Chemical and electrochemical generation of $[Fe(bpy)_2(S)_2]^{2+}$ (bpy = 2,2′-bipyridine, S = H_2O or CH_3CN). A route for synthesis of coordinatively dissymmetrical iron(II) polypyridine complexes and supramolecular structures containing a $Fe(bpy)_3^{2+}$ moiety

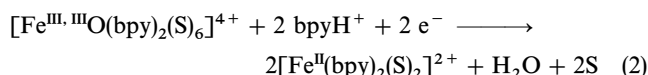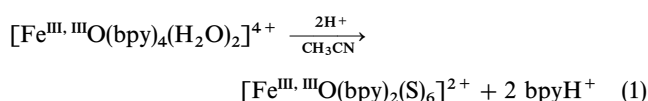**Marie-Noëlle Collomb, Alain Deronzier,* Karine Gorgy and Jean-Claude Leprêtre**

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A route for the synthesis of coordinatively dissymmetrical iron(II) polypyridine complexes $[Fe(L)_2L']^{2+}$ (L and L′ are two different 2,2′-bipyridine derivatives) is described. The procedure is based on the use of the precursor $[Fe(L)_2(CH_3CN)_2]^{2+}$ (L = 2,2′-bipyridine), which can be easily prepared by electrochemical or chemical reduction of the μ-oxo diaqua diiron(III) complex $[Fe_2O(bpy)_4(H_2O)_2]^{4+}$ in acidic CH_3CN solution. In addition, it is shown that this procedure can be applied with success to the synthesis of covalently linked heterodinuclear complexes containing, for instance, $Fe(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ moieties. The electrochemical behaviour of all these new complexes is reported.

Iron(II) complexes of the type $[Fe(L)_2L']^{2+}$ containing two different diimine ligands (L, L′) such as 2,2′-bipyridine derivatives are very rare.[1] This is mainly due to the lack of easy synthetic routes producing precursors like $[Fe(L)_2X_2]^{2+}$, where X is a labile unidentate ligand (CH_3CN for instance). We recently demonstrated[2] that the electrochemical reduction of the μ-oxo diaqua diiron(III) complex $[Fe_2^{III,III}O(bpy)_4(H_2O)_2]^{4+}$ (bpy = 2,2′-bipyridine) in CH_3CN in the presence of two added protons ($HClO_4$) per complex leads to the quantitative formation of $[Fe^{II}(bpy)_2(S)_2]^{2+}$ species, S = CH_3CN or H_2O. Eqns. (1) and (2) summarize the process involved:

$$[Fe^{III,III}O(bpy)_4(H_2O)_2]^{4+} \xrightarrow[CH_3CN]{2H^+}$$
$$[Fe^{III,III}O(bpy)_2(S)_6]^{2+} + 2\ bpyH^+ \quad (1)$$
$$[Fe^{III,III}O(bpy)_2(S)_6]^{4+} + 2\ bpyH^+ + 2\ e^- \longrightarrow$$
$$2[Fe^{II}(bpy)_2(S)_2]^{2+} + H_2O + 2S \quad (2)$$

In this paper we report a simpler procedure to electro-generate $[Fe(bpy)_2(S)_2]^{2+}$ and chemical routes for its *in situ* utilization. We also take advantage of this behaviour to propose a synthetic technique to prepare a series of new $[Fe(bpy)_2L']^{2+}$ complexes (Scheme 1; L′ = L_{1-3}). Two of these L′ ligands contain an electropolymerizable substituent in order to elaborate new modified electrodes. Moreover, this procedure has been applied with success to the synthesis of a supramolecular structure, like a covalently linked heterodinuclear Fe(II)-Ru(II) polypyridyl complex $[Fe(bpy)_2(L_4)(bpy)_2Ru]^{4+}$ (Scheme 1). Heteronuclear metallic systems incorporating the $Ru(bpy)_3^{2+}$ moiety are of a great interest since they construct efficient intramolecular electron or energy transfer systems.[3] Only a few examples have been described in the literature, using alkyl-linked bis bipyridine as a bridging ligand,[4–7] and none of them contain a $Fe(bpy)_3^{2+}$ moiety.

Experimental

Elemental analyses were performed by the Service Central d'Analyse du CNRS at Vernaison (France).

Materials
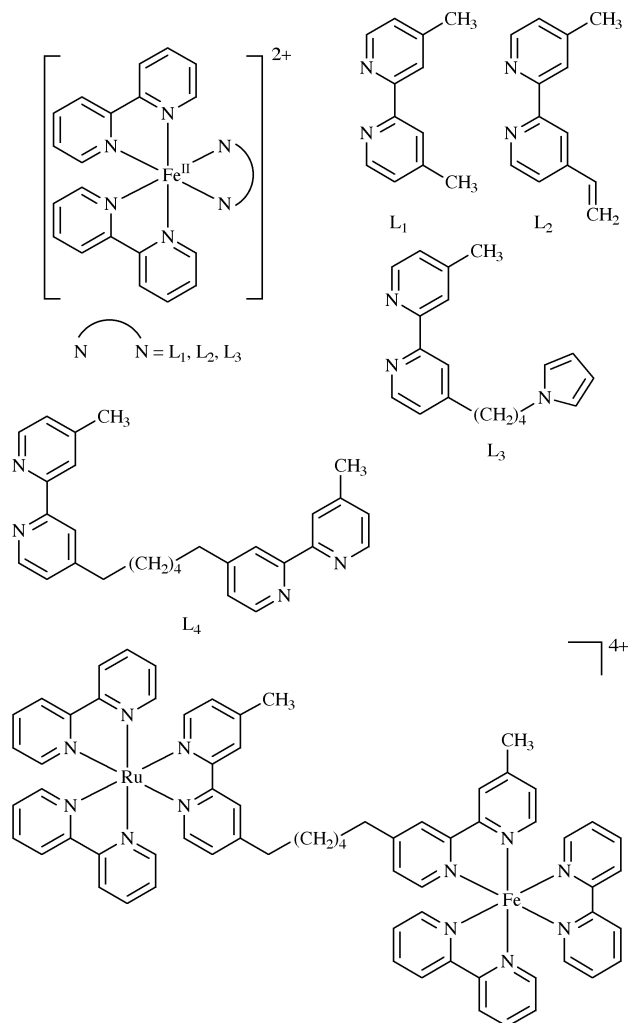
KPF_6 (Fluka 99%), NH_4PF_6 (Fluka 99%), $NaClO_4$ (Fluka 99%), tetrabutylammonium tetraphenylborate (Fluka 99%), ascorbic acid ($AscH_2$, Aldrich 99%), 2,2′-bipyridine (bpy, Aldrich 99%), 4,4′-dimethyl-2,2′-bipyridine (L′ = L_1, Fluka, 99%) and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ (Alfa) were used as received. Ligands L_2 and L_3, and the $[Fe_2O(bpy)_4(H_2O)_2](ClO_4)_4$ complex, were prepared according to literature procedures.[2,8,9]

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small quantities of these compounds should be prepared and handled behind suitable protective shields.

The determination of the x value for $Fe(ClO_4)_3 \cdot xH_2O$ (Aldrich) has been made by the following procedure. A 10 mL acetonitrile solution containing $Fe(ClO_4)_3 \cdot xH_2O$ (5.2 mg, ~1 mM) in the presence of an excess of 2,2′-bipyridine (7.8 mg, 5 mM) was exhaustively reduced using a 10×10 mm^2 vitreous carbon sheet at 0.00 V, leading to the formation of $[Fe^{II}(bpy)_3]^{2+}$. The UV-visible titration at 510 nm ($\varepsilon = 8540$ M^{-1} cm^{-1}) of the electrochemically produced $[Fe^{II}(bpy)_3]^{2+}$ species gave the value $x = 12$ by comparison with the initial amount of starting material.

Synthesis

Chemical reduction of $[Fe_2O(bpy)_4(H_2O)_2](ClO_4)_4$. (*a*) By ascorbic acid. To a 20 mL deoxygenated CH_3CN solution at $-30\,°C$ containing $[Fe_2O(bpy)_4(H_2O)_2](ClO_4)_4$ (25 mg, 21 μmol), 1.5 mol equiv. of ascorbic acid (5.3 mg, 31.5 μmol) were added. After 2 h, the resulting orange solution was filtered off

Scheme 1 Structure of the ligands and dissymmetrical iron complexes.

$L' = L_1$ (yield 72%). ^{1}H NMR (CD$_3$CN, 250 MHz): δ 2.53 (s, 6H), 7.19 (m, 4H), 7.38 (m, 8H), 8.08 (m, 4H), 8.36 (m, 2H), 8.48 (d, 4H). Anal. calcd for C$_{32}$H$_{28}$N$_6$Cl$_2$O$_8$Fe·H$_2$O: C, 49.94; H, 3.90; N, 10.92; Fe, 7.26. Found: C, 49.83; H, 4.08; N, 10.54; Fe, 7.24. ES-MS (4.5 eV) m/z: 276.2 [FeC$_{32}$H$_{28}$N$_6$]$^{2+}$. UV/vis (CH$_3$CN) λ_{max}/nm (ε/M^{-1} cm^{-1}) 525 (7850).

$L' = L_2$ (yield 68%). ^{1}H NMR (CD$_3$CN, 250 MHz): δ 1.61 (m, 2H), 1.76 (m, 2H), 2.53 (s, 6H), 2.77 (t, 2H), 3.89 (t, 2H), 5.99 (d, 2H), 6.63 (d, 2H), 7.17 (m, 4H), 7.37 (m, 8H), 8.08 (m, 4H), 8.29 (s, 1H), 8.36 (s, 1H), 8.50 (m, 4H). Anal. calcd for C$_{39}$H$_{37}$N$_7$Cl$_2$O$_8$Fe·0.5H$_2$O: C, 53.99; H, 4.39; N, 11.30. Found: C, 54.00; H, 4.52; N, 10.72. ES-MS (4.5 eV) m/z: 329.6 [FeC$_{39}$H$_{37}$N$_7$]$^{2+}$. UV/vis (CH$_3$CN) λ_{max}/nm (ε/M^{-1} cm^{-1}) 526 (7880).

$L' = L_3$ (yield 73%). ^{1}H NMR (CD$_3$CN, 250 MHz): δ 2.54 (s, 3H), 6.02 (dd, 2H), 6.86 (dd, 1H), 7.27 (m, 1H), 7.38 (m, 10H), 7.44 (m, 1H), 8.10 (m, 4H), 8.49 (m, 6H). Anal. calcd for C$_{33}$H$_{28}$N$_6$Cl$_2$O$_8$Fe·H$_2$O: C, 50.77; H, 3.84; N, 10.75. Found: C, 50.55; H, 3.75; N, 10.42. ES-MS (4.5 eV) m/z: 282.1 [FeC$_{33}$H$_{28}$N$_6$]$^{2+}$. UV/vis (CH$_3$CN) λ_{max}/nm (ε/M^{-1} cm^{-1}) 524 (7840).

[Fe(bpy)$_2$L$_4$(bpy)$_2$Ru](PF$_6$)$_4$. (*a*) Preparation of the ligand L$_4$. The synthesis of L$_4$ was identical to that described in the literature[10] starting from 1,4-diiodobutane (1.9 g, 0.8 mL, 6.12 mmol) and 4,4'-dimethyl-2,2'-bipyridine (2.25 g, 12.2 mmol) in THF at $-78\,^\circ$C (acetone–liq N$_2$ bath). Chromatography on silica gel eluted with a 0 to 5% MeOH–CH$_2$Cl$_2$ mixture yielded the desired white ligand (620 mg; yield: 24%).

(*b*) [Ru(bpy)$_2$(L$_4$)](PF$_6$)$_2$. [Ru(bpy)$_2$(L$_4$)](PF$_6$)$_2$ was prepared according to the following procedure. Reaction of L$_4$ (76 mg, 0.18 mmol) and [Ru(bpy)$_2$(Cl)$_2$] (76 mg, 0.155 mmol) in 15 mL ethanol at reflux for 3 h afforded an orange solution. After cooling to room temperature, addition of aqueous NH$_4$PF$_6$ solution (0.29 g in 25 mL H$_2$O) allowed precipitation of the complex. After filtration, the crude product was redissolved in CH$_2$Cl$_2$ and dried over Na$_2$SO$_4$. Chromatography on silica gel eluting with CH$_3$CN–H$_2$O (70:30) containing 1 mM KPF$_6$ yielded the desired complex (174 mg, yield: 70%). ^{1}H NMR (CD$_3$CN, 250 MHz): δ 1.37 (m, 4H), 1.66 (m, 4H), 2.43 (s, 3H), 2.50 (s, 3H), 2.67 (t, 2H), 2.77 (t, 2H), 7.21 (m, 4H), 7.38 (m, 4H), 7.50 (m, 2H), 7.70 (m, 4H), 8.06 (m, 4H), 8.30 (m, 4H), 8.51 (m, 6H). UV/vis (CH$_3$CN) λ_{max}/nm (ε/M^{-1} cm^{-1}) 454 (14650).

This complex has to be stored at $-30\,^\circ$C in the dark to avoid the slow formation of [Ru(bpy)(L$_4$)]$^{2+}$ by the loss of one bpy ligand. This evolution can be prevented using L$_4$H$^+$ instead of L$_4$ to obtain [Ru(bpy)$_2$(L$_4$H)]$^{3+}$.

(*c*) [Ru(bpy)$_2$(L$_4$H)](PF$_6$)$_3$. This synthesis followed the same procedure as above except that 1 mol equiv. of perchloric acid is added to the ethanol solution of L$_4$. After 3 h the crude product was precipitated by addition of diethyl ether. The orange solid was redissolved in 10 mL CH$_2$Cl$_2$ and washed three times with a 0.1 M NH$_4$PF$_6$ aqueous solution. The organic layer was then dried over Na$_2$SO$_4$ and the complex precipitated by addition of diethyl ether (yield: 68%). Anal. calcd for C$_{48}$H$_{47}$N$_8$RuP$_3$F$_{18}$: C, 45.25; H, 3.29; N, 8.79. Found: C, 45.72; H, 3.69; N, 8.44. FAB-MS (positive mode) m/z: 981 [M $-$ (PF$_6$)$_2$]$^{2+}$; 836 [M $-$ (PF$_6$)$_3$]$^{3+}$. ^{1}H NMR (CD$_3$CN, 250 MHz): δ 1.43 (m, 4H), 1.72 (m, 4H), 2.51 (s, 3H), 2.59 (s, 3H), 2.81 (m, 4H), 7.20 (m, 2H), 7.36 (m, 4H), 7.51 (m, 2H), 7.59 (m, 2H), 7.70 (m, 4H), 8.02 (m, 4H), 8.31 (m, 4H), 8.47 (m, 6H), 8.60 (m, 2H).

(*d*) [Ru(bpy)$_2$(L$_4$)(bpy)$_2$Fe](PF$_6$)$_4$. To a freshly prepared 2 mM solution of [Fe(bpy)$_2$(S)$_2$](ClO$_4$)$_2$ (5 mL), 11.8 mg of a freshly prepared sample of [Ru(bpy)$_2$(L$_4$)](PF$_6$)$_2$ (10 μmol) was added, leading to the formation of the red-orange complex [Ru(bpy)$_2$(L$_4$)(bpy)$_2$Fe]$^{4+}$, which was precipitated by addition of 200 mL of diethyl ether. The crude product was

in order to eliminate the oxidized form of the reducing agent. The [Fe(bpy)$_2$(S)$_2$](ClO$_4$)$_2$ solution was used without further purification for the synthesis of dissymmetrical iron complexes (see below).

(*b*) By tetraphenylborate salt. To a 20 mL CH$_3$CN deoxygenated solution containing [Fe$_2$O(bpy)$_4$(H$_2$O)$_2$](ClO$_4$)$_4$ (474 mg, 0.4 mmol), 2 mol equiv. of 70% aqueous perchloric acid (69 μL, 0.8 mmol) and 20 mL of a CH$_3$CN solution containing tetra-*n*-butylammonium tetraphenylborate (0.56 g, 1.1 mmol) were added at $-30\,^\circ$C. After 2 h the deep orange complex [Fe(bpy)$_2$(S)$_2$](BPh$_4$)$_2$ precipitated. The filtered complex was then successively washed with cold acetonitrile ($-30\,^\circ$C), a cold acetonitrile–diethyl ether (50:50) mixture and then diethyl ether. After drying under vaccum, 320 mg of [Fe(bpy)$_2$(S)$_2$](BPh$_4$)$_2$ were obtained (yield: 39%). ^{1}H NMR (CD$_3$CN, 250 MHz): δ 6.82 (t, 8H), 6.96 (t, 16H), 7.25 (m, 16H), 7.31 (m, 4H), 7.77 (m, 4H), 8.07 (t, 4H), 8.77 (d, 4H).

[Fe(bpy)$_2$(L')](ClO$_4$)$_2$. To a freshly prepared millimolar [Fe(bpy)$_2$(S)$_2$](ClO$_4$)$_2$ solution (10 mL), 1 mol equiv. of L' was added at $-30\,^\circ$C. The solution immediately turned red, attesting to the formation of the dissymmetrical complex [Fe(bpy)$_2$(L')]$^{2+}$. The complex was then precipitated by addition of 100 mL of diethyl ether; the solid was washed with a cold acetonitrile–diethyl ether (50:50) mixture and with diethyl ether. The purity of the dissymmetrical complex could be estimated by TLC on silica gel using CH$_3$CN + 0.01 M NaClO$_4$ as eluent (see later) {for instance: R_f[Fe(bpy)$_3^{2+}$] = 0.3, R_f[Fe(L$_1$)$_3^{2+}$] = 0.14, R_f[Fe(bpy)$_2$(L$_1$)$^{2+}$] = 0.2}.

then redissolved in 10 mL CH_2Cl_2 and washed successively by 0.1 M aqueous KPF_6 and water. After drying over Na_2SO_4, the organic solvent was removed under vaccum. Finally, the complex was redissolved in a minimum amount of acetonitrile, the resulting solution filtered off, and the complex precipitated by addition of 100 mL of diethyl ether. After filtration and drying under vacuum 6 mg of complex were obtained (yield: 32%). ^1H NMR (CD_3CN, 250 MHz): δ 1.42 (m, 4H), 1.68 (m, 4H), 2.51 (s, 6H), 2.81 (t, 4H), 7.20 (m, 6H), 7.38 (m, 6H), 7.52 (m, 2H), 7.70 (m, 4H), 8.06 (m, 8H), 8.38 (m, 4H). UV/vis (CH_3CN) λ_{max}/nm (ε/M^{-1} cm^{-1}) 460 (15600), 520 (8200).

Electrochemical and spectroscopic studies

Most electrochemical experiments were run under an inert atmosphere in a glovebox at room temperature. Acetonitrile (CH_3CN, Rathburn, HPLC grade) was used as received and stocked under an argon atmosphere in the glove box. The supporting electrolyte, tetra-n-butylammonium perchlorate (TBAP) was purchased from Fluka, recrystallized from ethyl acetate–cyclohexane and dried under vacuum at 80 °C for 3 days.

Cyclic voltammetry and controlled potential electrolysis experiments were performed using a PAR model 273 potentiostat/galvanostat or a PAR model 173 potentiostat/ galvanostat, a PAR model 175 universal programmer and a PAR model 179 digital coulometer. The standard three-electrode electrochemical cell was used. Potentials are referred to an Ag | 10 mM $AgNO_3$ reference electrode in CH_3CN + 0.1 M TBAP. Potentials referenced to this system can be converted to the ferrocene/ferricinium couple by adding 70 mV. The working electrodes were platinum and vitreous carbon disks (5 mm diameter) polished with 1 μm diamond paste. Exhaustive electrolyses were carried out with $10 \times 10 \times 4$ mm^3 carbon felt electrodes (RCV 2000, 65 mg cm^{-3}, from Le Carbone Lorraine).

Electronic absorption spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer equipped with a Compacq 286 computer. Initial and electrolyzed solutions were transferred to a conventional cuvette cell in the glove box. The cell was inserted into an optical translator connected to the spectrophotometer through a fibre optic system (Photonetics Spectrofip System). The optical fibres pass through the wall of the dry box *via* optical seals.

^1H NMR spectra were recorded on a Brucker AC250 spectrometer. Fast atom bombardment mass spectra (FAB-MS) were obtained using an AEI Kratos MS 50 spectrometer fitted with an Ion Tech Ltd ion gun.

Results and discussion

Chemical synthesis

$[Fe^{II}(bpy)_2(S)_2]^{2+}$. We have previously seen that obtaining $[Fe^{II}(bpy)_2(S)_2]^{2+}$ from $[Fe_2^{III,III}O(bpy)_4(H_2O)_2]^{4+}$ requires the exchange of two electrons in the presence of two protons per molecule of the oxo diiron complex.[2] With the goal to achieve a chemical synthesis of $[Fe^{II}(bpy)_2(S)_2]^{2+}$, two different mild reducing agents have been tested, ascorbic acid ($AscH_2$) and Bu_4NBPh_4.

$AscH_2$ is known to act as a two-electron reducing agent[11] with the release of two protons and consequent transformation into dehydroascorbic acid (DHA), following eqn. (3):

$$AscH_2 \rightarrow DHA + 2\,e^- + 2\,H^+ \tag{3}$$
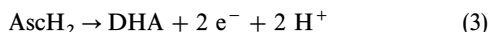
Addition of a slight excess (1.5 mol equiv.) of $AscH_2$ to a CH_3CN solution of $[Fe_2^{III,III}O(bpy)_2(H_2O)_2]^{4+}$ at -30 °C induces its slow and quantitative reduction into $[Fe^{II}(bpy)_2(S)_2]^{2+}$. The process can be followed by UV-vis

spectroscopy, the initial absorption at 360 nm being progressively replaced by that of $[Fe^{II}(bpy)_2(S)_2]^{2+}$ located at 470 nm ($\varepsilon = 6590$ M^{-1} cm^{-1}).[2]

The presence of a marked isosbestic point at 405 nm demonstrates the selectivity of the reduction. Keeping the temperature at -30 °C during the reduction is a crucial point. At higher temperature some slow conversion of $[Fe(bpy)_2(S)_2]^{2+}$ into $[Fe(bpy)_3]^{2+}$ occurs. Unfortunately, all attempts to precipitate $[Fe(bpy)_2(S)_2]^{2+}$ by addition of an excess of an electroinactive counter anion like PF_6^-, BF_4^- or ClO_4^- were unsuccessful, preventing its isolation.

BPh_4^- acts as an one-electron reducing agent and addition of perchloric acid is required. The reduction is also carried out at -30 °C in CH_3CN (see experimental for details). The resulting precipitate, $[Fe(bpy)_2(S)_2](BPh_4)_2$, is filtered and washed with a cold mixture of CH_3CN–diethyl ether (50 : 50), followed by cold diethyl ether to eliminate BPh_3 and biphenyl[12] resulting from oxidation of BPh_4^-, and dried under vacuum. This complex was characterized by ^1H NMR, UV-vis spectroscopy and cyclic voltammetry.

In CD_3CN solution the ^1H NMR spectrum of the dry complex exhibits the expected 4 sets of resonances of the bpy ligand and the 3 sets from BPh_4^-. In CD_3NO_2 an additional signal located at 3.4 ppm is detected, whereas no signal relative to a CH_3 group is seen. The value of the integration of this signal shows that 4 protons are involved, seeming to indicate that S = H_2O rather than CH_3CN in the dry complex. This is confirmed by the absence of any ^{13}C NMR signals typical of a methyl or a nitrile group. However, no definitive conclusion can be drawn from these experiments since addition of D_2O to the solution induces a total transformation of $[Fe(bpy)_2(S)_2]^{2+}$ into $[Fe(bpy)_3]^{2+}$. On the other hand, we have previously established that in CH_3CN solutions of this kind of complex some rapid exchange of the aqua ligands with solvent occurs.[2]

The cyclic voltammograms of $[Fe(bpy)_2(S)_2](BPh_4)_2$ in CH_3CN + 0.1 M TBAP exhibits in the cathodic region the same pattern as that of an electrogenerated sample (see further in the text). A first irreversible peak is seen at $E_{p_c} = -1.54$ V, followed by the three ligand-based reversible reduction waves of the $[Fe^{II}(bpy)_3]^{2+}$ issued from the irreversible reduction of $[Fe(bpy)_2(S)_2]^{2+}$. In the anodic region, besides the expected reversible system $[Fe(bpy)_2(S)_2]^{2+/3+}$ ($E_{1/2} = 0.95$ V),[2] the irreversible oxidation peak of the BPh_4^- counter anion is observed at $E_{p_a} = 0.70$ V.[11]

Iron(II) dissymmetric complexes $[Fe(bpy)_2(L')]^{2+}$; ($L' = L_1–L_3$) and $[Fe(bpy)_2(L_4)(bpy)_2Ru]^{4+}$

As recalled in the introduction there is no existing procedure for incorporation of two different bidentate ligands into the coordination sphere of Fe(II). The synthetic technique described here provides a general route for the preparation of this kind of Fe(II) complex. To a solution of $[Fe^{II}(bpy)_2(S)_2]^{2+}$ in CH_3CN prepared, for instance, by reduction of the oxo binuclear complex with $AscH$, kept at -30 °C, is added a stoichiometric amount of a bidentate ligand L' in CH_3CN solution. The two labile ligands S are easily replaced in the coordination sphere by L'. The resulting $[Fe^{II}(bpy)_2L'](ClO_4)_2$ complex immediately formed is precipitated by addition of cold diethyl ether and purified as described in the experimental section.

The purity of the complexes was checked by NMR and TLC. Best results are obtained when the synthesis is carried out at -30 °C. Only one spot is then observed on the chromatogram. If reactions are conducted at room temperature, other spots corresponding to the $[Fe(bpy)_3]^{2+}$, $[Fe(L')_3]^{2+}$ and $[Fe(bpy)(L')_2]^{2+}$ complexes are obtained, revealing that some ligand exchanges occur in solution at higher temperatures. This phenomena is confirmed by TLC analysis of

the evolution of an analytically pure sample of $[Fe(bpy)_2(L')]^{2+}$ in CH_3CN solution. After 1 h of standing at room temperature the presence of the other mixed complexes seen above are detected. So NMR and voltammetry cyclic experiments are made immediately after the dissolution of the complexes in acetonitrile. The same synthetic procedure has been used to prepare the heterobinuclear $[Fe(bpy)_2(L_4)(bpy)_2Ru]^{4+}$ complex.

Electrochemical synthesis and behaviour of $[Fe(bpy)_2(S)_2]^{2+}$

As previously reported[2] exhaustive reduction at $E = 0.00$ V of $[Fe_2^{III}O(bpy)_4(H_2O)_2]^{4+}$ in $CH_3CN + 0.1$ M TBAP in the presence of 2 added moles of H^+ per complex allows the quasi-quantitative generation of $[Fe(bpy)_2(S)_2]^{2+}$. A simpler procedure to electrogenerate this complex, avoiding the synthesis and the isolation of the μ-oxo diferric complex, has been finalized.

Indeed, simple mixing of $Fe^{III}(ClO_4)_3 \cdot xH_2O$ (2 mM) and bpy (4 mM) ligand in CH_3CN results in the quantitative *in situ* formation of $[Fe_2^{III}O(bpy)_2(S)_6]^{4+}$ [eqn. (4)].

$$2\,Fe^{3+} + 4\,bpy + H_2O + 6\,S \rightarrow$$

$$[Fe_2O(bpy)_2(S)_6]^{4+} + 2\,bpyH^+ \quad (4)$$
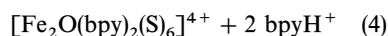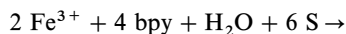
It should be noted that a knowledge of the quantity of H_2O contained (x) in $Fe(ClO_4)_3$ is crucial to ensure completion of the reaction [eqn. (4)] and to prevent formation of by products like $[Fe(bpy)_3]^{2+}$. The value of x $(x = 12)$ has been evaluated by an electrochemical technique (see experimental). Fe^{III} is acidic enough to deprotonate H_2O and to form the oxo bridge. The formed H^+ are trapped by the two free bpy ligands.

Quantitative formation of $[Fe_2O(bpy)_2(S)_6]^{4+}$ is displayed by comparison of the visible and NMR spectra and cyclic voltammogram of the resulting solution to those of a solution of $[Fe_2O(bpy)_4(H_2O)_2]^{4+}$ in CH_3CN in the presence of two added H^+.[2] For instance, in the cathodic region the typical irreversible peak at 0.08 V is observed, associated with some shoulders at 0.21 and 0.25 V. On the reverse scan the $[Fe(bpy)_2(S)_2]^{2+}$ quasi-reversible oxidation peak system is detected at $E_{1/2} = 0.95$ V while the peak system due to $[Fe(bpy)_3]^{2+}$ $(E_{1/2} = 0.76$ V) is missing (Fig. 1, curve *a*). Exhaustive reduction carried out at 0 V consumed 2 electrons per mol, in accordance with eqn. (2), and produces quantitatively $[Fe(bpy)_2(S)_2]^{2+}$ as judged by the CV of the electrolyzed solution, which exhibits in the anodic region only the quasi-reversible $[Fe(bpy)_2(S)_2]^{3+/2+}$ peak system at $E_{1/2} = 0.95$ V. In addition, the electronic absorption of this orange solution is typical of $[Fe(bpy)_2(S)_2]^{2+}$ at a concentration close to 2 mM with a maximum absorption band lying at $\lambda_{max} = 470$ nm. In the negative potential area (Fig. 1, curve *b*) the CV shows the three waves of the ligand-based reversible reduction of the $[Fe^{II}(bpy)_3]^{2+}$ complex. An irreversible peak $(E_{p_c} = -1.50$ V) corresponding to the reduction of the bis bpy complex is seen before the first reduction system of $[Fe(bpy)_3]^{2+}$. This means that the $[Fe(bpy)_2(S)_2]^{2+}$ complex is quickly converted into the more stable $[Fe^{II}(bpy)_3]^{2+}$ complex after the first reduction of the bpy ligand of $[Fe(bpy)_2(S)_2]^{2+}$. This analytical observation has been confirmed by the result of a controlled-potential reduction of the solution at -1.38 V. Coulometric measurement shows that 0.6 electron per molecule of $[Fe(bpy)_2(S)_2]^{2+}$ has been consumed. Analysis of the resulting electrolyzed red solution by cyclic voltammetry (Fig. 1, curve *c*) and visible absorption reveals that 1.33 mM of $[Fe(bpy)_3]^{2+}$ has formed. Formation of this complex in bulk solution is accompanied by coating of the platinum working electrode by a dark-brown material, which is presumably metallic iron. The amount of Fe^0 deposited has been evaluated by dissolution of the coating in aqueous acidic medium (1 M HNO_3). The solution was neutralized by addition of sodium acetate and addition of an
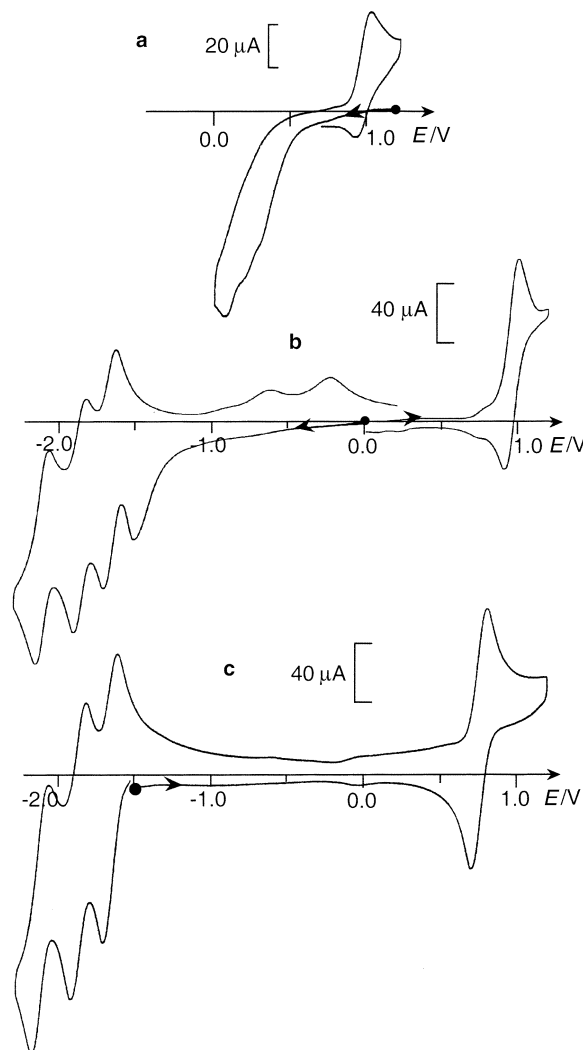
Fig. 1 Cyclic voltammograms in $CH_3CN + 0.1$ M TBAP at a vitreous carbon electrode (diameter 5 mm), scan rate 100 mV s^{-1}, of (*a*) 2 mM $Fe(ClO_4)_3 \cdot 12H_2O + 4$ mM bpy mixture, (*b*) after exhaustive reduction at 0.00 V of the resulting solution, (*c*) after reduction at -1.40 V of the solution obtained in (*b*).

excess of bpy allowed the concentration of Fe^{2+} to be determined to be 0.47 mM, instead of 0.66 mM as expected. Eqn. (5) summarizes the overall process implied in the reduction of $[Fe(bpy)_2(S)_2]^{2+}$:

$$[Fe(bpy)_2(S)_2]^{2+} + 2/3\,e^- \rightarrow$$

$$2/3\,[Fe(bpy)_3]^{2+} + 1/3\,Fe + 2\,S \quad (5)$$
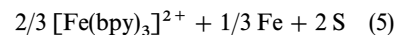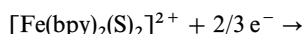
Electrochemical behaviour of $[Fe(bpy)_2(L')]^{2+}$ and $Fe(bpy)_2L_4(bpy)_2Ru]^{4+}$

$[Fe(bpy)_2(L')]^{2+}$ ($L' = L_1$–L_3). All these complexes exhibit the expected three successive one-electron reduction waves of the bpy ligand.[13] For $[Fe(bpy)_2(L_2)]^{2+}$ some adsorption phenomena are observed due to the electroinduced fomation of a polyvinyl film derivative.[14] Although this monomer contains only one vinyl group, films of $[Fe(bpy)_2(L_2)]^{2+}$ are easily obtained by continuously cycling the potential between 0 and -2.0 V or by potentiostatting the working electrode at -2.00 V.

Fig. 2 shows the CV of the resulting modified electrode in electrolyte free of monomer, obtained after 3.0 mC have passed at -2.00 V. The stability of this poly$[Fe(bpy)_2(L_2)]^{2+}$ film toward electrochemical cycling between the Fe(II) and Fe(III) redox states is excellent. Negligible loss of integrated peak current was typically observed after 20 cycles at 100 mV
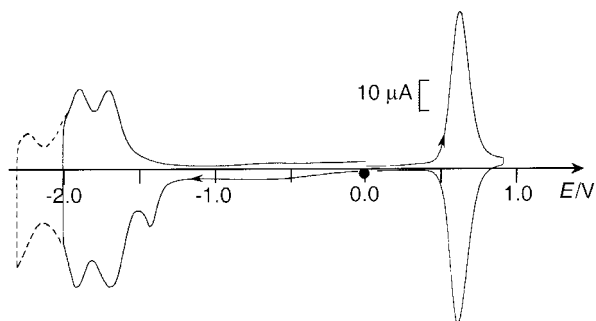
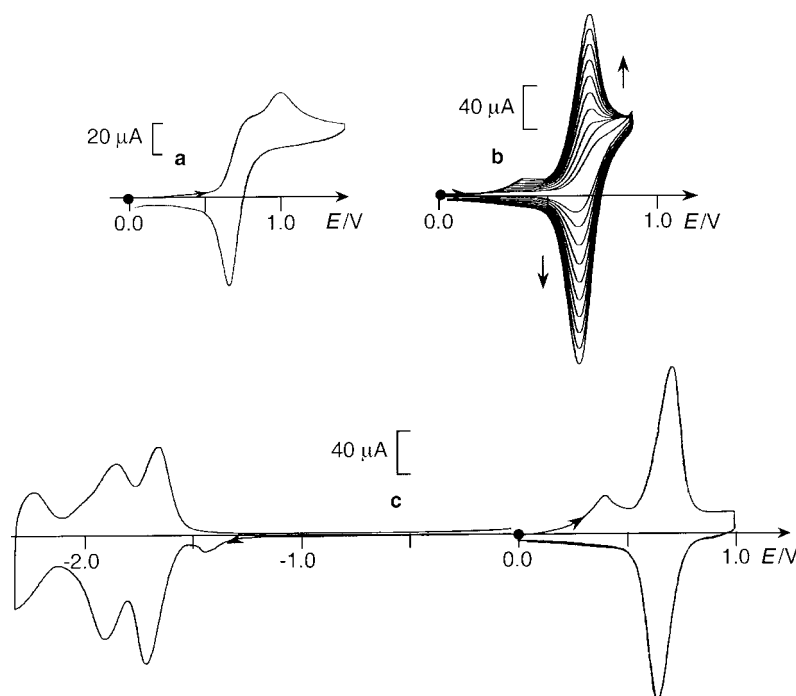**Fig. 2** Cyclic voltammograms in $CH_3CN + 0.1$ M TBAP of poly[Fe(bpy)$_2$(L$_2$)](ClO$_4$)$_2$ at a vitreous carbon electrode (diameter 5 mm) prepared by cycling between 0.00 and -2.00 V of a millimolar solution of monomer, potential ranges: 0.9 to -2.0 V (bold line), 0.9 to -2.4 V (dotted line); scan rate 100 mV s^{-1}.

s^{-1}, between 0 and 0.95 V. Finally, poly[Fe(bpy)$_2$(L$_2$)]$^{2+}$ films appear as stable as the more cross-linked poly[Fe(L$_2$)$_3$]$^{2+}$ films, previously described,[14] obtained from the [Fe(L$_2$)$_3$]$^{2+}$ monomer. It is noteworthy that the second one-electron reduction wave, [Fe(bpy)$_2$(L$_2$)]$^+$/[Fe(bpy)$_2$(L$_2$)]^0, is split. Besides the main peak system at $E_{1/2} = -1.92$ V, a weak system appears at a more cathodic potential ($E_{1/2} = -2.08$ V), especially if the electrode is cycled up to -2.40 V on the third one-electron reduction wave. As reported previously for some Ru-bpy polymeric films,[15] this phenomenon is probably due to the presence of two distinct ionic process associated with the redox one. Since the second ligand-based reduction leads to formation of the neutral species [Fe(bpy)$_2$(L$_2$)]^0, electroneutrality in the film can be maintained by the release of anions or by the incorporation of cations coming from the electrolyte.

The CV of the [Fe(bpy)$_2$(L')]$^{2+}$ complexes in the anodic region shows the reversible Fe^{II}/Fe^{III} oxidation system. For [Fe(bpy)$_2$(L$_3$)]$^{2+}$ this wave is followed by the irreversible oxidation peak at $E_{pa} = 0.96$ V of the pyrrole group into polypyrrole (Fig. 3, curve a). By continuous cycling between 0 and 0.9 V, sustained film growth take place at a Pt electrode. The

CV response is quickly dominated by the Fe^{II}/Fe^{III} wave of the complex immobilized in the film (Fig. 3, curve b) while a small reversible peak system appears at $E_{1/2} = 0.38$ V due to the electroactivity of the polypyrrole itself.[16] The resulting poly[Fe(bpy)$_2$(L$_3$)]$^{2+}$ modified electrode, upon transfer into monomer-free $CH_3CN + 0.1$ M TBAP, exhibits the same basic electrochemical behaviour as the poly[Fe(bpy)$_2$(L$_2$)]$^{2+}$ modified one (Fig. 2), with a slight split of the [Fe(bpy)$_2$(L$_3$)]$^+$/[Fe(bpy)$_2$(L$_3$)]^0 reduction wave. The observation and persistance of the polypyrrole electroactivity ($E_{1/2} = 0.38$ V) is strongly dependent on the anodic limit of the potential scanning.[16] If the electrode is cycled above 0.80 V this signal disappears, as a consequence of the overoxidation of the polypyrrole matrix. Electropolymerization can also be accomplished by controlled-potential oxidation at 0.80 V. Modified electrodes prepared by both methods exhibit toward electrochemical cycling between the Fe(II) and Fe(III) states an excellent stability, comparable to those obtained with a more cross-linked polypyrrole backbone.[17] A slight loss of electroactivity is observed after one cycle while the intensity of the signal remains identical for twenty subsequent anodic scans. All the potential data of the [Fe(bpy)$_2$(L')]$^{2+}$ complexes and of the corresponding modified electrodes are summarized in Table 1.

On the other hand, it should be noted that the electrodeposition yield is poor ($\sim 10\%$), indicating that the electropolymerization produces soluble polymer and/or oligomers. Indeed, this particular behaviour is evidenced by the analysis of solutions resulting from exhaustive oxidation. In the case of [Fe(bpy)$_2$(L$_3$)]$^{2+}$ the amount of soluble iron species (80% of the starting material) can be estimated by measurement of the anodic current relative to the Fe^{II}/Fe^{III} system and comparison to the one of the initial solution, and by UV-vis titration at 520 nm. The CV of the resulting solution exhibits, besides the regular reversible Fe^{II}/Fe^{III} electroactivity, reduction of the released protons during the electropolymerization process. After exhaustive reduction of the protons one can observe that repeated cycles in the negative potential region induce a continuous increase of an electroactive film at the surface of the electrode. This phenomenon, already described,[15] is due to a

Fig. 3 Cyclic voltammograms of 1 mM [Fe(bpy)$_2$(L$_3$)](ClO$_4$)$_2$ in $CH_3CN + 0.1$ M TBAP on a vitreous carbon electrode (diameter 5 mm), scan rate 100 mV s^{-1} (a) First scan between 0.00 and 1.40 V, (b) elaboration of the modified electrode by 10 potential scans between 0.00 and 0.90 V, (c) cyclic voltammogram of the resulting modified electrode in monomer-free CH_3CN solution.

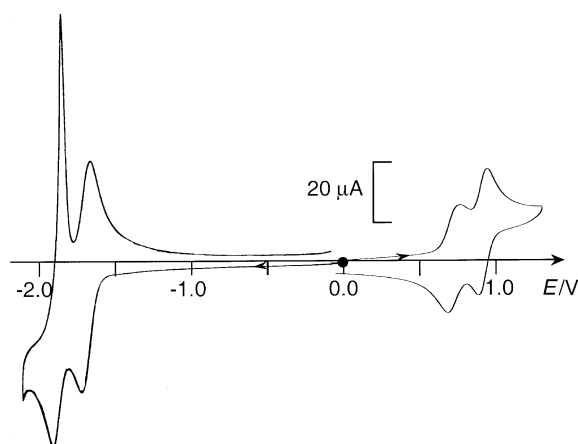**Table 1** Electrochemical data of $[Fe(bpy)_2(L')]^{2+}$ ($L' = L_1-L_3$), $[Ru(bpy)_2(L_4)]^{2+}$ and of the corresponding modified electrodes

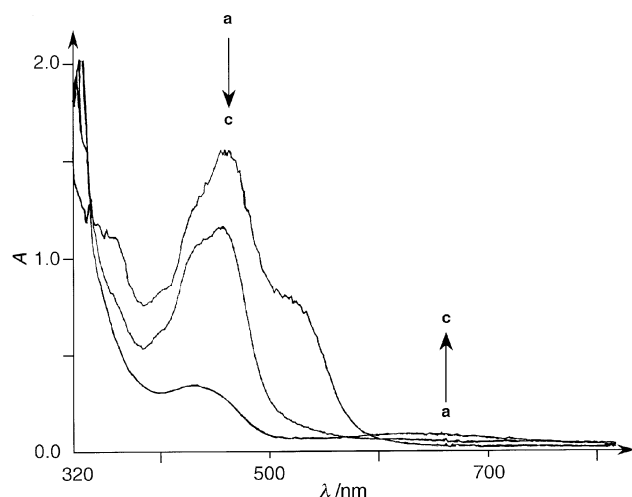| Complex	$E_{1/2}$ ox/V (ΔE_p/mV)		$E_{1/2}$red/V (ΔE_p/mV)		
	$3+/2+$	other	$2+/+$	$+/0$	$0/-$
$[Fe(bpy)_2(L_1)]^{2+}$	0.69 (75)		−1.68 (90)	−1.88 (100)	−2.13
$[Fe(bpy)_2(L_2)]^{2+}$	0.70 (70)		−1.64 (95)	—[a]	—[a]
poly$[Fe(bpy)_2(L_2)]^{2+}$	0.63 (20)		−1.70 (40)	−1.90 (30)	−2.24
$[Fe(bpy)_2(L_3)]^{2+}$	0.69 (70)	0.95-pyrrole	−1.68 (92)	−1.92 (105)	−2.15 (100)
poly$[Fe(bpy)_2(L_3)]^{2+}$	0.67 (70)	0.38-polypyrrole	−1.65 (45)	−1.85 (63)	−2.26 (100)
$[Ru(bpy)_2(L_4)]^{2+}$	0.91 (70)		−1.68 (90)	−1.88 (105)	−2.20 (100)

[a] These values cannot be measured since the waves are strongly distorted by adsorption phenomena (see the text).

poor solubility of the reduced forms of the polymers and oligomers compared to the starting material.

$[Ru(bpy)_2(L_4)]^{2+}$. As expected the CV of this complex shows the reversible one-electron oxidation peak system of the metal and the three successive reversible one-electron bpy-based reduction ones. An additional partially reversible reduction wave is seen at a more cathodic potential corresponding to the reduction of the uncomplexed bpy part of the complex, if a vitreous carbon electrode is used as working electrode instead of a platinum one.[18] Corresponding potentials are reported in Table 1. Exhaustive electrolysis at 1.15 V furnished the corresponding Ru^{3+} species after one electron had been consumed. The absorption spectrum of this solution shows typical bands at 434 and 620 nm, close to those of the $[Ru(bpy)_3)]^{3+}$ species.[19]

$[Fe^{II}(bpy)_2L_4(bpy)_2Ru^{II}]^{4+}$. Oxidation waves of the two different metals are well-separated (Fig. 4): $E_{1/2}$ Fe^{II}/Fe^{III} = 0.71 V (ΔE_p = 100 mV); $E_{1/2}$ Ru^{II}/Ru^{III} = 0.91 V (ΔE_p = 70 mV). Obviously, these two values are close respectively to those of the $[Fe(bpy)_2(L_1)]^{2+}$ and $[Ru(bpy)_2(L_4)]^{2+}$ complexes (see Table 1), in accordance with the lack of metal-metal coupling. Taking into account the large difference of potential between the Fe^{II}/Fe^{III} and Ru^{II}/Ru^{III} redox systems ($\Delta E_{1/2}$ = 200 mV), the mixed valent Fe^{III}-Ru^{II} species is perfectly stable. Indeed, two successive exhaustive electrolyses carried out at 0.80 and 1.0 V consumed one electron per complex and allowed the bulk build up of $[Fe^{III}(bpy)_2L_4(bpy)_2Ru^{II}]^{5+}$ and $[Fe^{III}(bpy)_2L_4(bpy)_2Ru^{III}]^{6+}$ species, respectively. This is illustrated by the evolution of the solution after these sequential electrolyses (Fig. 5). The typical initial band of the Fe^{II} species (520 nm) has disappeared after one electron per complex, has been passed. After exchange of another electron the band of the Ru^{II} species (λ_{max} = 454 nm) has been replaced by those of the Ru^{III} one (λ_{max} = 431 and 628 nm). Since the reduction of the bpy ligands in the regular $[Fe(bpy)_3]^{2+}$ and $[Ru(bpy)_3)]^{2+}$ moieties occurs at very similar potentials the reduction pattern of this complex involves three successive two-electron waves. However, only the first two-electron reduction wave is clearly seen ($E_{1/2}$ = −1.67 V, ΔE_p = 90 mV). The two other subsequent waves ($E_{1/2}$ = −1.88 and −2.20 V) are strongly distorted by some electroprecipitation-redissolution phenomena (Fig. 4, where only the two first waves are shown).

Fig. 4 Cyclic voltammogram of 1 mM $[Ru(bpy)_2(L_4)(bpy)_2Fe]$-$(PF_6)_4$ in CH_3CN + 0.1 M TBAP solution at a vitreous carbon electrode (diameter 5 mm); scan rate 100 mV s^{-1}.

Fig. 5 UV-visible spectra of 1 mM $[Ru(bpy)_2(L_4)(bpy)_2Fe](PF_6)_4$ in CH_3CN + 0.1 M TBAP solution (l = 1 mm): (a) initial solution, (b) after exhaustive oxidation at 0.80 V, (c) after exhaustive oxidation at 1.00 V.

Conclusion

It appears that reduction of a CH_3CN solution of the μ-oxo diferric complex $[Fe_2O(bpy)_4(H_2O)_2]^{4+}$ by ascorbic acid, followed by addition of a bidentate ligand L', is a convenient route to prepare the mononuclear coordinatively dissymmetrical iron(II) complexes $[Fe(bpy)_2L']^{2+}$. This route can be easily applied to the design of new complexes having unusual properties like electropolymerization capacity or containing a photoredox center such as a $Ru(bpy)_3{}^{2+}$ moiety. The studies

the photochemical properties of this last class of compounds is now underway.

Acknowledgements

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