b-13a} = 11.9 Hz). **¹³C-NMR** (151 MHz, d₆-acetone / 10% OD₂, 25°C) δ (ppm): 199.4 (C28), 162.4 (C8), 160.5 (C5), 156.3 (C24), 153.4 (C12), 150.4 (C20), 149.4 (C1), 139.9 (C22), 138.7 (C3), 137.2 (C10), 126.8 (C26), 125.5 (C2), 125.0 (C11), 123.4 (C4), 122.9 (C21), 122.3 (C9), 120.9 (C16, C19), 118.1 (C26), 112.5 (C25), 108.9 (C17, C18), 69.7 (C7), 68.4 (C6), 66.2 (C13), 46.7 (C15), 36.4 (C27), 25.2 (C14). **NOEs:** H9-H7b; H27-H12; H6a-H20; H6b-H4; H1-H20; H23-H25. For the NMR signal assignment we have used the numbering scheme shown in Fig. 2. **IR** (ν_{max}, cm⁻¹): 3662 (w), 1616 (m), 1488 (m), 1091 (m), 831 (s), 555 (m). **E_{1/2}** (IV/II), (phosphate buffer pH = 7): 0.32 V vs SSCE. **E_{1/2}** (IV/II), CH₂Cl₂: 0.95 V vs SSCE. **UV-vis** (CH₂Cl₂): λ_{max}, nm (ε, M⁻¹ cm⁻¹) 245 (10368), 268 (8380), 355 (5476). **ESI-MS** (MeOH): m/z (relative intensity, assignment) = 586.1 (18%, [M - H₂O - 2PF₆⁻ + F]⁺), 598.1 (100%, [M - H₂O + MeO - 2PF₆⁻]⁺), 283.5 (43%; [M - H₂O - 2PF₆⁻]²⁺).

Instrumentation and measurements

FT-IR spectra were taken in a Mattson-Galaxy Satellite FT-IR spectrophotometer containing a MKII Golden Gate Single

Reflection ATR System. UV-vis spectroscopy was performed on a Cary 50 Scan (Varian) UV-vis spectrophotometer with 1 cm quartz cells. The ¹H and ¹³C-NMR spectroscopy was carried out on a Bruker DPX 200 MHz or a Bruker 600 MHz. Samples were run in d₆-acetone or CDCl₃, with internal references (residual protons and/or tetramethylsilane). Elemental analyses were performed using a CHNS-O Elemental Analyser EA-1108 from Fisons. ESI-MS experiments were performed on a Navigator LC/MS chromatograph from Thermo Quest Finnigan, using acetonitrile as a mobile phase. Cyclic voltammetric (CV) experiments were performed in a IJ-Cambria IH-660 potentiostat using a three electrode cell. Glassy carbon electrodes (3 mm diameter) from BAS or carbon felt from SOFACEL were used as working electrode, platinum wire as auxiliary and SSCE as the reference electrode. All cyclic voltammograms presented in this work were recorded under nitrogen atmosphere. All E_{1/2} values were calculated as the average of the oxidative and reductive peak potentials (E_{pa}+E_{pc})/2 at a scan rate of 100 mV/s. Unless explicitly mentioned, the concentration of the complexes was approximately 1 mM. In aqueous solution the pH was adjusted from 0-2 with HCl. Potassium chloride was added to keep a minimum ionic strength of 0.1 M. From pH 2-10, 0.1 M phosphate buffers were used, and from pH 10-12 diluted, CO₂ free, NaOH.

X-ray structure determination

Suitable crystals of **2a** and **2b** were obtained by slow diffusion of pentane or diethylether into a solution of the complexes in dichloromethane. Measurement of the crystals were performed on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from an X-Ray tube. Data collection, Smart V. 5.631 (Bruker AXS 1997-02); data reduction, Saint+ Version 6.36A (Bruker AXS 2001); absorption correction, SADABS version 2.10 (Bruker AXS 2001) and structure solution and refinement, SHELXTL Version 6.14 (Bruker AXS 2000-2003). CCDC 990320 (**2a**) and 990321 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.uk/data_request/cif.

Anchoring of the complexes onto an electrode surface

The electropolymerization was carried out through consecutive scanning of potential between 0 and 1.3 V on a 1 mM solution of the corresponding complex in CH₂Cl₂ + 0.1 M TBAH. The number of cycles is indicated in each case. The modified electrode is afterwards transferred to a clean electrolyte solution and five further cycles are registered. The amount of complex immobilized has been determined through the Faraday's law from the overall charge of the Ru(III/II) anodic peak in each case.

Catalytic studies

Experiments have been performed in anhydrous dichloromethane at room temperature. In a typical run, a modified **C-felt/poly-4** electrode was immersed in a dichloromethane solution (5 mL) containing the alkene (50 mM), the oxidant PhI(OAc)₂ (50 mM) and biphenyl as internal standard. The mixture was stirred at room temperature for 32 h and the epoxide formed was determined by gas chromatography

(GC) analysis in a Shimadzu GC-17A gas chromatography apparatus with a TRA-5 column (30 m x 0.25 mm diameter) incorporating a flame ionization detector.

Conclusions

We have prepared and characterized a new family of complexes containing the bpea-pyr tridentate ligand together with Cl⁻, dmsO or pyridylcarbene (CN-Me) ligands. The compounds with general formula [Ru^{II}(CN-Me)(bpea-pyr)(X)]ⁿ⁺ (with X = Cl or H₂O, complexes **3** and **4**) have been anchored onto an electrode surface through repetitive voltammetric cycles, generating the corresponding C/poly-**3** and C/poly-**4** modified electrodes, which display a good stability despite the low level of cross-linking expected from the presence of a unique pyrrole unit per complex. Catalyst **4** has been anchored onto a carbon felt electrode and tested in heterogeneous epoxidation catalysis using iodobenzene diacetate as oxidant, displaying excellent TON values and good selectivity for the epoxide product. C-felt/poly-**4** constitutes, to the best of our knowledge, the first report of a Ru-polypyrrole system in olefin epoxidation catalysis.

Acknowledgements

This research has been financed by MINECO of Spain through projects, CTQ2010-21532-C02-01, CTQ2012-32436 and CTQ2009-08328. The authors acknowledge STR from UdG for technical support. Johnson & Matthey LTD are acknowledged for a RuCl₃·nH₂O loan. MD thanks AECID (MAEC) of Spain for the allocation of a MAEC-AECID grant.

Notes and references

^a Departament de Química i Serveis Tècnics de Recerca, Universitat de Girona, Campus de Montilivi, E-17071 Girona, Spain. E-mail: montse.rodriguez@udg.edu, marisa.romero@udg.edu.

^b Laboratoire des Matériaux et Systèmes Interfaciaux, Département de Chimie, Faculté des Sciences, B.P.: 2121 93000 Tétouan, Morocco.

^c Departament de Química i Servei de RMN Universitat Autònoma de Barcelona, Cerdanyola del Vallès, E-08193 Barcelona, Spain.

Electronic Supplementary Information (ESI) available: crystal data for the X-ray structures of complexes **2a** and **2b**; possible diastereoisomers for complex **3**; NMR spectra (1D and 2D) of all complexes described in this work; cyclic voltammograms of complex **3**, **4** and C/poly-**3**; linear regression of $E_{1/2}$ values vs. pH for the cyclic voltammograms of complex **4**. See DOI: 10.1039/b000000x/

- (a) Z. Ma and F. Zaera, in *Heterogeneous Catalysis by Metals. Encyclopedia of Inorganic and Bioinorganic Chemistry*, John Wiley & Sons, 2011; (b) C. N. Satterfield, in *Heterogeneous Catalysis in Industrial Practice*, Krieger Publishing: Malabar, 1996.
- (a) A. E. C. Collis and I. T. Horvath, *Catal. Sci. Technol.*, 2011, **1**, 912; (b) S. Shylesh, M. Jia and W. R. Thiel, *Eur. J. Inorg. Chem.* 2010, 4395; (c) C. Baleizão and H. Garcia, *Chem. Rev.*, 2006, **106**, 3987.
- (a) B. M. L. Dooos, I. F. J. Vankelecom and P. A. Jacobs, *Adv. Synth. Catal.*, 2006, **348**, 1413; (b) C. M. Elliott, S. Caramori and C. A. Bignozzi, *Langmuir*, 2005, **21**, 3022.
- (a) X.-Q. Yu, J.-S. Huang, W.-Y. Yu and C.-M. Che, *J. Am. Chem. Soc.*, 2000, **122**, 5337; (b) C. Poriel, Y. Ferrand, P. Le Maux, J. Rault-Berthelot and J. G. Simonneaux, *Inorg. Chem.*, 2004, **43**, 5086; (c) J. A. Gladysz, *Pure Appl. Chem.*, 2001, **73**, 1319.
- (a) A. Deronzier and J.-C. Moutet, *Coord. Chem. Rev.*, 1996, **147**, 339; (b) S. J. Higgins, *Chem. Soc. Rev.*, 1997, **26**, 247; (c) S. Cosnier, *Anal. Lett.*, 2007, **40**, 1260.
- (a) M. N. Collomb-Dunand-Sauthier, A. Deronzier, H. Le Bozec and M. Navarro, *J. Electroanal. Chem.*, 1996, **410**, 21; (b) A. Deronzier and J. C. Moutet, *Acc. Chem. Res.*, 1989, **22**, 249.
- (a) V. Saumya, K. P. Prathish, S. Dhanya and T. P. Rao, *J. Electroanal. Chem.*, 2011, **663**, 53; (b) X. Y. Li, M. Y. Zhu and B. Dai, *Appl. Catal. B-Environ.*, 2013, **142**, 234.
- (a) M. Yuasa, K. Oyaizu, H. Murata, K. Tanaka, M. Yamamoto and S. Sasaki, *Electrochemistry*, 2007, **75**, 800; (b) S. Fujii, S. Matsuzawa, Y. Nakamura, A. Ohtaka, T. Teratani, K. Akamatsu, T. Tsuruoka and H. Nawafune, *Langmuir*, 2010, **26**, 6230.
- (a) V. A. Zinovyeva, M. A. Vorotyntsev, I. Bezverkhyy, D. Chaumont and J. C. Hierso, *Adv. Funct. Mater.*, 2011, **21**, 1064; (b) T. V. Magdesieva, O. M. Nikitin, O. A. Levitsky, V. A. Zinovyeva, I. Bezverkhyy, E. V. Zolotukhina and M. A. Vorotyntsev, *J. Mol. Catal. A-Chem.*, 2012, **353**, 50.
- (a) S. Fujii, S. Matsuzawa, H. Hamasaki, Y. Nakamura, A. Bouleghlimat and N. J. Buurma, *Langmuir*, 2012, **28**, 2436; (b) D. A. Torelli, D. P. Harrison, A. M. Lapidés and T. J. Meyer, *ACS Appl. Mater. Inter.*, 2013, **5**, 7050.
- (a) M. Navarro, M.-N. Collomb and A. Deronzier, *J. Electroanal. Chem.*, 2002, **520**, 150; (b) J. A. Moss, R. M. Leasure and T. J. Meyer, *Inorg. Chem.*, 2000, **39**, 1052.
- (a) D. L. Wise, G. E. Winek, D. J. Trantolo, T. M. Cooper and J. D. Gresser, in *Electrical and Optical Polymer Systems*; Marcel Dekker Inc.: New York, vol. 17, 1998; (b) J. Rodriguez, H. J. Grande and T. F. Otero, in *Handbook of Organic Conductive Molecules and*

- Polymers*, ed. H. S. Nalwa, John Wiley & Sons: New York, 1997, p. 415.
- 13 (a) F. Bedioui, S. Griveau, T. Nyokong, A. J. Appleby, C. A. Caro, M. Gulppi, G. Ochoa and J. H. Zagal, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3383; (b) A. Ehsani, M. G. Mahjani, M. Jafarian and A. Naeemy, *Electrochim. Acta*, 2012, **71**, 128; (c) Y. Zhao, L. Zhan, J. Tian, S. Nie and Z. Ning, *Electrochim. Acta*, 2011, **56**, 1967; (d) M. R. Majidi, A. Jouyban and K. Asadpour-Zeynali, *Electrochim. Acta*, 2007, **52**, 6248.
- 14 (a) G. Cauquis, S. Cosnier, A. Deronzier, B. Galland, D. Limonin and J.-C. Moutet, *J. Electroanal. Chem.*, 1993, **352**, 181; (b) N. P. Rodrigues, J. Obirai, T. Nyokong and F. Bedioui, *Electroanal.*, 2005, **17**, 186; (c) F. Bedioui, J. Devynck and C. Bied-Charreton, *J. Mol. Cat. A*, 1996, **113**, 3.
- 15 (a) D. Chatterjee, *Coord. Chem. Rev.*, 2008, **252**, 176; (b) M. K. Tse, S. Bhor, M. Klawonn, G. Anilkumar, H. J. Jiao, A. Spannenberg, C. Dobler, W. Magerlein, H. Hugl and M. Beller, *Chem. Eur. J.*, 2006, **12**, 1875; (c) G. A. Barf, D. Van Den Hoek and R. A. Sheldon, *Tetrahedron*, 1996, **52**, 12971.
- 16 (a) P. Fackler, S. M. Huber and T. Bach, *J. Am. Chem. Soc.*, 2012, **134**, 12869; (b) M. K. Tse, C. Dobler, S. Bhor, M. Klawonn, W. Magerlein, H. Hugl and M. Beller, *Angew. Chem. Int. Ed.*, 2004, **43**, 5255; (c) N. End and A. Pfaltz, *Chem. Commun.*, 1998, 589.
- 17 (a) W. F. De Giovanni and A. Deronzier, *J. Electroanal. Chem.*, 1992, **337**, 285; (b) K. C. Cheung, P. Guo, M. H. So, Z. Y. Zhou, L. Y. S. Lee and K. Y. Wong, *Inorg. Chem.*, 2012, **51**, 6468; (c) M. Rodríguez, I. Romero, C. Sens, A. Llobet and A. Deronzier, *Electrochim. Acta*, 2003, **48**, 1047.
- 18 J. Mola, E. Mas-Marza, X. Sala, I. Romero, M. Rodríguez, C. Viñas, T. Parella and A. Llobet, *Angew. Chem. Int. Ed.*, 2008, **47**, 5830.
- 19 J. Mola, I. Romero, M. Rodríguez, F. Bozoglian, A. Poater, M. Sola, T. Parella, J. Benet-Buchholz, X. Fontrodona and A. Llobet, *Inorg. Chem.*, 2007, **46**, 10707.
- 20 (a) M. Rodríguez, I. Romero, A. Llobet, A. Deronzier, M. Biner, T. Parella and H. Stoeckli-Evans, *Inorg. Chem.*, 2001, **40**, 4150; (b) X. Sala, A. Poater, A. Von Zelewsky, T. Parella, X. Fontrodona, I. Romero, M. Solà, M. Rodríguez and A. Llobet, *Inorg. Chem.*, 2008, **47**, 8016; (c) S. Fukui, A. Kajihara, T. Hirano, F. Sato, N. Suzuki and H. Nagao, *Inorg. Chem.*, 2011, **50**, 4713.
- 21 V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.
- 22 (a) M. Dakkach, X. Fontrodona, T. Parella, A. Atlamsani, I. Romero and M. Rodríguez, *Adv. Synth. Catal.*, 2011, **353**, 231; (b) M. Dakkach, I. López, I. Romero, M. Rodríguez, A. Atlamsani, T. Parella, X. Fontrodona and A. Llobet, *Inorg. Chem.*, 2010, **49**, 7072;
- (c) J. Mola, C. Dinoi, X. Sala, M. Rodríguez, I. Romero, T. Parella, X. Fontrodona and A. Llobet, *Dalton Trans.*, 2011, 3640.
- 23 M. Dakkach, A. Atlamsani, X. Fontrodona, T. Parella, I. Romero and M. Rodríguez, *Inorg. Chem.*, 2013, **52**, 5077.
- 24 E. Masllorens, M. Rodríguez, I. Romero, A. Roglans, T. Parella, J. Benet-Buchholz, M. Poyatos and A. Llobet, *J. Am. Chem. Soc.*, 2006, **128**, 5306.
- 25 (a) W.-H. Fung, W.-Y. Yu and C.-M. Che, *J. Org. Chem.*, 1998, **63**, 7715; (b) L. K. Stultz, R. A. Binstead, M. S. Reynolds and T. J. Meyer, *J. Am. Chem. Soc.*, 1995, **117**, 2520.
- 26 I. Romero, M. Rodríguez, A. Llobet, M.-N. Collomb-Dunand-Sauthier, A. Deronzier, T. Parella and H. Stoeckli-Evans, *J. Chem. Soc., Dalton Trans.*, 2000, 1689.
- 27 S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *J. Am. Chem. Soc.*, 2002, **124**, 10473.
- 28 I. P. Evans, A. Spencer and J. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, **2**, 204.