Synthesis and molecular hyperpolarisabilities of donor–acceptor bipyridyl metal complexes (M = Re, Zn, Hg)

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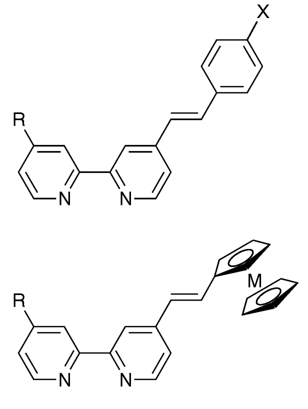
A series of rhenium(I), zinc(II) and mercury(II) complexes of π-donor-substituted vinyl bipyridines [donor = 4-$R_2N-C_6H_4-$; 4-$RO-C_6H_4-$; $(C_5H_5)Fe(C_5H_4-)$; $(C_5H_5)Ru(C_5H_4-)$] has been prepared and characterized by ^1H NMR and UV-visible spectroscopy. The second-order nonlinear optical properties of bipyridyl ligands and of their complexes have been investigated using EFISH experiments at 1.34 μm. A significant increase of the molecular hyperpolarizability β is observed upon coordination. The role of the nature of both the donor group and the metallic moiety on the NLO properties is discussed in detail.

Synthèse et hyperpolarisabilités moléculaires de complexes "donneur–accepteur" à ligands bipyridines (M = Re, Zn, Hg). Divers complexes de rhénium(I), zinc(II) et mercure(II) à ligands vinyl-bipyridines substitués par des groupements π-donneurs [donneur = 4-$R_2N-C_6H_4-$; 4-$RO-C_6H_4-$; $(C_5H_5)Fe(C_5H_4-)$; $(C_5H_5)Ru(C_5H_4-)$] ont été synthétisés et caractérisés par spectroscopies RMN ^1H et UV-visible. Les propriétés optiques non-linéaires du second-ordre des ligands bipyridyles et de leurs complexes ont été étudiées par des expériences EFISH à 1.34 μm. La complexation induit une augmentation significative du coefficient d'hyperpolarisabilité moléculaire β. Le rôle de la nature du groupement donneur et de l'entité métallique sur les propriétés ONL est discuté.

The search for active nonlinear optical materials has mainly focused on π-donor–acceptor organic compounds. However, investigations of organotransition metal chromophores have greatly increased in the past ten years.[1,2] One reason is the wide range of metals with different oxidation states, as well as a large choice of ligands and geometries, which can give rise to enhanced nonlinearities in thermally and/or photochemically stable compounds. Among these, dipolar metalloorganic molecules containing nitrogen ligands such as pyridines,[3] diimines,[4] Schiff bases,[5] phthalocyanines[6] and porphyrins[7] have shown promising microscopic NLO responses. Large octupolar nonlinearities have also been recently demonstrated in octahedral tris-bipyridine ruthenium complexes.[8,9]

We have previously developed the synthesis of new 4-alkenyl-2,2′-bipyridines bearing π-donor substituents (Scheme 1).[10] Their optical UV-visible absorption spectra showed characteristically intense solvatochromic intramolecular charge-transfer transitions, usually correlated with high first-order hyperpolarisabilities β. In the present work we report the synthesis, linear optical spectroscopy and molecular hyperpolarisability of a series of donor–acceptor complexes containing the bipyridyl ligands L—L represented in Scheme 1. We have focused our study on two different types of compounds in which the organometallic fragment acts as an acceptor: octahedral rhenium(I) carbonyl complexes of general formula $(L-L)Re(CO)_3X$ and tetrahedral zinc and mercury complexes of general formula $(L-L)MX_2$, where X can be halogeno, acetato or trifluorosulfonato ligands. By comparing the NLO responses of the ligands with those of the complexes we show (*i*) a significant enhancement of the molecular hyperpolarisability β upon coordination and (*ii*) that the NLO properties can be fine tuned by varying the nature of the metallic moieties as well as of the donor substituents on the bipyridines. A part of this work has already been published as a preliminary communication.[11]



	X	R
a	Me_2N	Me
b	$Bu^n{}_2N$	Me
c	(Me)(Oct)N	Me
d	OctO	Me
e	MeO	Nonyl

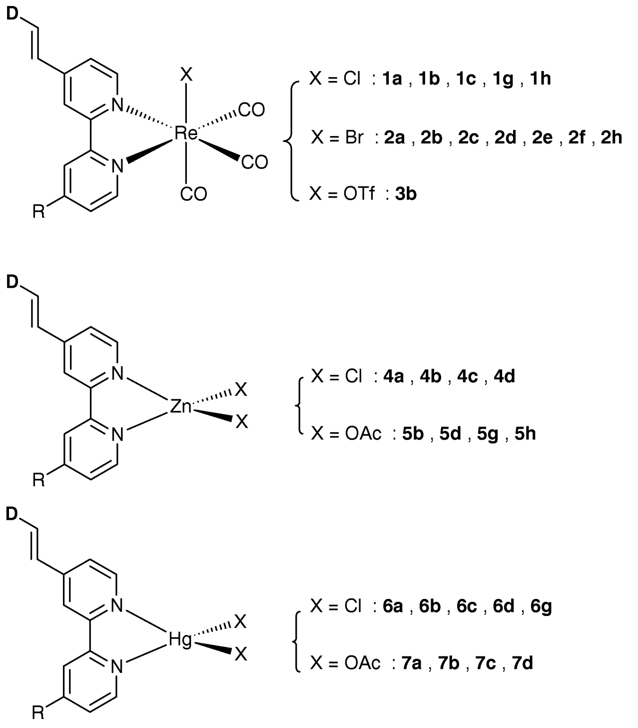
	M	R
f	Fe	Me
g	Fe	Nonyl
h	Ru	Me

Scheme 1

Results and Discussion

Synthesis and NMR characterization

The structures of the rhenium, zinc and mercury complexes synthesized in this work are shown in Scheme 2. Reaction of $Re(CO)_5X$ (X = Cl, Br, OTf) with the ligands **a**–**h** (Scheme 1) in refluxing toluene gave the stable red $Re(L-L)(CO)_3X$ complexes in high yield. The carbonyl stretching frequencies were in agreement with a facial geometry.[12] Only the triflato-rhenium complexes were moisture and solvent sensitive due to the enhanced lability of the $CF_3SO_3^-$ ligand in polar media. The zinc and mercury derivatives were readily prepared upon room temperature treatment of the ligands **a**–**h** with MX_2 (X = Cl, OAc). These complexes were stable in non-



Scheme 2

coordinating solvents but ligand exchange occurred slowly in coordinating solvents such as acetone.

The ^1H NMR spectra of compounds **1**–**7** show two expected doublets for the olefinic protons with strong vicinal coupling constants ($J_{HH} \approx 16$ Hz), which are characteristic of an *E* geometry. In some cases, especially for complexes containing an alkoxystyryl or a ruthenocenylvinyl substituent, the ^1H NMR spectra reveal the presence of a small amount of the corresponding *Z* isomers ($Z/E < 1/10$). These isomers show a distinctive AB quartet at higher field with $J_{HH} \approx 12$ Hz. Like in the free ligand, the aromatic region shows six different signals due to the dissymmetry of the bipyridines with a downfield shift of the $H^{6,6'}$ and $H^{5,5'}$ and a upfield shift of the $H^{3,3'}$ resonances upon complexation.

UV-visible spectroscopy

The UV-visible spectra recorded in dichloromethane (see Table 1 and experimental section) exhibit charge-transfer bands that are sensitive to the nature of both the organometallic moiety and the conjugated donor group. Fig. 1 shows solution spectra for the ligand **b** and the corresponding rhenium and zinc complexes **2b** and **5b**. The rhenium complexes **1**–**3** containing the dialkylaminostyryl bipyridine ligands **a**–**c** are characterized by an intense intraligand charge-transfer band (ILCT) in the region of 460–480 nm ($\varepsilon \approx 25\,000$–$30\,000$) that is considerably red-shifted (70–90 nm) when compared to the corresponding CT band of the free bipyridine ligand.[10] Replacement of the chloro or bromo ligand with the more electron withdrawing triflato ligand as in **3b** also causes a significant bathochromic shift ($\Delta\lambda \approx 20$ nm) of the ILCT band. The alkoxystyryl bipyridine rhenium derivatives **2d**–**e** have a substantially blue-shifted ILCT band ($\lambda_{max} \approx 365$ nm) when compared to the corresponding dialkylamino compounds, due to the weaker electron donating nature of the alkoxy group. Each of the rhenium complexes also exhibits a less intense absorption near 380 nm, which can be assigned to a $d\pi(Re) \rightarrow \pi^*(bpy)$ transition.

The electronic spectra of the ferrocenylvinyl-bipyridine rhenium complexes **1g** and **2f** exhibit one absorption band at *ca.* 525 nm ($\varepsilon \approx 4000$), a more intense one in the 350 nm region ($\varepsilon = 10\,000$) and a shoulder around 380 nm. The shoulder can be reasonably attributed to a $d\pi(Re) \rightarrow \pi^*(bpy)$ transition. The lowest and highest energy bands are typical for donor–acceptor chromophores containing ferrocene as the donor and has been assigned by Marder and coworkers[13] to a metal-to-ligand CT transition and to a π–π^* transition, respectively.[14] Similar transitions are observed for the ruthenocene

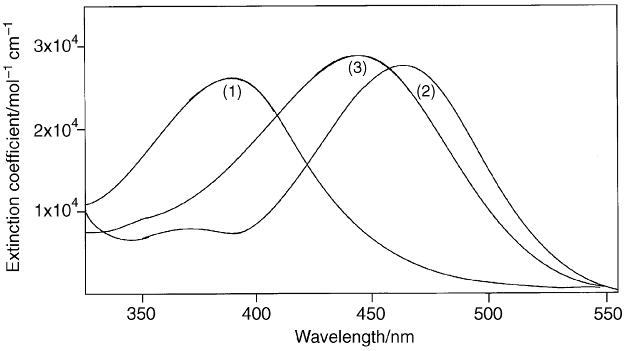


Fig. 1 UV-visible spectra of ligand **b** (curve 1) and complexes **2b** (curve 2) and **5b** (curve 3) in dichloromethane.

Table 1 Linear[a] and nonlinear optical data[b] for the ligands and complexes

Molecule	λ_{max}/ nm	μ^c/ D	$\mu\beta^c$/ 10^{-48} esu	β/ 10^{-30} esu	$\mu\beta(0)$/ 10^{-48} esu	$\beta(0)$/ 10^{-30} esu
b	388	5.1	70	14	41	8
d	329	6.5	27	4	20	3
g	469	2.6	24	9	—	—
h	345	3.2	21	7	—	—
2b	475	9.9	703	71	307	31
2d	367	11.6	128	11	81	7
1g	524	10.0	170	17	—	—
1h	460	11.3	170	15	—	—
4b	460	11.7	1780	152	831	71
5b	447	7.9	916	116	450	57
6b	442	11.7	760	65	374	32
7b	441	9.9	495	50	248	25
5d	358	10.0	190	19	130	13
6d	361	10.7	193	18	154	12
7d	360	10.4	187	18	125	12
5g	508	11.7	199	17	—	—
5h	441	11.5	207	18	—	—

[a] In CH_2Cl_2. [b] EFISH measurements were done in $CHCl_3$ at 1.34 μm. [c] The error in the measurements is estimated to be ±10%.

derivative **2h**, but the lower energy band is hypsochromically shifted by *ca.* 100 nm ($\lambda_{max} = 423$ and 335 nm), as expected from the replacement of ferrocene by the less electron-rich ruthenocene, for which the energy of the d orbitals is lowered as compared to that of the iron ones.

The low-energy spectra of the amino- and alkoxy-styryl bipyridine zinc and mercury complexes **4**–**7** consist only in an intense broad ILCT transition in the region of 360–460 nm. The bathochromic shift is consistent with the relative values of the donor strengths: $N(Bu^n)_2 > N(Me)(Oct) > N(Me)_2 \gg O(Oct)$. The energy of the CT is also sensitive to the nature of the organometallic fragment, then providing an estimate of the relative values of the acceptor strengths. With a given donor group, the ordering is: $ZnCl_2 > Zn(OAc)_2 > HgCl_2 > Hg(OAc)_2$. A positive solvatochromism, *i.e.*, a red shift with increasing polarity of the solvent can be observed for the ILCT transition. For example, for **5b** in solvents such as dichloromethane and toluene, the shift is 723 cm^{-1} [$\lambda_{max} =$ 433 nm (toluene); 447 nm (CH_2Cl_2)]. Like the rhenium complexes the zinc and mercury complexes containing the metallocenylvinyl bipyridine ligands exhibit two typical transitions at *ca.* 500 and 400 nm for the ferrocene derivatives **5g** and **6g** and at 396 and 325 nm for the ruthenocene compound **5h**.

Hyperpolarisability studies

Solution-phase hyperpolarisabilities β of several ligands and complexes were determined by the electric-field-induced second harmonic generation (EFISH) method.[15] All measurements were performed in chloroform solutions at a fundamental wavelength of 1.34 μm. The values of the zero-frequency β(0) were deduced from the experimental β values using the two-level dispersion model as proposed in ref. 15, which leads to the following expression for β:

$$\beta(-2\omega;\,\omega,\,\omega) = \frac{W^4}{[W^2 - (h\omega)^2][W^2 - (2h\omega)^2]}\,\beta(0)$$

As two low-lying excited states may contribute to the NLO responses of the metallocenyl-bipyridine ligands **g**–**h** and complexes their β(0) values are not relevant and were not calculated. Dipole moments were measured separately in chloroform solutions by a classical method based on the Guggenheim law.[16] The experimental results are collected in Table 1.

The EFISH measurements on the free ligands indicate moderate β values ranging from 4 to 14 × 10^{-30} esu, which are consistent with the weak acceptor strength of the pyridine group.[17] It is also apparent from these values that dibutylaminophenyl is by far the most effective electron-donor group and that metallocenes are comparable to octyloxyphenyl. The most important feature is the significant increase of the β values upon complexation. Interestingly, an enhancement factor ranging from 2 to 11 can be observed, depending on the nature of both the donor group and the metallic moiety. The inductive acceptor strength of the organometallic fragment contributes mainly to enhance the NLO response, whereas a conformational change of the bipyridine ligands upon chelation [(non-planar) *trans* → (planar) *cis* interconversion] may play a minor role. The ordering of the β values for the isostructural zinc and mercury complexes is the same as that found from the relative energies of the ILCT bands: the enhancement factor is larger with the stronger Lewis acids ZnX_2 (β from 17 to 152 × 10^{-30} esu) than with HgX_2 (β from 18 to 65 × 10^{-30} esu). The results in Table 1 also indicate that dichloro zinc and mercury complexes have increased β values over diacetato analogues, showing the non-negligible role of the electronegativity of the other ligands in the nonlinear response of the molecule. It is also worth noting that even though the rhenium complexes **1**–**2** show the most red-shifted ILCT bands, their β values (β from 11 to 71 × 10^{-30} esu) are smaller than those of the corresponding zinc complexes. The presence of two vectorially opposed charge-transfer axes (MLCT and ILCT) in the rhenium complexes only may contribute to the decrease in β. Finally, compound **4b** with dibutylaminophenyl as the electron donor and zinc dichloride as the electron acceptor is the most efficient [$\mu\beta(0) = 831 \times 10^{-48}$ esu; $\lambda_{max} = 460$ nm] and compares well with the optical nonlinearity of the prototypical chromophore DR1 [$\mu\beta(0) = 450 \times 10^{-48}$ esu; $\lambda_{max} = 495$ nm],[18] which should make these new types of NLO-active complexes good candidates for NLO materials, *e.g.* by inclusion into poled-polymer films.

Experimental

Materials

All reactions were conducted under argon or nitrogen atmosphere. The solvents were dried by standard methods. The complexes $Re(CO)_5Br$[19] and $Re(CO)_5(CF_3SO_3)$[20] were prepared according to the literature. For the synthesis of $Re(CO)_5Cl$[19] from $Re_2(CO)_{10}$, sulfuryl chloride was used instead of chlorine. $ZnCl_2$, $Zn(CH_3CO_2)_2 \cdot 2H_2O$, $HgCl_2$ and $Hg(CH_3CO_2)_2$ were commercial products.

Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer. Electronic absorption spectra were recorded on a Uvikon 941 + spectrophotometer. Proton (300.13 MHz) NMR spectra were recorded on a Bruker AM 300 spectrometer at 297 K using $CDCl_3$ or CD_2Cl_2 as solvents and referenced to TMS. High resolution mass spectra were obtained on a Varian MAT 311 at CRMPO, University of Rennes. Elemental analyses (%) were performed by the Service Central de Microanalyses du CNRS at Lyon, France.

EFISH measurements

Hyperpolarisability measurements were performed with a Q-switched mode-locked Nd^{3+} : YAG laser emitting at 1.34 μm using the EFISH method.[15,21] The molecules to be measured were dissolved in chloroform and the solutions were placed in a wedge-shaped cell. A high voltage electric pulse breaks the centrosymmetry of the liquid by a dipolar orientation of the molecules. Translation of this cell perpendicular to the beam direction will modulate the second harmonic signal into Maker fringes. The amplitudes and periodicity of the fringing pattern are respectively related to the macroscopic quadratic susceptibility $\Gamma(x)$ of the solution and to its coherence length, where x is the mass concentration. Calibrations are made with respect to the pure solvent: from the SHG intensity we can infer the value of the macroscopic susceptibility of the solution $\Gamma(x)$. $\Gamma(x)$ is related to the microscopic hyperpolarisabilities of the solvent γ_s and of the solute γ_c by

$$\Gamma(x) = \frac{Nf\rho}{1 + x}\left(\frac{\gamma_s}{M_s} + x\,\frac{\gamma_c}{M_c}\right)$$

where the index s stands for the solvent, index c for the dissolved molecules and $M_{s,\,c}$ is the molar mass of solvent and solute, respectively. γ_c is related to the second-order β and third-order γ hyperpolarisability through the following relation:

$$\gamma_c(-2\omega;\,\omega,\,\omega,\,0) = \gamma(-2\omega;\,\omega,\,\omega,\,0) + \frac{\mu\beta(-2\omega;\,\omega,\,\omega)}{5kT}$$

where μ is the ground-state dipole moment. Tests are performed at several concentrations (typically 10^{-2}–10^{-3} M or even less, depending on the solubility and the nonlinearity of the molecule). By neglecting the third-order contribution $\gamma(-2\omega;\,\omega,\,\omega,\,0)$,[22] the second-order polarisability β at the operating wavelength can be evaluated.

To complete these measurements the dipole moments are separately determined using a WTW dipole meter coupled with an Abbe refractometer, in order to measure the dielectric constant and the refractive index of the solutions. From these experimental data the dipole moment can be easily deduced using the Guggenheim model.[16] The relative error on the dipole moment is 5%, the total experimental error on the β values does not exceed 10%.

General procedure for the preparation of rhenium complexes

The bipyridyl ligand and $Re(CO)_5X$ were dissolved in a 1 : 1 ratio in 50 ml of toluene and refluxed for 2 h. A red solution progressively evolved during the reflux. The reaction mixture was cooled to room temperature and evaporated to dryness. The residue was dissolved in a minimum amount of dichloromethane and slowly added to a cold solution of pentane. The resulting orange-red precipitate was filtered and dried under vacuum.

[**a**]$Re(CO)_3Cl$, **1a**.—**1a** (0.58 g, 93%) was obtained from $Re(CO)_5Cl$ (0.36 g, 1 mmol) and bipyridine **a** (0.32 g, 1 mmol). IR (KBr): ν_{CO} 2013, 1904, 1870 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 459, 370 nm; ^1H NMR (CD_2Cl_2): δ 8.90 (d, 1H, $J = 5.6$ Hz), 8.85 (d, 1H, $J = 5.9$ Hz), 8.69 (d, 1H, $J = 1.5$ Hz), 8.57 (s, 1H), 7.76 (d, 1H, $J = 16.2$ Hz), 7.59 (d, 2H, $J = 9.0$ Hz), 7.41 (dd, 1H, $J = 5.9$ and 1.7 Hz), 7.29 (dd, 1H, $J = 5.0$ and 1.7 Hz), 7.13 (d, 1H, $J = 16.2$ Hz), 6.81 (d, 2H, $J = 9.0$ Hz), 3.05 (s, 6H), 2.61 (s, 3H). Anal. Calcd (found) for $C_{24}H_{21}ClN_3O_3Re$: C, 46.41 (46.53); H, 3.41 (3.51); N, 6.77 (6.68).

[**b**]$Re(CO)_3Cl$, **1b**.—**1b** (0.25 g, 71%) was obtained from $Re(CO)_5Cl$ (0.18 g, 0.5 mmol) and bipyridine **b** (0.20 g, 0.5 mmol). IR (KBr): ν_{CO} 2016, 1907, 1890 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 474, 376 nm; ^1H NMR (CD_2Cl_2): δ 8.68 (d, 1H, $J = 5.6$ Hz), 8.59 (d, 1H, $J = 5.9$ Hz), 8.05 (s, 1H), 8.04 (d, 1H, $J = 1.3$ Hz), 7.48 (d, 2H, $J = 8.5$ Hz), 7.35 (d, 1H, $J = 16.0$ Hz), 7.15 (dd, 1H, $J = 5.9$ and 1.5 Hz), 7.11 (d, 1H, $J = 5.6$ and 0.8 Hz), 6.65 (d, 1H, $J = 16.0$ Hz), 6.64 (d, 2H, $J = 8.5$ Hz), 3.32 (t, 4H, $J = 7.7$ Hz), 2.33 (s, 3H), 1.58 (m, 4H), 1.37 (m, 4H), 0.96 (t, 6H, $J = 7.3$ Hz). Anal. Calcd (found) for $C_{30}H_{33}ClN_3O_3Re \cdot 0.5CH_2Cl_2$: C, 48.99 (48.33); H, 4.58 (4.48); N, 5.62 (5.76). HRMS, Calcd (found): 705.1764 (705.1806).

[**c**]$Re(CO)_3Cl$, **1c**.—**1c** (0.32 g, 89%) was obtained from $Re(CO)_5Cl$ (0.18 g, 0.5 mmol) and bipyridine **c** (0.20 g, 0.5 mmol). IR (KBr): ν_{CO} 2017, 1911, 1890 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 468, 375 nm; ^1H NMR (CD_2Cl_2): δ 8.71 (d, 1H, $J = 5.6$ Hz), 8.63 (d, 1H, $J = 5.9$ Hz), 8.10 (s, 1H), 8.06 (s, 1H), 7.55 (d, 2H, $J = 7.5$ Hz), 7.38 (d, 1H, $J = 16.1$ Hz), 7.16 (dd, 1H, $J = 5.9$ and 1.6 Hz), 7.11 (dd, 1H, $J = 5.6$ and 1.6 Hz), 6.74 (d, 2H, $J = 7.5$ Hz), 6.70 (d, 1H, $J = 16.1$ Hz), 3.38 (t, 2H, $J = 7.6$ Hz), 3.02 (s, 3H), 2.36 (s, 3H), 1.80–1.10 (m, 12H), 0.90 (m, 3H). Anal. Calcd (found) for $C_{31}H_{35}ClN_3O_3Re \cdot 1.5 CH_2Cl_2$: C, 46.10 (45.66); H, 4.52 (4.36); N, 4.96 (5.08).

[**g**]$Re(CO)_3Cl$, **1g**.—**1g** (0.15 g, 94%) was obtained from $Re(CO)_5Cl$ (0.07 g, 0.2 mmol) and bipyridine **g** (0.10 g, 0.2 mmol). UV-vis: λ_{max} (CH_2Cl_2) 524, 390 nm; ^1H NMR ($CDCl_3$), δ 8.87 (d, 1H, $J = 5.6$ Hz), 8.82 (d, 1H, $J = 6.0$ Hz), 8.00 (s, 2H), 7.41 (dd, 1H, $J = 6.0$ and 1.5 Hz), 7.36 (d, 1H, $J = 16$ Hz), 7.29 (dd, 1H, $J = 5.6$ and 1.0 Hz), 6.65 (d, 1H, $J = 16.0$ Hz), 4.59 (m, 2H), 4.48 (m, 2H), 4.18 (s, 5H), 2.77 (t, 2H, $J = 7.7$ Hz), 1.68 (m, 2H), 1.50–1.10 (m, 12H), 0.88 (t, 3H, $J = 6.8$ Hz).

[**h**]$Re(CO)_3Cl$, **1h**.—**1h** (0.17 g, 98%) was obtained from $Re(CO)_5Cl$ (0.085 g, 0.24 mmol) and bipyridine **h** (0.10 g, 0.24 mmol). IR (KBr): ν_{CO} 2021, 1902 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 423, 333 nm; ^1H NMR ($CDCl_3$): δ 8.80 (d, 1H, $J = 5.9$ Hz), 8.75 (d, 1H, $J = 5.6$ Hz), 8.03 (s, 1H), 8.01 (d, 1H, $J = 1.6$ Hz), 7.36 (dd, 1H, $J = 5.9$ and 1.7 Hz), 7.31 (dd, 1H, $J = 5.6$ and 1.7 Hz), 7.28 (d, 1H, $J = 16.1$ Hz), 6.68 (d, 1H, $J = 16.1$ Hz), 4.96 (m, 2H), 4.73 (m, 2H), 4.55 (s, 5H), 2.53 (s, 3H).

[**a**]$Re(CO)_3Br$, **2a**.—**2a** (0.32 g, 96%) was obtained from $Re(CO)_5Br$ (0.2 g, 0.5 mmol) and bipyridine **a** (0.16 g, 0.5 mmol). IR (KBr): ν_{CO} 2010, 1910, 1890 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 456, 369 nm; ^1H NMR (CD_2Cl_2): δ 8.82 (d, 1H, $J = 5.6$ Hz), 8.76 (d, 1H, $J = 6.0$ Hz), 8.12 (d, 1H, $J = 1.5$ Hz), 8.08 (d, 1H, $J = 1.5$ Hz), 7.52 (d, 2H, $J = 8.9$ Hz), 7.46 (d, 1H, $J = 16.3$ Hz), 7.41 (dd, 1H, $J = 5.9$ and 1.7 Hz), 7.29 (dd, 1H, $J = 5.0$ and 1.7 Hz), 6.88 (d, 1H, $J = 16.3$ Hz), 6.73 (d, 2H, $J = 8.9$ Hz), 3.03 (s, 6H), 2.53 (s, 3H). Anal. Calcd (found) for $C_{24}H_{21}BrN_3O_3Re$: C, 43.31 (43.99); H, 3.18 (2.91); N, 6.31 (6.33).

[**b**]$Re(CO)_3Br$, **2b**.—**2b** (1.16 g, 96%) was obtained from $Re(CO)_5Br$ (0.63 g, 1.55 mmol) and bipyridine **b** (0.62 g, 1.55 mmol). IR (KBr): ν_{CO} 2017, 1911, 1887 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 475, 376 nm; ^1H NMR (CD_2Cl_2): δ 8.70 (d, 1H, $J = 5.6$ Hz), 8.61 (d, 1H, $J = 5.8$ Hz), 8.07 (s, 1H), 8.05 (s, 1H), 7.51 (d, 2H, $J = 8.3$ Hz), 7.35 (d, 1H, $J = 16.0$ Hz), 7.17 (dd, 1H, $J = 5.8$ and 1.5 Hz), 7.11 (dd, 1H, $J = 5.6$ and 0.8 Hz), 6.67 (d, 1H, $J = 16.0$ Hz), 3.33 (t, 4H, $J = 7.5$ Hz), 2.34 (s, 3H), 1.59 (m, 4H), 1.37 (m, 4H), 0.96 (t, 6H, $J = 7.3$ Hz). Anal. Calcd (found) for $C_{30}H_{33}BrN_3O_3Re \cdot 2CH_2Cl_2$: C, 41.95 (41.78); H, 3.95 (4.02); N, 4.77 (4.57).

[**c**]$Re(CO)_3Br$, **2c**.—**2c** (0.35 g, 92%) was obtained from $Re(CO)_5Br$ (0.2 g, 0.5 mmol) and bipyridine **c** (0.21 g, 0.5 mmol). IR (KBr): ν_{CO} 2020, 1918, 1897 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 468, 375 nm; ^1H NMR (CD_2Cl_2): δ 8.66 (d, 1H, $J = 5.7$ Hz), 8.59 (d, 1H, $J = 5.9$ Hz), 8.02 (s, 1H), 8.0 (d, 1H, $J = 1.5$ Hz), 7.46 (d, 2H, $J = 8.7$ Hz), 7.32 (d, 1H, $J = 16.3$ Hz), 7.15 (dd, 1H, $J = 6.0$ and 1.6 Hz), 7.07 (dd, 1H, $J = 6.0$ and 1.6 Hz), 6.66 (d, 1H, $J = 16.3$ Hz), 6.65 (d, 2H, $J = 8.7$ Hz), 3.31 (t, 2H, $J = 7.5$ Hz), 2.94 (s, 3H), 2.33 (s, 3H), 2.80–1.70 (m, 12H), 0.82 (m, 3H). Anal. Calcd (found) for $C_{31}H_{35}BrN_3O_3Re$: C, 46.21 (46.21); H, 4.85 (4.47); N, 5.78 (5.42).

[**d**]$Re(CO)_3Br$, **2d**.—**2d** (0.09 g, 65%) was obtained from $Re(CO)_5Br$ (0.07 g, 0.16 mmol) and bipyridine **d** (0.07 g, 0.16 mmol). IR (KBr): ν_{CO} 2018, 1926, 1886 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 367, 388 (sh) nm; ^1H NMR (CD_2Cl_2): *trans*: δ 8.73 (d, 1H, $J = 5.5$ Hz), 8.72 (d, 1H, $J = 6.0$ Hz), 8.09 (d, 1H, $J = 1.0$ Hz), 8.05 (s, 1H), 7.53 (d, 2H, $J = 8.7$ Hz), 7.41 (d, 1H, $J = 16.2$ Hz), 7.31 (dd, 1H, $J = 6.0$ and 1.5 Hz), 7.18 (d, 1H, $J = 5.5$ and 1.5 Hz), 6.89 (d, 2H, $J = 8.7$ Hz), 6.86 (d, 1H, $J = 16.2$ Hz), 3.94 (t, 2H, $J = 7.5$ Hz), 2.41 (s, 3H), 1.72 (m, 2H), 1.50–1.15 (m, 10H), 0.81 (m, 3H); *cis*: δ 8.74 (d, 1H, $J = 4.9$ Hz), 8.68 (d, 1H, $J = 5.9$ Hz), 7.91 (s, 1H), 7.56 (s, 1H), 7.25 (m, 2H), 7.17 (d, 2H, $J = 8.9$ Hz), 6.95 (d, 1H, $J = 12.0$ Hz), 6.80 (d, 2H, $J = 8.9$ Hz), 6.42 (d, 1H, $J = 12.0$ Hz), 3.89 (t, 2H, $J = 6.5$ Hz), 2.41 (s, 3H), 1.72 (m, 2H), 1.50–1.15 (m, 10H), 0.81 (m, 3H). Anal. Calcd (found) for $C_{30}H_{32}BrN_2O_4Re$: C, 47.99 (47.47); H, 4.30 (4.36); N, 3.73 (3.59).

[**e**]$Re(CO)_3Br$, **2e**.—**2e** (0.17 g, 99%) was obtained from $Re(CO)_5Br$ (0.09 g, 0.22 mmol) and bipyridine **e** (0.09 g, 0.22 mmol). IR (KBr): ν_{CO} 2021, 1919, 1897 cm^{-1}, UV-vis: λ_{max} (CH_2Cl_2) 364, 382 (sh) nm; ^1H NMR ($CDCl_3$): *trans*: δ 8.84 (d, 1H, $J = 5.7$ Hz), 8.81 (d, 1H, $J = 5.6$ Hz), 8.16 (d, 1H, $J = 1.7$ Hz), 8.06 (d, 1H, $J = 1.3$ Hz), 7.58 (d, 2H, $J = 8.6$ Hz), 7.49 (dd, 1H, $J = 5.9$ and 1.8 Hz), 7.48 (d, 1H, $J = 16.2$ Hz), 7.25 (dd, 1H, $J = 4.7$ and 1.8 Hz), 7.00 (d, 1H, $J = 16.2$ Hz), 6.95 (d, 2H, $J = 8.6$ Hz), 3.83 (s, 3H), 2.76 (t, 2H, $J = 8.6$ Hz), 1.64 (m, 2H), 1.70–1.10 (m, 12H), 0.86 (m, 3H); *cis*: δ 8.81 (d, 1H, $J = 5.6$ Hz), 8.75 (d, 1H, $J = 5.8$ Hz), 7.99 (d, 1H, $J = 1.5$ Hz), 7.59 (d, 1H, $J = 1.8$ Hz), 7.32 (m, 1H), 7.28 (m, 1H), 7.25 (d, 2H, $J = 8.9$ Hz), 7.01 (d, 1H, $J = 11.9$ Hz), 6.87 (d, 2H, $J = 8.9$ Hz), 6.50 (d, 1H, $J = 11.9$ Hz), 3.79 (s, 3H), 2.71 (t, 2H, $J = 7.3$ Hz), 1.64 (m, 2H), 1.70–1.10 (m, 12H), 0.86 (m, 3H). Anal. Cald (found) for $C_{31}H_{34}BrN_2O_4Re$: C, 48.60 (47.83); H, 4.44 (4.76); N, 3.66 (3.46).

[**f**]$Re(CO)_3Br$, **2f**.—**2f** (0.55 g, 85%) was obtained from $Re(CO)_5Br$ (0.36 g, 0.88 mmol) and bipyridine **f** (0.34 g, 0.88 mmol). IR (KBr): ν_{CO} 2015, 1900, 1860 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 525, 380 (sh), 357 nm; ^1H NMR ($CDCl_3$): δ 8.83 (d, 1H, $J = 5.7$ Hz), 8.79 (d, 1H, $J = 5.5$ Hz), 8.07 (d, 1H, $J = 1.5$

Hz), 8.05 (d, 1H, $J = 1.5$ Hz), 7.36 (d, 1H, $J = 16.0$ Hz), 7.35 (m, 2H), 6.64 (d, 1H, $J = 16.0$ Hz), 4.71 (m, 2H), 4.57 (m, 2H), 4.27 (s, 5H) 2.54 (s, 3H). Anal. Calcd (found) for $C_{26}H_{20}BrN_2O_3FeRe$: C, 42.74 (42.22); H, 2.74 (2.81); N, 3.84 (3.73).

[**h**]Re(CO)$_3$Br, **2h**.—**2h** (0.15 g, 82%) was obtained from Re(CO)$_5$Br (0.10 g, 0.24 mmol) and bipyridine **h** (0.10 g, 0.24 mmol). IR (KBr): ν_{CO} 2017, 1917, 1890 cm^{-1}; UV-vis: λ_{max} (CH_2Cl_2) 423, 335 nm; ^1H NMR ($CDCl_3$): *trans*: δ 8.82 (d, 1H, $J = 6.0$ Hz), 8.78 (d, 1H, $J = 5.7$ Hz), 8.04 (s, 1H), 8.02 (d, 1H, $J = 1.6$ Hz), 7.38 (dd, 1H, $J = 6.0$ and 1.6 Hz), 7.32 (dd, 1H, $J = 6.0$ and 0.8 Hz), 7.28 (d, 1H, $J = 15.8$ Hz), 6.65 (d, 1H, $J = 15.8$ Hz), 4.96 (m, 2H), 4.73 (m, 2H), 4.56 (s, 5H), 2.56 (s, 3H); *cis*: δ 8.81 (m, 2H), 8.18 (s, 1H), 7.87 (s, 1H), 7.56 (dd, 2H, $J = 6.0$ and 1.8 Hz), 6.61 (d, 1H, $J = 11.6$ Hz), 6.22 (d, 1H, $J = 11.6$ Hz), 4.68 (m, 2H), 4.65 (m, 2H), 4.55 (s, 5H), 2.53 (s, 3H).

[**b**]Re(CO)$_3$(OSO_2CF_3), **3b**.—**3b** (0.27 g, 66%) was obtained from Re(CO)$_5$(OSO_2CF_3) (0.25 g, 0.5 mmol) and bipyridine **b** (0.16 g, 0.5 mmol). IR (KBr): ν_{CO} 2028, 1920, 1899 cm^{-1}, UV-vis: λ_{max} (CH_2Cl_2) 488 nm; ^1H NMR (CD_2Cl_2): δ 8.79 (d, 1H, $J = 5.6$ Hz), 8.72 (d, 1H, $J = 5.9$ Hz), 8.03 (s, 1H), 8.02 (s, 1H), 7.44 (d, 2H, $J = 8.9$ Hz), 7.38 (d, 1H, $J = 16.2$ Hz), 7.38 (dd, 1H, $J = 5.9$ and 1.7 Hz), 7.28 (dd, 1H, $J = 5.6$ and 0.8 Hz), 6.72 (d, 1H, $J = 16.2$ Hz), 6.66 (d, 2H, $J = 8.9$ Hz), 3.32 (t, 4H, $J = 7.7$ Hz), 2.47 (s, 3H), 1.58 (m, 4H), 1.36 (m, 4H), 0.96 (t, 6H, $J = 6.6$ Hz). Anal. Calcd (found) for $C_{31}H_{33}F_3N_3O_6SRe$: C, 47.32 (47.13); H, 4.20 (4.23); N, 5.30 (5.22).

General procedure for the preparation of zinc and mercury complexes

The bipyridyl ligand (0.5 mmol) and one equivalent of MX_2 (M = Zn, Hg; X = Cl, OAc) were dissolved in 30 ml of dichloromethane. The reaction mixture was stirred at room temperature for 2–6 h and then evaporated to dryness. The orange-red powder was washed three times with diethyl ether (2 × 3 ml) and then dried under vacuum. The resulting solid was recrystallized from dichloromethane–pentane or dichloromethane–diethyl ether.

[**a**]ZnCl$_2$, **4a**.—Yield: 74%. UV-vis: λ_{max} (CH_2Cl_2) 444 nm; ^1H NMR (CD_2Cl_2): δ 8.56 (d, 1H, $J = 5.4$ Hz), 8.53 (d, 1H, $J = 4.5$ Hz), 8.25 (s, 1H), 8.15 (s, 1H), 7.53 (m, 1H), 7.48 (d, 2H, $J = 8.9$ Hz), 7.46 (d, 1H, $J = 16.2$ Hz), 7.41 (m, 1H), 6.92 (d, 1H, $J = 16.2$ Hz), 6.71 (d, 2H, $J = 8.9$ Hz), 3.00 (s, 6H), 2.54 (s, 3H). Anal. Calcd (found) for $C_{21}H_{21}N_3Cl_2Zn$: C, 55.84 (55.15); H, 4.69 (4.65); N, 9.30 (9.27).

[**b**]ZnCl$_2$, **4b**.—Yield: 73%. UV-vis: λ_{max} (CH_2Cl_2) 460 nm; ^1H NMR (CD_2Cl_2): δ 8.65 (d, 1H, $J = 6.7$ Hz), 8.63 (d, 1H, $J = 5.3$ Hz), 8.57 (s, 1H), 8.56 (s, 1H), 7.76 (d, 1H, $J = 16.0$ Hz), 7.76 (m, 1H), 7.69 (m, 1H), 7.54 (d, 2H, $J = 8.9$ Hz), 7.07 (d, 1H, $J = 16.0$ Hz), 6.77 (d, 2H, $J = 8.9$ Hz), 3.43 (t, 4H, $J = 7.5$ Hz), 2.63 (s, 3H), 1.64 (m, 4H), 1.41 (m, 4H), 0.98 (t, 6H, $J = 7.3$ Hz). Anal. Calcd (found) for $C_{27}H_{33}N_3Cl_2Zn \cdot H_2O$: C, 58.55 (59.16); H, 6.37 (6.30); N, 7.59 (7.55).

[**c**]ZnCl$_2$, **4c**.—Yield: 76%. UV-vis: λ_{max} (CH_2Cl_2) 455 nm; ^1H NMR (CD_2Cl_2): δ 8.57 (d, 1H, $J = 5.3$ Hz), 8.56 (s, 1H), 8.51 (d, 1H, $J = 5.8$ Hz), 8.50 (s, 1H), 7.72 (d, 1H, $J = 16.2$ Hz), 7.72 (dd, 1H, $J = 5.7$ and 1.4 Hz), 7.60 (dd, 1H, $J = 5.3$ and 1.0 Hz), 7.50 (d, 2H, $J = 8.9$ Hz), 7.00 (d, 1H, $J = 16.2$ Hz), 6.74 (d, 2H, $J = 8.9$ Hz), 3.43 (t, 4H, $J = 7.5$ Hz), 3.02 (s, 3H), 2.56 (s, 3H), 1.64 (m, 2H), 1.40–1.20 (m, 10H), 0.86 (t, 3H, $J = 6.9$ Hz).

[**d**]ZnCL$_2$, **4d**.—Yield: 78%. UV-vis: λ_{max} (CH_2Cl_2 367 nm; ^1H NMR ($CDCl_3$): *trans*: δ 8.52 (d, 1H, $J = 5.5$ Hz), 8.51 (d, 1H, $J = 5.5$ Hz), 8.20 (d, 1H, $J = 1.0$ Hz), 8.15 (s, 1H), 7.56 (dd, 1H, $J = 4.5$ and 1.5 Hz), 7.55 (d, 1H, $J = 16.0$ Hz), 7.47 (dd, 1H, $J = 5.4$ and 1.5 Hz), 7.19 (d, 2H, $J = 8.7$ Hz), 6.96 (d, 1H, $J = 16.0$ Hz), 6.93 (d, 2H $J = 8.7$ Hz), 3.99 (t, 2H, $J = 6.6$ Hz), 2.55 (s, 3H), 1.73 (m, 2H), 1.50–1.10 (m, 10H), 0.85 (t, 3H, $J = 7.0$ Hz); *cis*: δ 8.54 (d, 1H, $J = 3.7$ Hz), 8.52 (d, 1H, $J = 6.2$ Hz), 8.01 (s, 1H), 7.67 (s, 1H), 7.56 (d, 2H, $J = 8.9$ Hz), 7.50 (dd, 1H, $J = 5.6$ and 1.4 Hz), 7.44 (dd, 1H, $J = 6.1$ and 1.4 Hz), 7.01 (d, 1H, $J = 12.0$ Hz), 6.82 (d, 2H, $J = 8.8$ Hz), 6.51 (d, 1H, $J = 12.0$ Hz), 3.92 (t, 2H, $J = 6.6$ Hz), 2.49 (s, 3H), 1.73 (m, 2H), 1.50–1.10 (m, 10H), 0.85 (m, 3H).

[**b**]Zn(OAc)$_2$, **5b**.—Yield: 92%. UV-vis: λ_{max} (CH_2Cl_2) 447 nm; ^1H NMR (CD_2Cl_2): δ 8.69 (d, 1H, $J = 5.2$ Hz), 8.63 (d, 1H, $J = 5.2$ Hz), 8.08 (s, 1H), 8.04 (s, 1H), 7.48 (d, 1H, $J = 4.9$ Hz), 7.43 (d, 2H, $J = 8.9$ Hz), 7.42 (d, 1H, $J = 16.0$ Hz), 7.36 (d, 1H, $J = 5.2$ Hz), 6.77 (d, 1H, $J = 16.0$ Hz), 6.59 (d, 2H, $J = 8.9$ Hz), 3.25 (t, 4H, $J = 7.7$ Hz), 2.45 (s, 3H), 1.88 (s, 6H), 1.52 (m, 4H), 1.30 (m, 4H), 0.90 (t, 6H, $J = 7.3$ Hz). Anal. Calcd (found) for $C_{31}H_{39}N_3O_4Zn \cdot CH_2Cl_2$: C, 63.86 (63.52); H, 6.74 (6.85); N, 7.21 (7.07).

[**d**]Zn(OAc)$_2$, **5d**.—Yield: 75%. UV-vis: λ_{max} (CH_2Cl_2) 358 nm; ^1H NMR (CD_2Cl_2): δ 8.71 (m, 2H), 8.15 (s, 1H), 8.05 (s, 1H), 7.53 (d, 2H, $J = 8.0$ Hz), 7.48 (m, 1H), 7.47 (d, 1H, $J = 16.4$ Hz), 7.38 (m, 1H), 6.97 (d, 1H, $J = 16.4$ Hz), 6.92 (d, 2H, $J = 8.0$ Hz), 3.98 (t, 2H, $J = 6.4$ Hz), 2.52 (s, 3H), 1.93 (s, 6H), 1.77 (m, 2H), 1.50–1.20 (m, 10H), 0.87 (t, 3H, $J = 5.5$ Hz). Anal. Calcd (found) for $C_{31}H_{38}N_2O_5Zn \cdot H_2O$: C, 61.85 (61.54); H, 6.70 (6.54).

[**g**]Zn(OAc)$_2$, **5g**.—Yield: 81%. UV-vis: λ_{max} (CH_2Cl_2) 508, 410 nm; ^1H NMR ($CDCl_3$): δ 8.86 (d, 1H, $J = 5.4$ Hz), 8.83 (d, 1H, $J = 5.7$ Hz), 8.00 (s, 1H), 7.98 (s, 1H), 7.57 (dd, 1H, $J = 5.7$ and 1.3 Hz), 7.42 (dd, 1H, $J = 5.4$ and 1.3 Hz), 7.35 (d, 1H, $J = 16.0$ Hz), 6.70 (d, 1H, $J = 16.0$ Hz), 4.57 (m, 2H), 4.46 (m, 2H), 4.18 (s, 5H), 2.80 (t, 2H, $J = 7.5$ Hz), 1.74 (s, 6H), 1.71 (m, 2H), 1.40–1.20 (m, 12H), 0.87 (t, 3H, $J = 6.3$ Hz). Anal. Calcd (found) for $C_{35}H_{42}N_2O_4FeZn \cdot H_2O$: C, 60.60 (61.20); H, 6.39 (6.20); N, 4.04 (4.13).

[**h**]Zn(OAc)$_2$, **5h**.—Yield: 43%. UV-vis: λ_{max} (CH_2Cl_2) 396, 325 nm; ^1H NMR ($CDCl_3$): δ 8.70 (d, 1H, $J = 5.3$ Hz), 8.67 (d, 1H, $J = 5.9$ Hz), 8.03 (m, 2H), 7.45 (m, 1H), 7.39 (m, 1H), 7.26 (d, 1H, $J = 16.1$ Hz), 6.65 (d, 1H, $J = 16.1$ Hz), 4.95 (m, 2H), 4.71 (m, 2H), 4.55 (s, 5H), 2.52 (s, 3H), 1.92 (s, 6H). Anal. Calcd (found) for $C_{27}H_{26}N_2O_4RuZn \cdot 0.5CH_2Cl_2$: C, 50.70 (51.22); H, 4.20 (4.60); N, 4.30 (4.24).

[**a**]HgCl$_2$, **6a**.—Yield: 66%. UV-vis: λ_{max} (CH_2Cl_2) 424 nm; ^1H NMR (CD_2Cl_2): δ 8.53 (d, 1H, $J = 5.4$ Hz), 8.50 (d, 1H, $J = 5.6$ Hz), 8.16 (s, 1H), 8.09 (s, 1H), 7.65 (dd, 1H, $J = 5.6$ and 1.6 Hz), 7.49 (dd, 1H, $J = 5.4$ and 0.8 Hz), 7.49 (d, 2H, $J = 8.9$ Hz), 7.47 (d, 1H, $J = 16.3$ Hz), 6.92 (d, 1H, $J = 16.3$ Hz), 6.71 (d, 2H, $J = 8.9$ Hz), 3.01 (s, 6H), 2.56 (s, 3H). Anal. Calcd (found) for $C_{21}H_{21}N_3Cl_2Hg$: C, 39.33 (39.93); H, 3.45 (3.39); N, 6.25 (6.66).

[**b**]HgCl$_2$, **6b**.—Yield: 87%. UV-vis: λ_{max} (CH_2Cl_2) 442 nm; ^1H NMR (CD_2Cl_2): δ 8.43 (d, 1H, $J = 5.3$ Hz), 8.38 (d, 1H, $J = 5.5$ Hz), 8.07 (s, 1H), 8.04 (s, 1H), 7.56 (dd, 1H, $J = 5.5$ and 1.5 Hz), 7.47 (dd, 1H, $J = 5.6$ and 1.4 Hz), 7.39 (d, 2H, $J = 8.9$ Hz), 7.37 (d, 1H, $J = 16.1$ Hz), 6.77 (d, 1H, $J = 16.1$ Hz), 6.59 (d, 2H, $J = 8.9$ Hz), 3.26 (t, 4H, $J = 7.7$ Hz), 2.47 (s, 3H), 1.51 (m, 4H), (m, 4H), 1.30 (m, 4H), 0.90 (t, 6H, $J = 7.4$ Hz). Anal. Calcd (found) for $C_{27}H_{33}N_3Cl_2Hg \cdot H_2O$: C, 46.38 (47.05); H, 6.11 (6.10).

[**c**]HgCl$_2$, **6c**.—Yield: 71%. UV-vis: λ_{max} (CH_2Cl_2) 436 nm; ^1H NMR (CD_2Cl_2): δ 8.50 (d, 1H, $J = 5.3$ Hz), 8.45 (d, 1H, $J = 5.5$ Hz), 8.13 (d, 1H, $J = 1.2$ Hz), 8.04 (s, 1H), 7.57 (dd, 1H, $J = 5.5$ and 1.5 Hz), 7.47 (d, 2H, $J = 8.9$ Hz), 7.46 (d, 1H, $J = 16.2$ Hz), 7.44 (dd, 1H, $J = 5.3$ and 1.4 Hz), 6.86 (d, 1H, $J = 16.2$ Hz), 6.68 (d, 2H, $J = 8.9$ Hz), 3.35 (t, 4H, $J = 7.5$ Hz), 2.98 (s, 3H), 2.53 (s, 3H), 1.60 (m, 2H), 1.35–1.15 (m, 10H), 0.86 (t, 3H, $J = 7.0$ Hz). Anal. Calcd (found) for $C_{28}H_{35}N_3Cl_2Hg \cdot H_2O$: C, 47.80 (47.25); H, 5.30 (5.16); N, 5.98 (5.71).

[**d**]HgCl$_2$, **6d**.—Yield: 83%. UV-vis: λ_{max} (CH_2Cl_2) 361 nm; ^1H NMR ($CDCl_3$): *trans*: δ 8.53 (d, 1H, $J = 5.6$ Hz), 8.51 (d, 1H, $J = 5.2$ Hz), 8.18 (s, 1H), 8.10 (s, 1H), 7.63 (m, 1H), 7.55 (d, 2H, $J = 8.7$ Hz), 7.49 (d, 1H, $J = 16.3$ Hz), 7.45 (m, 1H), 6.97 (d, 1H, $J = 16.3$ Hz), 6.92 (d, 2H, $J = 8.7$ Hz), 3.98 (t, 2H, $J = 6.5$ Hz), 2.53 (s, 3H), 1.78 (m, 2H), 1.60–1.30 (m, 10H), 0.86

(t, 3H, $J = 7.0$ Hz), *cis*: δ 8.49 (d, 1H, $J = 4.4$ Hz), 8.48 (d, 1H, $J = 5.4$ Hz), 7.99 (s, 1H), 7.59 (s, 1H), 7.45 (d, 2H, $J = 8.5$ Hz), 7.40 (m, 2H), 6.96 (d, 1H, $J = 12.0$ Hz), 6.82 (d, 2H, $J = 8.5$ Hz), 6.50 (d, 1H, $J = 12.0$ Hz), 3.91 (t, 2H, $J = 6.7$ Hz), 2.44 (s, 3H), 1.78 (m, 2H), 1.60–1.30 (m, 10H), 0.86 (t, 3H, $J = 7.0$ Hz). Anal. Calcd (found) for $C_{27}H_{32}N_2Cl_2OHg \cdot H_2O$: C, 46.99 (46.55); H, 4.97 (4.89); N, 4.06 (3.91).

[**g**]$HgCl_2$, **6g**.—Yield: 79%. UV-vis: λ_{max} (CH_2Cl_2) 512, 390 nm; ^1H NMR ($CDCl_3$): δ 8.58 (d, 1H, $J = 5.3$ Hz), 8.54 (d, 1H, $J = 5.4$ Hz), 8.02 (s, 1H), 8.01 (s, 1H), 7.59 (d, 1H, $J = 5.4$ Hz), 7.44 (d, 1H, $J = 5.3$ Hz), 7.35 (d, 1H, $J = 16.1$ Hz), 6.69 (d, 1H, $J = 16.1$ Hz), 4.57 (m, 2H), 4.46 (m, 2H), 4.18 (s, 5H), 2.79 (t, 2H, $J = 7.6$ Hz), 1.72 (m, 2H), 1.40–1.20 (m, 12H), 0.90 (t, 3H, $J = 6.3$ Hz). Anal. Calcd (found) for $C_{31}H_{36}N_2Cl_2FeHg \cdot H_2O$: C, 47.61 (47.88); H, 4.90 (4.72).

[**a**]$Hg(OAc)_2$, **7a**.—Yield: 69%. UV-vis: λ_{max} (CH_2Cl_2) 425 nm; ^1H NMR (CD_2Cl_2): δ 8.63 (d, 1H, $J = 5.2$ Hz), 8.61 (d, 1H, $J = 5.5$ Hz), 8.20 (s, 1H), 8.12 (s, 1H), 7.59 (dd, 1H, $J = 5.5$ and 1.5 Hz), 7.48 (d, 2H, $J = 8.9$ Hz), 7.45 (d, 1H, $J = 16.0$ Hz), 7.44 (dd, 1H, $J = 5.5$ and 0.8 Hz), 6.90 (d, 1H, $J = 16.0$ Hz), 6.70 (d, 2H, $J = 8.9$ Hz), 3.00 (s, 6H), 2.53 (s, 3H), 1.94 (s, 6H). Anal. Calcd (found) for $C_{25}H_{27}N_3O_4Hg$: C, 47.35 (47.14); H, 4.29 (4.37); N, 6.63 (6.38).

[**b**]$Hg(OAc)_2$, **7b**.—Yield: 74%. UV-vis: λ_{max} (CH_2Cl_2) 441 nm; ^1H NMR (CD_2Cl_2): δ 8.60 (d, 1H, $J = 5.5$ Hz), 8.55 (d, 1H, $J = 5.3$ Hz), 8.10 (s, 1H), 8.05 (s, 1H), 7.52 (dd, 1H, $J = 5.5$ and 1.4 Hz), 7.39 (d, 2H, $J = 9.0$ Hz), 7.38 (d, 1H, $J = 16.2$ Hz), 7.38 (m, 1H), 6.79 (d, 1H, $J = 16.2$ Hz), 6.59 (d, 2H, $J = 9.0$ Hz), 3.26 (t, 4H, $J = 8.0$ Hz), 2.47 (s, 3H), 1.90 (s, 6H) 1.52 (m, 4H), 1.30 (m, 4H), 0.90 (t, 3H, $J = 7.3$ Hz). Anal. Calcd (found) for $C_{31}H_{39}N_3O_4Hg \cdot CH_2Cl_2$: C, 47.84 (48.64); H, 5.15 (5.33); N, 5.23 (5.45).

[**c**]$Hg(OAc)_2$, **7c**.—Yield: 50%. UV-vis: λ_{max} (CH_2Cl_2) 434 nm; ^1H NMR (CD_2Cl_2): δ 8.64 (d, 1H, $J = 5.2$ Hz), 8.60 (d, 1H, $J = 5.4$ Hz), 8.16 (s, 1H), 8.10 (s, 1H), 7.57 (dd, 1H, $J = 5.5$ and 1.5 Hz), 7.46 (d, 2H, $J = 8.9$ Hz), 7.45 (m, 1H), 7.44 (d, 1H, $J = 16.2$ Hz), 6.86 (d, 1H, $J = 16.2$ Hz), 6.67 (d, 2H, $J = 8.9$ Hz), 3.34 (t, 4H, $J = 7.5$ Hz), 2.97 (s, 3H), 2.52 (s, 3H), 1.94 (s, 6H), 1.60 (m, 2H), 1.35–1.20 (m, 10H), 0.86 (t, 3H, $J = 6.8$ Hz). Anal. Calcd (found) for $C_{32}H_{41}N_3O_4Hg \cdot H_2O$: C, 51.23 (51.61); H, 5.78 (5.64); N, 5.60 (5.46).

[**d**]$Hg(OAc)_2$, **7d**.—Yield: 75%. UV-vis: λ_{max} (CH_2Cl_2) 360 nm; ^1H NMR ($CDCl_3$): *trans*: δ 8.78 (d, 1H, $J = 5.3$ Hz), 8.76 (d, 1H, $J = 5.0$ Hz), 8.18 (s, 1H), 8.10 (s, 1H), 7.63 (m, 1H), 7.52 (d, 2H, $J = 8.8$ Hz), 7.46 (m, 1H), 7.43 (d, 1H, $J = 16.2$ Hz), 6.97 (d, 1H, $J = 16.2$ Hz), 6.93 (d, 2H, $J = 8.8$ Hz), 4.00 (t, 2H, $J = 6.7$ Hz), 2.56 (s, 3H), 2.06 (s, 6H), 1.80 (m, 2H), 1.50–1.10 (m, 10H), 0.88 (t, 3H, $J = 6.6$ Hz); *cis*: δ 8.72 (d, 1H, $J = 5.5$ Hz), 8.70 (d, 1H, $J = 5.6$ Hz), 7.98 (s, 1H), 7.59 (s, 1H), 7.40 (m, 2H), 7.17 (d, 2H, $J = 8.7$ Hz), 6.96 (d, 1H, $J = 12.0$ Hz), 6.83 (d, 2H, $J = 8.7$ Hz), 6.48 (d, 1H, $J = 12.0$ Hz), 3.94 (t, 2H, $J = 6.6$ Hz), 2.45 (s, 3H), 2.06 (s, 6H), 1.80 (m, 2H), 1.50–1.10 (m, 10H), 0.88 (t, 3H, $J = 6.6$ Hz). Anal. Calcd (found) for $C_{31}H_{38}N_2O_5Hg \cdot 0.5C_5H_{12}$: C, 53.27 (53.31); H, 5.83 (5.67); N, 3.71 (3.82).

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References

1 H. S. Nalwa, *Appl. Organomet. Chem.*, 1991, **5**, 349.
2 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21.
3 L.-T. Cheng, W. Tam and D. F. Eaton, *Organometallics*, 1990, **9**, 2856; D. W. Bruce and A. Thornton, *Mol. Cryst. Liq. Cryst.*, 1993, **231**, 253; D. R. Kanis, P. G. Lacroix, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10089.
4 J. C. Calabrese and W. Tam, *Chem. Phys. Lett.*, 1987, **133**, 244; S. D. Cummings, L.-T. Cheng and R. Eisenberg, *Chem. Mater.*, 1997, **9**, 440.
5 S. Di Bella, I. Fragala, I. Ledoux, M. A. Diaz-Garcia, P. G. Lacroix and T. J. Marks, *Chem. Mater.*, 1994, **6**, 881; P. G. Lacroix, S. Di Bella and I. Ledoux, *Chem. Mater.*, 1996, **8**, 541.
6 A. Sastre, T. Torres, M. A. Diaz-Garcia, F. Agullo-Lopez, C. Dhenaut, S. Brasselet, I. Ledoux and J. Zyss, *J. Am. Chem. Soc.*, 1996, **118**, 2746.
7 S. M. LeCours, H.-W. Guan, S. G. DiMagno, C. H. Wang and M. J. Therien, *J. Am. Chem. Soc.*, 1996, **118**, 1497.
8 J. Zyss, C. Dhenaut, T. Chau Van and I. Ledoux, *Chem. Phys. Lett.*, 1993, **206**, 409.
9 C. Dhenaut, I. Ledoux, I. D. W. Samuel, J. Zyss, M. Bourgault and H. Le Bozec, *Nature* (*London*), 1995, **374**, 339.
10 M. Bourgault, T. Renouard, B. Lognoné, C. Mountassir and H. Le Bozec, *Can J. Chem.*, 1997, **75**, 318.
11 M. Bourgault, C. Mountassir, H. Le Bozec, I. Ledoux, G. Pucetti and J. Zyss, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1623.
12 J. C. Luong, L. Nadjo and M. S. Wrighton, *J. Am. Chem. Soc.*, 1974, **96**, 998; P. J. Giordano and M. S. Wrighton, *J. Am. Chem. Soc.*, 1979, **101**, 2888.
13 J. C. Calabrese, L.-T. Cheng, J. C. Green, S. R. Marder and W. Tam, *J. Am. Chem. Soc.*, 1991, **113**, 7227; V. Alain, A. Fort, M. Barzoukas, C.-T. Chen, M. Blanchard-Desce, S. R. Marder and J. W. Perry, *Inorg. Chim. Acta.*, 1996, **242**, 43.
14 By contrast, ZINDO calculations have suggested that the lower energy band is a ligand field transition and that the higher lying transition is MLCT: D. R. Kanis, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 10338.
15 J. L. Oudar, *J. Chem. Phys.*, 1977, **67**, 446.
16 E. A. Guggenheim, *Trans. Faraday Soc.*, 1949, **45**, 203.
17 M. Barzoukas, M. Blanchard-Desce, D. Josse, J.-M. Lehn and J. Zyss, in *Materials for Nonlinear and Electro-Optics*, ed. M. H. Lyons, Institute of Physics Conf. Ser., IOP Publishing, Bristol, U.K., 1989, vol. 103, 239.
18 K. D. Singer, J. E. Sohn, L. A. King, H. M. Gordon, H. E. Katz and C. W. Dirk, *J. Opt. Soc. Am. B*, 1989, **6**, 1339.
19 S. P. Schmidt, W. C. Trogler and F. Basolo, in *Inorganic Syntheses*, ed. S. Kirschner, Wiley-Interscience, New York, 1985, vol. 23, p. 41.
20 R. J. Shaver, D. P. Rillema and C. Woods, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 179.
21 I. Ledoux and J. Zyss, *Chem. Phys.*, 1982, **73**, 203.
22 M. Barzoukas , P. Fremaux, D. Josse, F. Kajzar and J. Zyss, *Mater. Res. Symp. Proc.*, 1988, **109**, 171.

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