

Spectroscopic and electrochemical sensing of lanthanides with  $\pi$ -extended chromophores incorporating ferrocenes and a coordinative end†Carmino Coluccini,<sup>a</sup> Arvind K. Sharma,<sup>a</sup> Daniele Merli,<sup>a</sup> Douglas Vander Griend,<sup>b</sup> Barbara Mannucci<sup>c</sup> and Dario Pasini<sup>\*a,d</sup>

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In this study, we report the synthesis and characterization of three novel “push–pull” chromophores, in which multiple phenylenevinylene units are endcapped by ferrocene as donor units and malonate moieties as acceptor units. These chromophores have spectroscopic and electrochemical characteristics which consistently change according to the extension of the conjugated bridge, thus to the variation of the HOMO–LUMO band gap. The 1,3-dicarbonyl units, directly incorporated into the conjugated molecular structures, are able to coordinate Lewis acid-like cations, such as lanthanides, as confirmed by UV/Vis, <sup>1</sup>H NMR and cyclic voltammetry studies. The UV/Vis spectroscopic response upon complexation with Sc<sup>3+</sup> or Eu<sup>3+</sup> as the triflate salts is rather unselective and nonlinear in going from the least to the most  $\pi$ -extended chromophore. Binding studies in MeCN, analyzed *via* equilibrium-restricted factor analysis, give values between  $\log K_a = 1.21$  and 3.07 and affirm a 1 : 1 stoichiometry of the host:guest complexes in all cases. On the other hand, cyclic voltammetry reveals a selectivity in the response to Sc<sup>3+</sup> coordination over Ln<sup>3+</sup> (Eu<sup>3+</sup>, but also Lu<sup>3+</sup> and Er<sup>3+</sup> were tested) for the two shorter chromophores, whereas the ligand with the longest  $\pi$ -bridge is able to sense Er<sup>3+</sup> ( $\Delta E_{1/2}$  complexed/uncomplexed chromophore = 20 mV) selectively over the other lanthanides.

## Introduction

Ferrocene compounds continue to attract attention due to their combination of electronic and physical properties; research efforts have focused in the recent past both on biological and on material science applications.<sup>1</sup> Particular activity in the last two decades has been devoted to donor–acceptor chromophores, in which the ferrocenyl moiety has been incorporated as an organometallic donor into push–pull assemblies with nonlinear optical (NLO) properties.<sup>2</sup> The favourable electrochemical properties of ferrocene moieties have also been developed for sensing; in this context, functionalities capable of molecular recognition towards suitable analytes are placed in direct conjugation with the ferrocene unit: the binding event causes a perturbation of the electronic properties of the whole unit, and therefore electrochemical response, upon coordination of the analyte.<sup>3</sup>

Some of us have previously reported on the characterization of supramolecular complexes involving push–pull chromophores in which the electron-withdrawing molecular fragment is a malonate moiety, able to coordinate metal cations (such as lanthanides).<sup>4</sup> 1,3-Dicarbonyl units (either ketones or esters, such as acetylacetone, *etc.*) are commonly used as bidentate ligands for lanthanide and transition metal ions, traditionally in inorganic chemistry but also in organic catalysis.<sup>5</sup> Modified malonate functionalities with  $\pi$ -systems in direct conjugation with the two carbonyl moieties, to form  $\pi$ -extended ligands for metal cations, have not been, to the best of our knowledge, extensively investigated. We have previously studied ferrocene-containing model systems of such kind, in which an oligoethylene chain joins as an ester derivative the two carboxylate ends of the 1,3-dicarbonyl moieties, forming functionalized malonate crown ethers.<sup>4a</sup>

Our motivation in this work was to analyze the complexation and sensing behaviour towards lanthanides of ferrocene-containing push–pull chromophores bearing identical donor–acceptor moieties (ferrocene as a donor, dimethylmalonate esters as the acceptors) endcapping progressively longer  $\pi$ -conjugated bridges, with multiple *p*-phenylenevinylene units sequentially introduced.

## Results and discussion

## Ligand preparation and spectroscopic characterization

The synthesis of the compounds is shown in Scheme 1. The synthetic scheme follows the introduction of *p*-phenylenevinylene

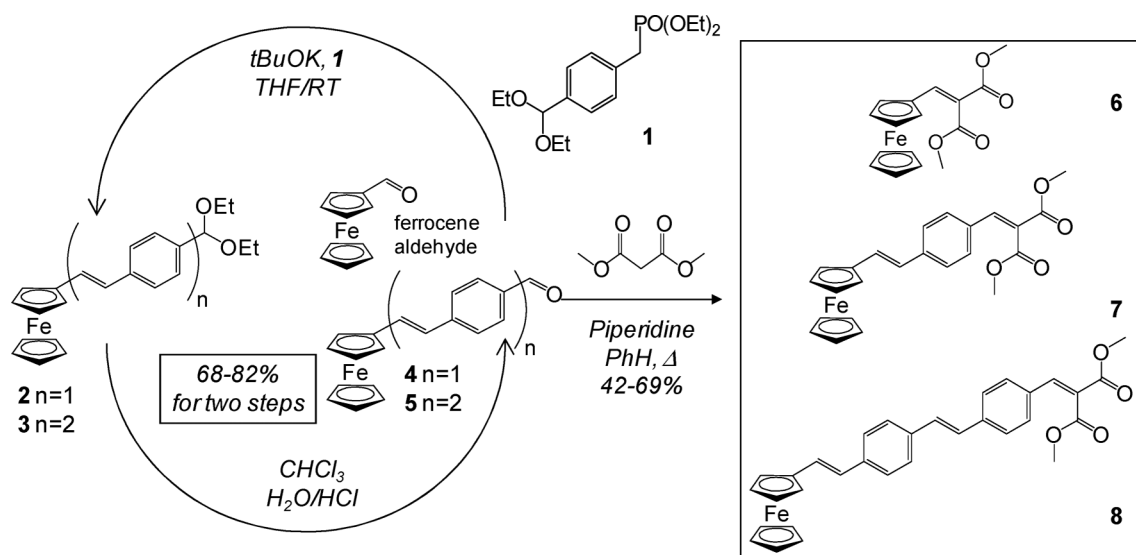
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† Electronic supplementary information (ESI) available: Copies of NMR spectra for all compounds, additional NMR and UV/Vis spectroscopic data. See DOI: 10.1039/c1dt11031d



Scheme 1 Synthesis of the ligands 6–8.

units making use of the acetal protected phosphonate **1**.

Compound **1** was prepared through substantial modifications of previously published procedures, as reported in the ESI.† Horner–Wadsworth–Emmons olefinations with **1** in basic conditions (THF, *t*-BuOK) afforded acetal-protected aldehydes **2** and **3**, used without further purification, which could be easily deprotected under mild acidic conditions, to afford elongated aldehydes **4** and **5**. Final endcapping (a Knoevenagel reaction) on **4** and **5**, or on the commercially available ferrocenealdehyde, was conducted in the presence of dimethyl malonate and a catalytic amount of base with the use of a Dean–Stark apparatus to afford, after purification by column chromatography, the air stable, “push–pull” ligands **6–8**.

<sup>1</sup>H NMR spectroscopy confirmed that, within the limit of detection of the technique, all the newly formed carbon–carbon double bonds are in the *trans* configuration exclusively (peaks between 7.20 and 6.70 ppm, <sup>3</sup>J<sub>HH</sub> coupling constants of *ca.* 16 Hz in all cases). Representative spectra for the aromatic portion of ligands **7** and **8** are shown in Fig. 1. The chemical shifts for the protons endcapping the conjugated molecular structures (the vinyl proton next to the malonate unit and the ferrocene protons) appear slightly different for the shorter compound **6** (7.65 and 4.47–4.22 ppm, respectively) when compared to both **7** and **8** (7.77–7.78 and 4.42–4.16 ppm, respectively) in CDCl<sub>3</sub> (Table S1†), evidencing a different electronic distribution within the conjugated framework.

A previous study has rationalized the UV/Vis spectroscopic properties of a series of conjugated “push–pull” ferrocenes and proposed a general model,<sup>2c</sup> which has been used in subsequent reports.<sup>2j</sup> According to this model, the highest occupied molecular orbitals correspond to the predominately non-bonding, nearly degenerate d orbitals of the metal (labelled hereafter M). The next highest orbital is formed from a combination of the highest occupied cyclopentadienyl orbital and the highest occupied π-bridge orbital (labelled hereafter π).

The LUMO (labelled hereafter A) is largely localized on the acceptor, but also has a small bridge contribution. The UV/Vis spectra of the ferrocene-containing chromophores **6–8**

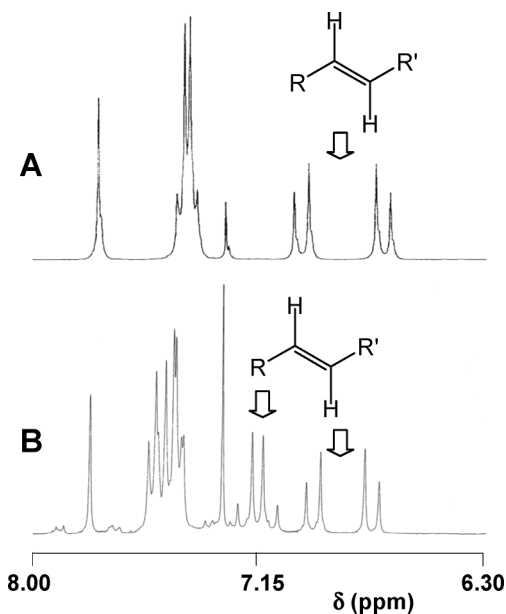


Fig. 1 Enlargement of <sup>1</sup>H NMR spectra (300 MHz, CDCl<sub>3</sub>) for ligands **7** (A) and **8** (B).

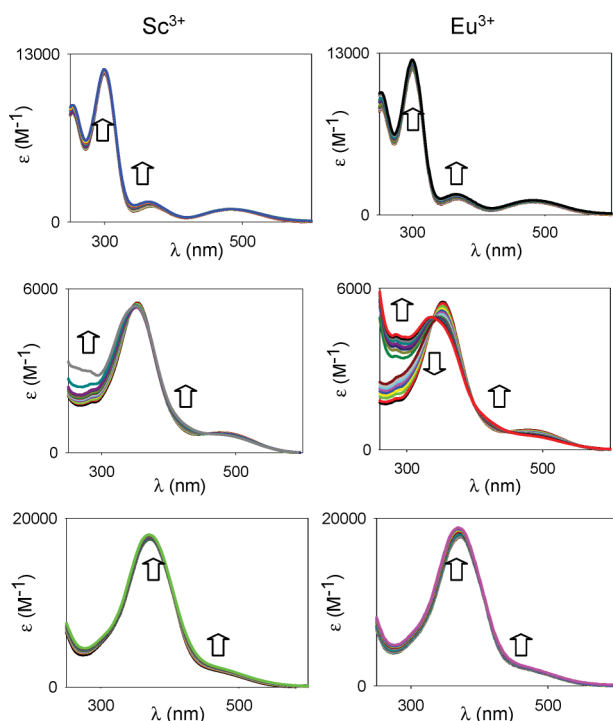
show stronger higher energy transition (HE) bands and weaker lower energy transition (LE) bands. The LE bands are M→A transitions, while the HE absorption is a π→A transition; both types are present in the UV/Vis spectra of ligands **6–8** (Table 1). The presence of two LE bands for compound **6** is consistent with previously reported analogous monosubstituted ferrocenes with electron-withdrawing substituents and with ferrocene itself.<sup>6</sup> Increasing the length of the π bridge causes a redshift of the HE band, which goes progressively from 299 to 373 nm, with some variations in the molar absorptivity values. However, the LE bands remain relatively insensitive to the effect of a longer conjugated bridge. This is in agreement with the previously published model, in which the LE transition, involving only metal- and acceptor-localized orbitals, is not affected by an extension of the conjugation length.

**Table 1** UV-Vis data on the HE and LE bands of **6–8** (in MeCN)

Compound	$\lambda_{\max}$ (nm)	$\epsilon$ ( $M^{-1} \text{ cm}^{-1}$ )
<b>6</b>	299 (HE)	11 600
	368 (LE)	1220
	484 (LE)	990
<b>7</b>	353 (HE)	5480
	480 (LE)	730
<b>8</b>	373 (HE)	17 670
	480 (shoulder, LE)	1700

**Complexation response with  $\text{Eu}^{3+}$  and  $\text{Sc}^{3+}$** 

The comparison of the recognition properties, and of the response induced by the binding event, within the class of the three conjugated ligands, was then pursued. Together with our previously used probe  $\text{Eu}^{3+}$ ,<sup>4</sup> we also analyzed the behaviour of  $\text{Sc}^{3+}$ ; having a different ionic radius and polarizability properties with respect to lanthanides,  $\text{Sc}^{3+}$  is in any case commonly used for coordinating 1,3-dicarbonyl moieties as a lanthanide analogue,<sup>7</sup> and it can be used in  $^1\text{H}$  NMR titrations as it is diamagnetic. UV/Vis studies were conducted in MeCN using the anhydrous triflate salts of  $\text{Sc}^{3+}$  and  $\text{Eu}^{3+}$ , and all titrations are reported in Fig. 2.

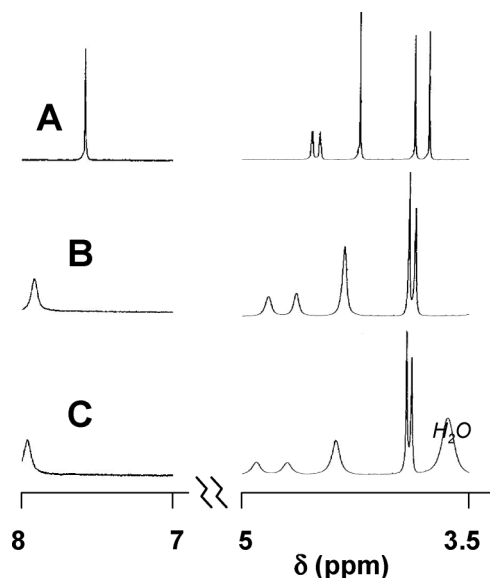


**Fig. 2** UV/Vis titration experiments with  $\text{Sc}(\text{OTf})_3$  and  $\text{Eu}(\text{OTf})_3$  in MeCN for ligands **6** (top), **7** (center), **8** (bottom). Ligand concentrations were in the range:  $5.2 \times 10^{-5} \text{ M}$ – $1.8 \times 10^{-4} \text{ M}$ . Between 6 and 12 equivalents of metal salt were added.

In general, small but detectable variations in the UV/Vis spectra were observed in all titrations, testifying to an effective interaction between the ligands (kept at a constant concentration) and the metal cations. A blueshift in the HE band is appreciable in the case of ligand **7**, in the presence of either  $\text{Sc}^{3+}$  and  $\text{Eu}^{3+}$ , whereas effects are drastically less evident in the cases of **6** and **8**. In all cases, however, isosbestic points are not present. The blueshift for both the HE and LE bands upon complexation in

the case of **7** can be considered a consequence of the electronic change in the acceptor group caused by the coordination of the metal ion to the 1,3-dicarbonyl moiety. The coordination event destabilizes the acceptor moiety which, according to the previously cited model, contributes largely to the LUMO level. The minimal effects observed for ligands **6** and **8** on the orbital energies upon complexation can be ascribed to concomitant stabilization and destabilization effects on HOMO and LUMO levels; there are indeed changes in the intensities of the corresponding HE and LE bands upon complexation (see below and Fig. S1†).

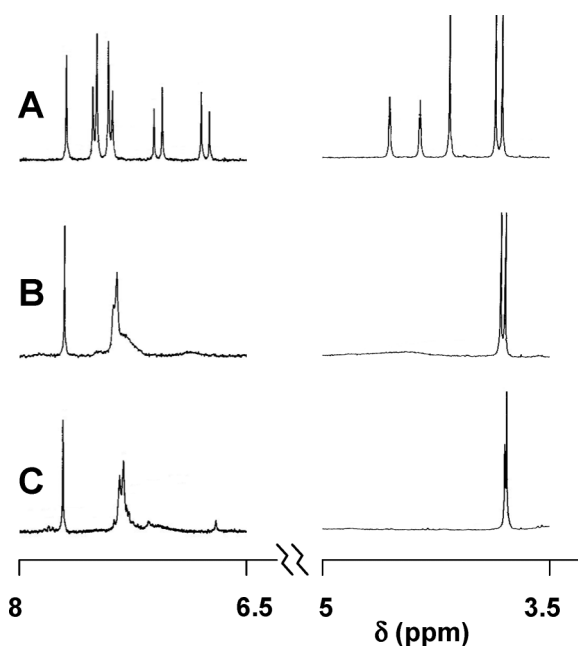
The complexation properties were further investigated by  $^1\text{H}$  NMR spectroscopy with  $\text{Sc}(\text{OTf})_3$ . It is evident (Fig. 3 and 4) how, in both ligands **6** and **7**, the coordination of the  $\text{Sc}^{3+}$  ion severely perturbs the  $\pi$ -conjugated system. As in the UV/Vis titrations, in the  $^1\text{H}$  NMR titrations there are differences between the two resulting complexes: in the case of **6** (Fig. 3), broadening and a downfield shift for resonances of the vinyl and ferrocene protons could be observed (0.38 ppm downfield for the vinyl proton resonance at 7.58 ppm, and 0.45–0.5 downfield shift for the ferrocene proton resonances between 4.2 and 4.5 ppm). The downfield shift in these regions is in agreement with a decreased electron density in the conjugated bridge caused by the coordination of the positively charged ion to the malonate acceptor end.



**Fig. 3** Titration of ligand **6** (0.0105 M in  $\text{CD}_3\text{CN}$ ) with  $\text{Sc}(\text{OTf})_3$ : (A) 0 equivalents; (B) 0.6 equivalents; (C) 0.8 equivalents.

The effect is similar in the case of ligand **7** (Fig. 4), although the broadening is more pronounced for both the ferrocene and  $\pi$ -bridge proton resonances, which seem to disappear under the baseline.

The vinyl proton resonance (7.71 ppm) shifts in this case only marginally downfield (0.02 ppm). For both compounds **6** and **7**, upon complex formation, the methyl ester proton resonances get closer in terms of chemical shifts; the coordination of the metal cation seems to reduce the difference between the  $-\text{COOME}$  group chemical shifts, which, in ligands **6** and **7** on their own, is a consequence of the carbon–carbon double bond defining *cis* and *trans* environments for the two COOME groups. The reduction of



**Fig. 4** Titration of ligand **7** ( $2.5 \times 10^{-3}$  M in  $\text{CD}_3\text{CN}$ ) with  $\text{Sc}(\text{OTf})_3$ : (A) 0 equivalents; (B) 0.3 equivalents; (C) 1.5 equivalents.

this difference can be the indication of a reduced barrier to carbon–carbon double bond *cis*–*trans* isomerization occurring upon complexation; in any case, this observation reinforces evidence for a coordination of the cation at the 1,3-dicarbonyl end.

To better ascertain the species present and the thermodynamic relationships between them, sets of absorbance data like those shown in Fig. 2, for  $\text{Sc}(\text{OTf})_3$  and  $\text{Eu}(\text{OTf})_3$  titrated with **6–8**, were modelled using a factor analysis program called *Sivvu*, which takes into account *all* available wavelengths, and can potentially account for any set of equilibria.<sup>8</sup> When ligands **6–8** are titrated with  $\text{Sc}(\text{OTf})_3$ , the best models seem to simply identify a 1 : 1 complex. The data, especially for **6**, does not exhibit much change in the spectroscopic range. There is also some evidence with **8** that there is another complex, likely  $\text{ScL}_2$ . When **6–8** are titrated with  $\text{Eu}(\text{OTf})_3$ , again the best models seem to simply identify a 1 : 1 complex. With  $\text{Eu}(\text{OTf})_3$  binding constants are generally higher (Table 2), and the free energy values are all quite consistent. The data with **8** does exhibit a 4th factor, likely  $\text{EuL}_2$ , but also possibly  $\text{EuL}_3$ . The root-mean-square of the residuals over all of the spectroscopic data points were just 0.0025 as the maximum value. The modelled curves for the 1 : 1 complexes are shown in Fig. S1.†<sup>9</sup>

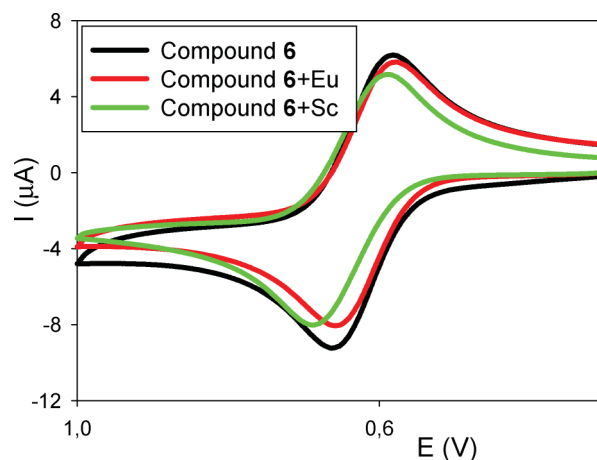
**Table 2** Association constants for the 1 : 1 complexes between  $\text{Sc}(\text{OTf})_3$  and  $\text{Eu}(\text{OTf})_3$  and ligands **6–8**, measured by UV/Vis titrations at 298 K in MeCN

Compound	$\text{Sc}(\text{OTf})_3$	$\text{Eu}(\text{OTf})_3$	RMS residual <sup>a</sup>	
	$\text{Log } K_a/\text{M}^{-1}$	$\text{Log } K_a/\text{M}^{-1}$	(Sc, Eu)	$R^2$
<b>6</b>	1.21	3.07	0.00144, 0.00202	99.988%, 99.994%
<b>7</b>	2.92	2.47	0.00194, 0.00088	99.998%, 99.996%
<b>8</b>	2.52	2.89	0.00252, 0.00116	99.993%, 99.999%

<sup>a</sup> Root-mean-square of the point-by-point differences between the absorbance data and the calculated values for each set of absorbance curves assuming 1 : 1 binding.

## Electrochemical studies

The electrochemical properties of compounds **6–8** have been investigated in MeCN by means of cyclic voltammetry. Even though the voltammograms were acquired in the  $-800$  mV/ $+2000$  mV potential range, no oxidation or reduction peaks were found other than the ones in the  $+400/+600$  mV region here reported. The oxidation wave corresponds to the one electron reversible oxidation of the Fe(II) atom in the ferrocene moiety, while the corresponding reduction wave represent the opposite process, *i.e.* the reduction of Fe(III) to Fe(II).<sup>10</sup> A typical voltammogram is shown in Fig. 5.



**Fig. 5** Cyclic voltammetry of compound **6**, **6** + 1 eq of Sc, and **6** + 1 eq of Eu in an MeCN solution with  $\text{Bu}_4\text{N}^+\text{BF}_4^-$  (0.1 M) as the supporting electrolyte.

As expected, it can be noted that the redox potentials shift towards more positive values from ferrocene to **6** (Table 3), as the presence in the investigated molecules of the electron-attractive malonate moiety makes the oxidation more difficult since it decreases the electron density on the metal center.<sup>11</sup> This shift reduces gradually with a further extended  $\pi$ -bridge from **6** to **8**, hence with an increased distance between the malonate unit from the ferrocene and with a reduced HOMO–LUMO bandgap.

The addition of  $\text{HBF}_4$  up to 2 equivalents *vs.* ligand does not cause a change in voltammetric profile for **6–8**, meaning that, as expected, protonation of the compounds does not occur. To investigate the cation detection properties of compounds **6–8**, electrochemical studies were performed in MeCN in the presence of  $\text{Eu}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Lu}^{3+}$  triflates. During these experiments, the amounts of salts added were increased until a clear reproducible

**Table 3** Response behaviour in the coordination of Ln<sup>3+</sup> by the ferrocene chromophores<sup>a</sup>

Redox properties (mV)	<b>6</b>	<b>7</b>	<b>8</b>
$E_{1/2}$	620	460	440
$E_{1/2} + \text{Eu}$	620	463	445
$E_{1/2} + \text{Sc}$	640	480	450
$E_{1/2} + \text{Er}$	620	464	418
$E_{1/2} + \text{Lu}$	620	463	437
$\Delta E_{1/2}$ (Sc)	20	20	10
$\Delta E_{1/2}$ (Er)	—	—	22
RCE (Sc)	1.47	1.47	1.21
RCE (Er)	—	—	1.48

<sup>a</sup> See the Experimental section for electrochemical conditions. For ferrocene:  $E_{1/2} = 415$  mV.

and final shift of the oxidation potential of the Fe(II)/Fe(III) couple was observed; this final shift required the addition of equimolar amounts of metallic salts with respect to the ligands **6–8** in all cases. Addition of further quantities of metal triflates does not cause a further potential peak shift, confirming a 1 : 1 stoichiometry of the supramolecular complex between the cation and the ligand.

Some common trends appear (see Table 3); in particular, all the compounds were not electrochemically sensitive to the presence of Eu<sup>3+</sup> or Lu<sup>3+</sup>; **6** and **7** were also not sensitive to the presence of Er<sup>3+</sup>, thus showing a selectivity for the detection of Sc<sup>3+</sup>. Compound **8** showed a partial selectivity for the detection of Er<sup>3+</sup>, as a clear shift of the oxidation potential ( $\Delta E_{1/2} = 22$  mV) is observed after the addition of this cation, while its response to Sc<sup>3+</sup> is rather low (10 mV). Upon the addition of Sc<sup>3+</sup> to **6** or **7**, the anodic shift of the oxidation potential is more pronounced with respect to the shift of the correlated reduction wave, meaning a partial loss of reversibility which could be ascribed to a kinetic effect.<sup>12</sup> The magnitude in chemical shift ( $\Delta E_{1/2} = E_{1/2}$  complexed –  $E_{1/2}$  free) in complexation provides thermodynamic information, as the following equation is applicable:<sup>13</sup>

$$\Delta E_{1/2} = (RT/nF)\ln(K_{\text{red}}/K_{\text{ox}})$$

where  $K_{\text{red}}$  is the metal binding constant for the ligand in its reduced form, and  $K_{\text{ox}}$  is the metal binding constant for the oxidized form. The quantity  $K_{\text{red}}/K_{\text{ox}}$  has been defined<sup>3b</sup> as reaction coupling efficiency (RCE), and represents a quantitative measure of the perturbation of the redox center induced by complexation of the receptor unit. As shown in Table 3, the values found are quite small and homogeneous for the different ligands, as a confirmation that the complexation constants are not high. Moreover, from these data it is clear that the binding events are not strongly affected by the distance between the binding site and the ferrocene moiety, thus from the elongation of the  $\pi$ -conjugated bridge.

## Conclusions

We have reported the synthesis and characterization of a series of novel “push–pull” chromophores, in which the two termini (ferrocene as the donor and malonate ester as the acceptor) are separated by a  $\pi$ -conjugated bridge of progressively longer dimensions, given the insertion of 0, 1 or 2 phenylenevinylene units. There is a linearity of behaviour in the electrochemical and UV/Vis response of the ligands: with longer  $\pi$ -bridges, UV/Vis transitions

and the electrochemical potentials shift to lower energies, as expected for lower HOMO–LUMO band gaps. The coordination of Sc<sup>3+</sup> or Ln<sup>3+</sup> to the acceptor moiety, analyzed by using three different techniques (UV/Vis, <sup>1</sup>H NMR and electrochemistry) give instead nonlinear behaviour within the class of homologous ligands. Although the coordination of the cation clearly perturbs the  $\pi$ -system of the ligands, as shown by <sup>1</sup>H NMR titrations in MeCN, the UV/Vis response is marked in the case of the intermediate ligand **7**, and only marginal in the cases of the ligands **6** and **8**. The binding strength of the 1 : 1 complexes do not follow clearly molecular modifications in a structure–activity relationship; the preferred complex stoichiometry seems to be 1 : 1 in all cases, with log  $K_a$  between 2 and 3.5. Ligands **6** and **7** selectively show a shift in the redox potential only in the presence of Sc<sup>3+</sup>. Ligand **8**, possessing the most extended  $\pi$ -bridge, is able to electrochemically discriminate between the different lanthanides tested (Er<sup>3+</sup>, Lu<sup>3+</sup>, Eu<sup>3+</sup>) showing selective response in the presence of Er<sup>3+</sup>. These data will be useful in the design of organic conjugated oligomers and polymers in which macroscopic outputs can be tuned by a supramolecular coordination event.<sup>14</sup> Because of their unique optical properties such as line-like emission spectra and long luminescence lifetimes, trivalent lanthanide complexes have been exploited in a wide variety of applied outputs. The possibility of addressing lanthanide emission upon excitation of supramolecular complexes, which, when incorporating ferrocenes, could be also switched electrochemically, can be highly relevant for targeted technological applications.

## Experimental section

### General experimental

All available compounds were purchased from commercial sources and used as received. Compound **1** was prepared using substantial modifications, detailed in the ESI,<sup>†</sup> of previously reported procedures.<sup>15</sup> THF (Na, benzophenone), Et<sub>2</sub>O (Na, benzophenone) and CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>) were dried and distilled before use. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded from solutions in CDCl<sub>3</sub> on Bruker 200 or AMX300 with the solvent residual proton signal as a standard. The UV/Vis spectroscopic studies were conducted on a Perkin Elmer spectrophotometer. Mass spectra were recorded using an Electrospray Ionization instrument LCQ Decca (ThermoFinnigan). Analytical thin layer chromatography was performed on Macherey-Nagel ALUGRAM SIL G/UV<sub>254</sub> plates. Flash column chromatography was performed using Merck Silica gel 60 (230–400 Mesh).

Electrochemical measurements were performed using a three-electrode cell (volume 1 mL) with a glassy carbon working electrode (BAS, diameter 1.6 mm), a Pt wire auxiliary electrode, and Ag/AgCl (3 M NaCl) reference electrode. All electrochemical measurements were recorded using a computer-controlled electrochemical analyzer (BAS). In all cases, the cyclic voltammograms were acquired in MeCN containing 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte. Ligand concentration was 10<sup>−3</sup> M, scan speed 100 mV s<sup>−1</sup>. Voltammetric solution were purged with N<sub>2</sub> for 5 min to remove oxygen before every measurement cycle. Potentials are given with a precision of ±3 mV.  $E_{1/2}$  are the half the sum of anodic and cathodic peak potentials, the processes involved being reversible.

**Compound 4.** Potassium *tert*-butoxide (207 mg, 1.84 mmol) was added as a solid to a solution of ferrocenealdehyde (100 mg, 0.46 mmol) and **1** (134 mg, 0.46 mmol) in dry THF (20 mL) at 0 °C. After stirring at room temperature for 15 h, the solvent was removed *in vacuo* and H<sub>2</sub>O (20 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase dried (Na<sub>2</sub>SO<sub>4</sub>). The crude compound **2** was obtained as a purple solid and used directly without further purification. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, 25 °C)  $\delta$  = 7.45 (s, 4H; -ArH-), 6.82 (dd, 2H; -CH- vinyl), 5.46 (s, 1H; -CH(OEt)<sub>2</sub>), 4.53 (d, 4H; -FeH), 4.16 (s, 5H; -FeH), 3.62 (m, 4H; -OCH<sub>2</sub>CH<sub>3</sub>), 1.27 (t, 6H; -OCH<sub>2</sub>CH<sub>3</sub>). A solution of **2** in CHCl<sub>3</sub> (50 mL) and HCl 1 M (3 mL) was stirred for 15 h. A saturated aqueous NaHCO<sub>3</sub> solution (50 mL) was added, the organic layer separated, the aqueous layer extracted with CH<sub>2</sub>Cl<sub>2</sub> and the combined organic layers dried (Na<sub>2</sub>SO<sub>4</sub>) to yield **4** as a purple solid (120 mg, 82% for the two steps). MS(ESI): *m/z* 316 ([*M* + H]<sup>+</sup>, 100%), 339 ([*M* + Na]<sup>+</sup>, 25%), 348 ([*M* + MeOH]<sup>+</sup>, 37%), 655 ([2*M* + Na]<sup>+</sup>, 25%), 686 ([2*M* + Na + MeOH]<sup>+</sup>, 10%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C)  $\delta$  = 10.00 (s, 1H; -CHO), 7.85 (d, 2H; -ArH-), 7.58 (d, 2H; -ArH-), 7.10 (d, 1H; -CH- vinyl), 6.75 (d, 1H; -CH- vinyl), 4.45 (m, 4H; -FeH), 4.18 (s, 5H; -FeH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 25 °C)  $\delta$  = 191.5 (C=O), 143.9 (Cq), 134.5 (Cq), 131.4 (CH), 130.2 (CH), 125.9 (CH), 124.4 (CH), 82.1 (Cq), 69.6 (CH), 69.2 (CH), 67.2 (CH).

**Compound 5.** Potassium *tert*-butoxide (165 mg, 1.48 mmol) was added as a solid to a solution of compound **5** (115 mg, 0.37 mmol) and **1** (120 mg, 0.37 mmol) in dry THF (16 mL) at 0 °C. After stirring at room temperature for 15 h, the solvent was removed *in vacuo* and H<sub>2</sub>O (20 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase dried (Na<sub>2</sub>SO<sub>4</sub>). The crude compound **3** was obtained as a purple solid and used directly without further purification. A solution of **3** in CHCl<sub>3</sub> (50 mL) and HCl 1 M (4 mL) was stirred for 15 h. A saturated aqueous NaHCO<sub>3</sub> solution (50 mL) was added, the organic layer separated, the aqueous layer extracted with CH<sub>2</sub>Cl<sub>2</sub> and dried (Na<sub>2</sub>SO<sub>4</sub>) to yield **5** as a purple solid (105 mg, 68% for the two steps). MS(ESI): *m/z* 418 ([*M* + H]<sup>+</sup>, 100%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C)  $\delta$  = 10.02 (s, 1H; -CHO), 7.89 (d, 2H; -ArH-), 7.68 (d, 2H; -ArH-), 7.50 (m, 4H; -ArH-), 7.22 (m, 2H; -CH- vinyl), 6.84 (m, 2H; -CH- vinyl), 4.42 (m, 4H; -FeH), 4.17 (s, 5H; -FeH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 25 °C)  $\delta$  = 191.1 (C=O), 143.1 (Cq), 137.8 (Cq), 134.7 (Cq), 134.5 (Cq), 131.5 (CH), 129.8 (CH), 127.4 (CH), 126.8 (CH), 126.4 (CH), 126.1 (CH), 125.7 (CH), 124.9 (CH), 82.6 (Cq), 68.8 (CH), 66.5 (CH).

**Compound 6.** A solution of ferrocenealdehyde (100 mg, 0.46 mmol), dimethyl malonate (121 mg, 0.92 mmol) and three drops of piperidine in benzene (10 mL) was stirred at reflux with a Dean–Stark apparatus for 15 h. The solvent was removed *in vacuo* and the reaction mixture was then treated with H<sub>2</sub>O (20 mL) at room temperature, extracted with Et<sub>2</sub>O (3 × 20 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The reaction mixture was purified by flash column chromatography (SiO<sub>2</sub>; hexane/AcOEt: 97/3) to afford **6** as a red solid (72 mg, 48%). MS(ESI): *m/z* 351 ([*M* + Na]<sup>+</sup>, 100%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C)  $\delta$  = 7.64 (s, 1H; -CHC(COOMe)<sub>2</sub>), 4.47 (m, 4H; -FeH), 4.22 (s, 5H; -FeH), 3.86 (d, 6H; -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 25 °C)  $\delta$  = 167.7 (C=O), 164.7 (C=O), 144.5 (CH), 120.3 (Cq), 75.0 (Cq), 71.9 (CH), 70.3 (CH), 69.9 (CH), 52.3 (CH<sub>3</sub>), 52.2 (CH<sub>3</sub>).

**Compound 7.** A solution of compound **4** (114 mg, 0.36 mmol), dimethyl malonate (95 mg, 0.72 mmol) and three drops of piperidine in benzene (10 mL) was stirred at reflux with a Dean–Stark apparatus for 15 h. The solvent was removed *in vacuo* and the reaction mixture was then treated with H<sub>2</sub>O (20 mL) at room temperature, extracted with Et<sub>2</sub>O (3 × 20 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The reaction mixture was purified by flash column chromatography (SiO<sub>2</sub>; hexane/AcOEt: 95/5) to afford **7** as a purple solid (107 mg, 69%). MS(ESI): *m/z* 883 ([2*M* + Na]<sup>+</sup>, 95%), 898 ([2*M* + K]<sup>+</sup>, 20%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C)  $\delta$  = 7.76 (s, 1H; -CHC(COOMe)<sub>2</sub>), 7.43 (m, 4H; -ArH-), 7.00 (d, 1H; -CH- vinyl), 6.69 (d, 1H; -CH- vinyl), 4.42 (m, 4H; -FeH), 4.16 (s, 5H; -FeH), 3.90 (s, 3H; -OCH<sub>3</sub>), 3.87 (s, 3H; -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 25 °C)  $\delta$  = 167.3 (C=O), 164.5 (C=O), 142.5 (CH), 140.4 (Cq), 130.7 (Cq), 130.0 (CH), 129.7 (CH), 126.0 (CH), 124.6 (CH), 124.0 (Cq), 82.4 (Cq), 69.4 (CH), 69.2 (CH), 67.0 (CH), 52.6 (CH<sub>3</sub>), 52.5 (CH<sub>3</sub>).

**Compound 8.** A solution of compound **5** (98 mg, 0.24 mmol), dimethyl malonate (64 mg, 0.48 mmol) and three drops of piperidine in benzene (15 mL) was stirred at reflux with a Dean–Stark apparatus for 15 h. The solvent was removed *in vacuo* and the reaction mixture was then treated with H<sub>2</sub>O (20 mL) at room temperature, extracted with Et<sub>2</sub>O (3 × 20 mL) and dried (Na<sub>2</sub>SO<sub>4</sub>). The reaction mixture was purified by flash column chromatography (SiO<sub>2</sub>; hexane/AcOEt: 9/1) to afford **8** as a purple solid (53 mg, 42%). MS(ESI): *m/z* 532 ([*M* + H]<sup>+</sup>, 100%), 548 ([*M* + H<sub>2</sub>O]<sup>+</sup>, 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, 25 °C)  $\delta$  = 7.78 (s, 1H; CHC(COOMe)<sub>2</sub>), 7.48 (m, 8H; -ArH-), 7.12 (m, 2H; -CH- vinyl), 6.83 (m, 2H; -CH- vinyl), 4.41 (m, 4H; -FeH), 4.16 (s, 5H; -FeH), 3.90 (s, 3H; -OCH<sub>3</sub>), 3.88 (s, 3H; -OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz, 25 °C)  $\delta$  = 167.2 (C=O), 164.5 (C=O), 142.4 (CH), 139.9 (Cq), 137.8 (Cq), 135.1 (Cq), 131.5 (Cq), 130.4 (CH), 129.9 (CH), 127.5 (CH), 127.0 (CH), 126.7 (CH), 126.0 (CH), 125.4 (CH), 124.5 (Cq), 83.0 (Cq), 69.1 (CH), 66.8 (CH), 52.6 (CH<sub>3</sub>), 52.6 (CH<sub>3</sub>).

### General procedure for the titration experiments

MeCN (UV/Vis spectroscopic grade) was used. An analytical balance (with a precision of 10<sup>-4</sup> g) was used to weigh the samples for the stock solutions. Aliquots of these stock solutions were then taken *via* high precision syringes to prepare the cuvette samples for spectrophotometric analyses.

**Titration experiments.** The titration experiments were conducted as follows: to a stock solution of the ligand (solution A) in MeCN, were added several aliquots of the ligand (the lanthanide triflate, solution B). Solution B is formed by the lanthanide triflate at higher concentration dissolved in solution A, in order to maintain the ligand always at the same, constant concentration.

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