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Terpyridine Zn(II), Ru(III), and Ir(III) Complexes: The Relevant Role of the Nature of the Metal Ion and of the Ancillary Ligands on the Second-Order Nonlinear Response of Terpyridines Carrying Electron Donor or Electron Acceptor Groups

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Coordination of 4′-(C_6H_4-*p*-X)-2,2′:6′,2″-terpyridines [X = NO_2, NBu_2, (*E*)-CH═CH–C_6H_4-*p*-NBu_2, (*E*,*E*)-(CH═CH)$_2$–C_6H_4-*p*-NMe_2] to Zn(II), Ru(III), and Ir(III) metal centers induces a significant enhancement of the absolute value of the second-order nonlinear optical (NLO) response of the terpyridine, measured by means of both electric field induced second harmonic generation and solvatochromic methods. By varying the nature of the metal center, the enhanced second-order NLO response shifts from positive to negative. Such a shift is controlled by electronic charge-transfer transitions, such as metal-to-ligand or ligand-to-metal transitions, in addition to the intraligand charge transfer. The enhancement generated by coordination is also controlled by the chelation effect and by fine-tuning of the ancillary ligands.

Introduction

In recent years organometallic and coordination compounds have attracted increasing attention as new chromophores for second-order nonlinear optical (NLO) responses. In particular, they may offer additional flexibility by introducing new electronic charge-transfer transitions between the metal and the ligand, and a response, tunable by virtue of the nature, oxidation state, and coordination sphere of the metal center.[1,2] In particular, the effects of coordination of various push−pull ligands, such as substituted pyridines,[3a−e,g] bipyridines,[4] and phenanthrolines,[3b,f] have been extensively studied for a series of metal complexes. For instance when these push−pull ligands bear a NR_2 electron donor substituent, a significant increase was usually reported upon coordination of β_λ, which is the projection of the vectorial component of the quadratic hyperpolarizability tensor along the dipole moment direction,

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measured by the solution-phase dc electric field induced second harmonic (EFISH) generation method, working at an incident wavelength λ.[5] As suggested by solvatochromic investigations,[3d,e,6] this enhancement is mainly due to a bathochromic shift of the intraligand charge-transfer (ILCT) transition, the major origin of the second-order NLO response of these kinds of push−pull ligands. This shift is often strongly dependent upon the Lewis acceptor properties of the metal center.[3e,f] An important role is also played by chelation, which imposes a rather planar arrangement of π-delocalized chelating ligands, such as bipyridines. Such planar arrangements lead to a strong enhancement of the second-order NLO response, by stabilization of the π^* levels, involved in the ILCT transition,[3f,4b] through a higher conjugation of the π system. The second-order NLO response of complexes carrying stilbazoles or phenanthrolines with electron acceptor substituents is, on the contrary, mainly controlled by metal-to-ligand charge-transfer (MLCT) processes.[3b,e] The aim of this work is to show how the electronic nature of the metal ion can influence by coordination, the value, and sign of the second-order NLO response of a chelating nitrogen donor push−pull ligand, as, for example, a terpyridine substituted with an electron donor or electron acceptor group, acting either through a perturbation toward lower energy of the ILCT transition or by introducing new metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge-transfer transitions, which can control the overall second-order NLO response.

Metal complexes of terpyridines have been extensively studied for their photochemical and photophysical properties,[7] but they have never been investigated from a NLO point of view before our preliminary work[8a] and a few other examples concerning second-order[8b] or third-order[8c] NLO properties. Our work on the effect of coordination of 4′-(C_6H_4-*p*-NBu_2)-2,2′:6′,2″-terpyridine (T_0) (see Figure 1) to Zn(II), Ru(III), and Ir(III) ions indicated a relevant role of the nature of the metal ion and of the ancillary ligands on the value and sign of the quadratic hyperpolarizability of T_0. The value of the quadratic hyperpolarizability of T_0,[8a] upon coordination to a "ZnY_2" center (Y = Cl, CF_3CO_2), increases and remains positive as occurs in other Zn(II) complexes with chelated π-delocalized nitrogen donor ligands.[3f,4] On the other hand, upon coordination of T_0 to "$IrCl_3$" or "$Ru(CF_3CO_2)_3$" centers, $\beta_{1.34}$ not only increases significantly in absolute value, but it becomes negative. A careful solvatochromic investigation has shown that only in Zn(II) complexes is the increase due to the usual red-shift[3f] of the ILCT transition of T_0. With coordination to an Ir(III) center, the second-order NLO response is dominated by the significant negative contribution of a band at lower energy, tentatively assigned to a metal-to-ligand charge-transfer (MLCT) transition.[7f,g] On the other hand, by coordination to a Ru(III) center, the negative sign of $\beta_{1.34}$ originates from the high contribution of a relatively weak absorption band at very low energy, tentatively assigned to a ligand-to-metal charge-transfer (LMCT) transition.[9,10]

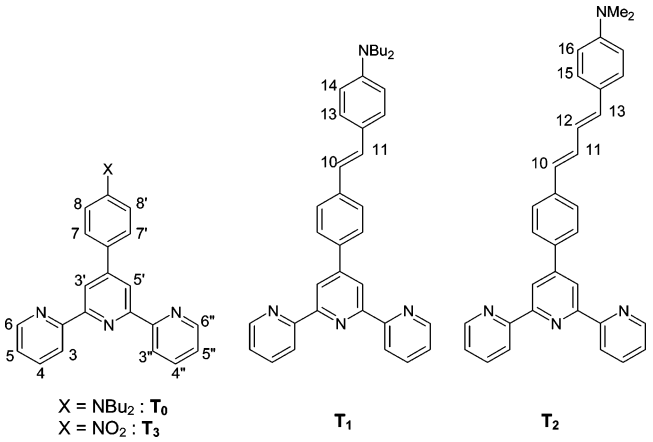

Figure 1. Terpyridinic ligands under investigation.

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To confirm these preliminary observations, we have extended our investigation to include two new terpyridines, T_1 and T_2 (see Figure 1), which should show a higher second-order NLO response with respect to T_0, due to the greater π-delocalization of the push−pull system, and to terpyridine T_3 (see Figure 1), which bears a strong electron acceptor group such as NO_2. In this latter case, our major objective was to confirm not only the correct assignment of the ILCT transitions but in particular the assignment as a MLCT to the band dominating with its negative contribution the sign of the second-order NLO response of $[IrCl_3T_0]$ and as a LMCT, the band at very low energy which generates the negative and dominating contribution to the second-order NLO response of $[Ru(CF_3CO_2)_3T_0]$. In the following we report the results of this investigation.

Experimental Section

General Comments. $ZnCl_2 \cdot xH_2O$, $Zn(CF_3CO_2)_2 \cdot 2H_2O$, $Ag(CF_3CO_2)$, 4-ethylbenzoic acid, 2-acetylpyridine, 4-(dibutylamino)-benzaldehyde, 4-(dimethylamino)cinnamaldehyde, 4-nitrobenzaldehyde, *p*-tolualdehyde, and triphenylphosphine were purchased from Sigma-Aldrich and $RuCl_3 \cdot xH_2O$ and $IrCl_3 \cdot xH_2O$ were purchased from Engelhard. All reagents and solvents were used without further purification. The terpyridine ligands were prepared under nitrogen atmosphere using flasks that were previously dried over flame and cooled under nitrogen flow. Ligands[11] and complexes, N-[2-(pyrid-2′-yl)-2-oxoethyl]pyridinium iodide[11a] and 4-EtC_6H_4-CO_2Ag,[12] were prepared using modified literature methods as described below. Products were characterized by ^{1}H NMR (with the exception of some paramagnetic Ru(III) complexes) (Bruker AC-200 and Bruker DRX-300 spectrometers) and UV−visible (Jasco V-530 spectrophotometer) spectroscopy, mass spectrometry (Varian VG9090 spectrometer), and elemental analysis. Dipole moments, μ, were measured in $CHCl_3$ by using a WTW-DM01 dipole meter (dielectric constant) coupled with an RX-5000 ATAGO digital refractometer (refractive index) according to the Guggenheim method.[13] Elemental analyses were carried out at the Dipartimento di Chimica Inorganica, Metallorganica e Analitica of the Università di Milano.

For the numbering used in the attribution of the ^{1}H NMR signals, see Figure 1 and Scheme 3.

Determination of the Second-Order NLO Response. (i) EFISH Measurements. The molecular quadratic hyperpolarizabilities of terpyridines and their complexes (Table 1) were measured in $CHCl_3$ solution by the solution-phase dc electric field induced second harmonic (EFISH) generation method,[5] which can provide direct information on the intrinsic molecular NLO properties through eq 1:

$$\gamma_{\mathrm{EFISH}} = (\mu\beta_\lambda/5kT) + \gamma\,(-2\omega;\,\omega,\,\omega,\,0) \qquad (1)$$

where $\mu\beta_\lambda/5kT$ represents the dipolar orientational contribution and $\gamma\,(-2\omega;\,\omega,\,\omega,\,0)$, a third-order term at frequency ω of the incident light, is the electronic contribution to γ_{EFISH}, which is negligible for the kind of molecules investigated here.[3d,e,14] β_λ is the vectorial projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, β_{VEC}, working with an incident wavelength λ. We usually worked with a nonresonant 1.34 μm wavelength, but in the case of some Ir(III) complexes, measurements were performed with an incident wavelength of 1.907 μm.

EFISH measurements at 1.34 μm were carried out at the École Normale Supérieure de Cachan in $CHCl_3$ solutions, while those at 1.907 μm were performed at the Dipartimento di Chimica Inorganica Metallorganica e Analitica dell'Università di Milano, using a Q-switched, mode-locked Nd^{3+}:YAG laser. All experimental EFISH β_λ values are defined according to the "phenomenological" convention.[15]

(ii) Solvatochromic Measurements. The quadratic hyperpolarizability along the charge-transfer direction (β_{CT}) of terpyridines and their corresponding Zn(II), Ru(III), and Ir(III) complexes was evaluated by the solvatochromic method, using UV−visible absorption spectra recorded in a series of solvents such as cyclohexane, carbon tetrachloride, toluene, chloroform, anisole, dichloromethane, ethyl acetate, 1,2-dichloroethane, acetone, and acetonitrile. The radius *a* of the cavity (which can be supposed to be pseudo-spherical taking into account the size and coordination sphere of the metal complexes investigated) occupied by the solute molecule in the solvent was evaluated from the molecular weight of the compound using eq 2:[6]

$$R = \left(\frac{3M}{4\pi Nd}\right)^{1/3} \qquad (2)$$

The quadratic hyperpolarizability tensor β_{CT} along the charge-transfer direction was calculated for each absorption band of the visible spectrum according to the Oudar two-level equation, eq 3:[16]

$$\beta_{\mathrm{CT}} = \frac{3}{2h^2c^2}\,\frac{\nu_a^{\,2} r_{eg}^{\,2} \Delta\mu_{eg}}{(\nu_a^{\,2} - \nu_L^{\,2})(\nu_a^{\,2} - 4\nu_L^{\,2})} \qquad (3)$$

where r_{eg} is the transition dipole moment related to the integrated intensity *f* of the absorption band, ν_a is the frequency of the charge-transfer absorption band, ν_L is the frequency of the incident radiation, and $\Delta\mu_{eg}$ is the variation of the dipole moment upon excitation.

The total value of β_{CT} was determined by adding the contributions of the various absorption bands (see Table 1).

Computational Details. Calculations, based on density functional theory and time-dependent DFT (TDDFT), were carried out for the 4′-(C_6H_4-*p*-NMe_2)-2,2′:6′,2″-terpyridine, analogous to T_0, but with a shorter aliphatic chain on the NR_2 donor group, to evaluate its optimized geometry, dipole moment, absorption spectrum, and EFISH quadratic hyperpolarizability. Geometry optimizations were performed in vacuo. The B3LYP exchange-correlation functional,[17] as implemented in the Gaussian03 program package,[18] was used together with a 3-21g* basis set.[19]

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Table 1. Electronic Spectra, Dipole Moments, and EFISH $\beta_{1.34}$ and $\beta_{CT,1.34}$ of Terpyridine Ligands T_0, T_1, T_2, and T_3 and Their Complexes with Zn(II), Ru(III), and Ir(III), Measured in $CHCl_3$ Solution

molecule	$\lambda_{max\ abs.}$[a] (nm)	μ[a,f] (D)	μEF[g]	$\beta_{1.34}$[a,h] ($\times10^{-30}$ esu)	$\beta_{1.34}$EF[i]	$\Delta\mu_{eg}$[j] (D)	f[a,k]	$\beta_{CT,134}$[l] ($\times10^{-30}$ esu)
T_0	360[b]	2.1		22		8.0	0.40	43
T_1	395[b]	3.6		52		8.3	0.26	43
T_2	399[b]	3.9		95		8.7	0.49	60
T_3	280[c]	1.7		−12		nd	nd	nd
$[ZnCl_2T_0]$	425[b]	8.0	3.8	67	3.0	10.8	0.33	98
$[Zn(CF_3CO_2)_2T_0]$	427[b]	10	4.8	88	4.0	8.2	0.34	79
$[Zn(CF_3CO_2)_2T_1]$	454[b]	8.3	2.3	181	3.5	5.3	0.32	64
$[Zn(CF_3CO_2)_2T_2]$	444[b]	8.9	2.3	137	1.4	7.2	0.17	42
$[Ru(CF_3CO_2)_3T_0]$[p]	416[b]	9.2	4.4	−70	3.2	12.7	0.15	48
	508[d]					5.4	0.20	75
	911[d]					15.8	0.04	−208
								−85
$[RuCl_3T_1]$	469[b]		2.9			2.4	0.42	59
	866[d]	10.3		nd	nd	1.2	0.01	−6
								53
$[Ru(CF_3CO_2)_3T_3]$	496[m]	8.1[n]	4.8[n]	nd	nd	10.2	0.05	2.6
$[IrCl_3T_0]$	465[b,e]	7.9	3.8	−109	5.0	−0.1	0.81	−4
	533[e]			−84[o]		−2.9	0.31	−79
								−83
$[Ir(4\text{-}EtPhCO_2)_3T_0]$	463[b,e]	8.8	4.2	−64[o]	nd	−0.4	0.20	−2
	531[e]					−15.9	0.05	−38
								−40[o]
$[IrCl_3T_1]$	476[b,e]	10.9	3.0	−30	0.6	−2.9	0.18	−22
	538[e]					−10.2	0.01	−11
								−33
$[Ir(4\text{-}EtPhCO_2)_3T_3]$	413[e]	9.1	5.3	−230	19	−21.4	0.05	−27
	521[e]			−126[o]		−27.2	0.03	−63
								−90

[a] In $CHCl_3$. [b] Assigned to the ILCT of the ligand. [c] Assigned to a $\pi-\pi^*$ transition centered on the ligand (LC). [d] Assigned to LMCT, according to refs 9, 10. [e] Assigned to MLCT, according to ref 7f,g. [f] Measured by the Guggenheim method, according to ref 13. [g] Dipole moment enhancement factor, given by $\mu_{complex}/\mu_{free\ ligand}$. [h] Measured by the EFISH technique. [i] $\beta_{1.34}$ enhancement factor, given by $\beta_{1.34\ complex}/\beta_{1.34\ free\ ligand}$. [j] $\Delta\mu_{eg}$ is the difference between excited- and ground-state molecular dipole moments, obtained from solvatochromic data; see ref 6. [k] f is the oscillator strength, obtained from the integrated absorption coefficient; see ref 6. [l] Quadratic hyperpolarizability tensor along the charge-transfer direction. [m] In CH_2Cl_2. [n] μ value obtained by DFT calculations according to the methodology reported in ref 20. [o] β measured in $CHCl_3$ with an incident wavelength of 1.907 μm. [p] The complex $[RuCl_3T_0]$, not soluble enough for dipole moment and EFISH measurements, shows three absorption bands at 416, 476, and 795 nm.

Calculations of the absorption spectrum were performed, within TDDFT, in chloroform solution by means of the nonequilibrium implementation[20a] of the polarizable continuum model (PCM) of solvation.[20b] Hyperpolarizability calculations were performed by numerical differentiation of analytic polarizabilities, obtained by a coupled-perturbed procedure and calculated at finite electric field values. The zzz component of the static first-order hyperpolarizability tensor is the only relevant component (all the other components are at least 2 orders of magnitude smaller), so that it can be directly related to the EFISH quadratic hyperpolarizability. Geometry optimizations in vacuo were also performed at the B3LYP/3-21G* level on the $[Ru(CF_3CO_2)_3T_3]$ complex, followed by a single point calculation in chloroform solution to evaluate its dipole moment.

Synthesis. (i) Synthesis of 4′-(C_6H_4-*p*-X)-2,2′:6′,2″-terpyridines. 4′-(Phenyl-*p*-dibutylamino)-2,2′:6′,2″-terpyridine (T_0). 2-Acetylpyridine (1.88 g, 15.4 mmol) was added to a stirred solution of ^{t}BuOK (2.6 g, 23.1 mmol) in anhydrous THF (40 mL). After the mixture was stirred at room temperature in an inert atmosphere for 2 h, a solution of 4-(dibutylamino)benzaldehyde (1.63 g, 7 mmol) in anhydrous THF (40 mL) was added. The reaction mixture was stirred overnight at room temperature. During this time a dark red color developed. NH_4OAc (18.5 g, 238 mmol) and EtOH (80 mL) were added sequentially and the mixture was heated at reflux for 4 h. Removal of the solvent in vacuo afforded a thick residue which solidified upon addition of a small amount of EtOH. This solid was washed with H_2O, EtOH, and Et_2O, affording 1.85 g of T_0 (60%) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.72 (d, 2H, $J_{6,5}$ = 4.7 Hz, H_6, $H_{6''}$), 8.69 (s, 2H, $H_{3'}$, $H_{5'}$), 8.65 (d, 2H, $J_{3,4}$ = 7.9 Hz, H_3, $H_{3''}$), 7.86 (ddd, 2H, $J_{4,3} = J_{4,5}$ = 7.6 Hz, J = 1.8 Hz, H_4, $H_{4''}$), 7.85 (d, 2H, J_{ortho} = 8.9 Hz, H_7, $H_{7'}$), 7.32 (ddd, 2H, $J_{5,4}$ = 7.4 Hz, $J_{5,6}$ = 4.8 Hz, J = 1.7 Hz, H_5, $H_{5''}$), 6.73 (d, 2H,

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J_{ortho} = 8.9 Hz, H_8, $H_{8'}$), 3.33 (t, 4H, J = 7.6 Hz, N−CH_2−CH_2−CH_2−CH_3), 1.61 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 1.39 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 0.97 (t, 6H, J = 7.3 Hz, N−CH_2−CH_2−CH_2−CH_3); MS-EI: *m*/*z* 436 (calcd for $C_{29}H_{32}N_4$ = 436). Anal. Calcd (found): C, 79.78 (79.96); H, 7.39 (7.24); N, 12.83 (13.20).

4′-(*p*-Tolyl)-2,2′:6′,2″-terpyridine (1). 2-acetylpyridine (2.42 g, 20 mmol) was added to a stirred solution of ^{t}BuOK (3.37 g, 30 mmol) in anhydrous THF (70 mL). After the mixture was stirred at room temperature in an inert atmosphere for 2 h, a solution of *p*-tolualdehyde (1.20 g, 10 mmol) in anhydrous THF (40 mL) was added. The reaction mixture was stirred overnight at room temperature. During this time a dark red color developed. NH_4OAc (35.9 g, 466 mmol) and MeOH (140 mL) were added sequentially and the mixture was heated at reflux for 4 h. Removal of the solvent in vacuo afforded a thick residue which solidified upon addition of a small amount of MeOH. This solid was recrystallized from MeOH, affording 1.29 g of **1** (40%) as crystalline needles.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.73 (s, 2H, $H_{3'}$, $H_{5'}$), 8.73 (d, 2H, $J_{6,5}$ = 5.1 Hz, H_6, $H_{6''}$), 8.66 (d, 2H, $J_{3,4}$ = 7.9 Hz, H_3, $H_{3''}$), 7.87 (ddd, 2H, $J_{4,3}$ = $J_{4,5}$ = 7.7 Hz, J = 1.8 Hz, H_4, $H_{4''}$), 7.81 (d, 2H, J_{ortho} = 8.1 Hz, H_7, $H_{7'}$), 7.35 (ddd, 2H, $J_{5,4}$ = 7.7 Hz, $J_{5,6}$ = 4.8 Hz, H_5, $H_{5''}$), 7.31 (d, 2H, J_{ortho} = 7.8 Hz, H_8, $H_{8'}$), 1.62 (s, 3H, CH_3). MS-EI: *m*/*e* 323 (calcd for $C_{22}H_{17}N_3$ *m*/*e* 323). Anal. Calcd (found): C, 81.70 (81.51); H, 5.23 (5.31); N, 12.91 (12.80).

4′-(Phenyl-*p*-bromomethyl)-2,2′:6′,2″-terpyridine (2). *N*-Bromosuccinimide (0.66 g, 3.71 mmol) and a catalytic amount of dibenzoylperoxide were added to a suspension of **1** (1.20 g, 3.71 mmol) in CCl_4 (20 mL). The mixture was stirred at reflux for 4 h, irradiating with a 100 W lamp. The floating succinimide was then separated by filtration and the liquid phase evaporated to dryness to afford a thick residue, which solidified by adding a small amount of EtOH to give 0.977 g of **2** (65%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.73 (s, 2H, $H_{3'}$, $H_{5'}$), 8.71 (d, 2H, $J_{6,5}$ = 5.1 Hz, H_6, $H_{6''}$), 8.66 (d, 2H, $J_{3,4}$ = 8.07 Hz, H_3, $H_{3''}$), 7.88 (d, 2H, J_{ortho} = 7.7 Hz, H_7, $H_{7'}$), 7.87 (m, 2H, H_4, $H_{4''}$), 7.53 (d, 2H, J_{ortho} = 8.4 Hz, H_8, $H_{8'}$), 7.35 (ddd, 2H, $J_{5,4}$ = 7.3 Hz, $J_{5,6}$ = 4.8 Hz, H_5, $H_{5''}$), 4.56 (s, 2H, CH_2Br). MS-EI: *m*/*e* 401, 322 (M − Br) (calcd for $C_{22}H_{16}N_3Br$ *m*/*e* 401). Anal. Calcd (found): C, 65.68 (65.72); H, 4.01 (3.70); N, 10.44 (10.29).

4-(2,2′:6′,2″-Terpyridyl-4′)-benzyl Triphenyl Phosponium Bromide (3). A solution of triphenylphosphine (0.89 g, 3.43 mmol) and **2** (1.378 g, 3.43 mmol) in toluene (16 mL) was refluxed for 3 h under magnetic stirring. During this time a white solid precipitate formed. The reaction mixture was cooled with an ice bath and the solid was collected by filtration, affording 1.90 g of **3** (83%) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.69 (d, 2H, $J_{6,5}$ = 6.6 Hz, H_6, $H_{6''}$), 8.65 (d, 2H, $J_{3,4}$ = 7.8 Hz, H_3, $H_{3''}$), 8.58 (s, 2H, $H_{3'}$, $H_{5'}$), 7.92−7.62 (m, 9H, H_4, $H_{4''}$, H_7, $H_{7'}$, C_6H_5P), 7.39−7.15 (m, 4H, H_5, $H_{5''}$, H_8, $H_{8'}$), 5.61 (d, 2H, CH_2P). Anal. Calcd (found): C, 72.29 (72.51); H, 4.70 (4.56); N, 6.32 (6.44).

4′-(4-{2-[4-(*N*,*N*-Dibutylamino)phenyl]ethenyl}phenyl)-2,2′:6′,2″-terpyridine (T_1). A sample of **3** (0.884 g, 1.33 mmol) was added to a solution of ^{t}BuOK (0.603 g, 5.38 mmol) in anhydrous DMF (30 mL). The black solution was stirred at room temperature for 10 min, after which 4-(dibutylamino)benzaldehyde (0.32 mL, 1.33 mmol) was added. The reaction mixture was heated at 80 °C for 4 h. Removal of the solvent in vacuo afforded a thick residue which was taken up with H_2O and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried over Na_2SO_4 and evaporated, to give a brown oily residue. This product was stirred with MeOH (5 mL) overnight to afford 0.38 g of T_1 (53%) as a bright yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.79 (s, 2H, $H_{3'}$, $H_{5'}$), 8.77 (d, 2H, $J_{6,5}$ = 4.7 Hz, H_6, $H_{6''}$), 8.70 (d, 2H, $J_{3,4}$ = 7.9 Hz, H_3, $H_{3''}$), 7.97 (d, 2H, J_{ortho} = 8.2 Hz, H_7, $H_{7'}$), 7.90 (ddd, 2H, $J_{4,3}$ = 7.8 Hz, $J_{4,5}$ = 5.8 Hz, J = 1.6 Hz, H_4, $H_{4''}$), 7.62 (d, 2H, J_{ortho} = 8.2 Hz, H_8, $H_{8'}$), 7.44 (d, 2H, J_{ortho} = 8.5 Hz, H_{13}, $H_{13'}$), 7.37 (dd, 2H, $J_{5,6}$ = 4.8 Hz, $J_{5,4}$ = 5.1 Hz, H_5, $H_{5''}$), 7.16 (d, 1H, J_{trans} = 16.2 Hz, H_{10} or H_{11}), 6.95 (d, 1H, J_{trans} = 16.2 Hz, H_{10} o H_{11}), 6.67 (d, 2H, J_{ortho} = 8.5 Hz, H_{14}, $H_{14'}$), 3.32 (t, 4H, J = 7.4 Hz, N−CH_2), 1.61 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 1.39 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 0.99 (t, 6H, J = 7.3 Hz, CH_3).

^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C, TMS): δ (ppm) 8.87 (s, 2H, $H_{3'}$, $H_{5'}$), 8.77 (m, 4H, H_6, $H_{6''}$, H_3, $H_{3''}$), 8.02 (ddd, 2H, $J_{4,3}$ = 7.6 Hz, $J_{4,5}$ = 5.8 Hz, J = 1.8 Hz, H_4, $H_{4''}$), 7.96(d, 2H, J_{ortho} = 8.3 Hz, H_7, $H_{7'}$), 7.78 (d, 2H, J_{ortho} = 8.3 Hz, H_8, $H_{8'}$), 7.50 (m, 4H, H_5, $H_{5''}$, H_{13}, $H_{13'}$), 7.30 (d, 1H, J_{trans} = 16.3 Hz, H_{10} or H_{11}), 7.08 (d, 1H, J_{trans} = 16.3 Hz, H_{10} o H_{11}), 6.73 (d, 2H, J_{ortho} = 8.8 Hz, H_{14}, $H_{14'}$), 3.39 (t, 4H, J = 7.4 Hz, N−CH_2), 1.63 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 1.42 (m, 4H, N−CH_2−CH_2−CH_2−CH_3), 0.98 (t, 6H, J = 7.3 Hz, CH_3). MS-EI: *m*/*e* 538 (calcd for $C_{37}H_{38}N_4$ *m*/*e* 538). Anal. Calcd (found): C, 82.50 (82.35); H, 7.10 (7.30); N, 10.40 (10.35).

4′-(4-{(*E*,*E*)-4-[4-(*N*,*N*-Dimethylamino)phenyl]-buta-1,3-dienyl}-phenyl)-2,2′:6′,2″-terpyridine (T_2). ^{t}BuOK (0.336 g, 3 mmol) was added to a solution of **3** (1.0 g, 1.50 mmol) in anhydrous DMF (20 mL). The black solution was stirred at room temperature for 30 min, after which 4-(dimethylamino)cinnamaldehyde (0.289 g, 1.65 mmol) was added. The reaction mixture was heated at 80 °C for 4 h, then cooled at room temperature. A yellow solid was collected and washed with a small amount of cold DMF. It was then dissolved in CH_2Cl_2 (200 mL) and washed with water (3 × 50 mL). The organic layer was dried over Na_2SO_4 and evaporated, to obtain 0.46 g of T_2 (64%) as a yellow powder.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.78 (s, 2H, $H_{3'}$, $H_{5'}$), 8.77 (d, 2H, $J_{6,5}$ = 6.0 Hz, H_6, $H_{6''}$), 8.70 (d, 2H, $J_{3,4}$ = 7.9 Hz, H_3, $H_{3''}$), 7.91 (d, 2H, J_{ortho} = 8.1 Hz, H_7, $H_{7'}$), 7.90 (m, 2H, H_4, $H_{4''}$), 7.57 (d, 2H, J_{ortho} = 8.3 Hz, H_8, $H_{8'}$), 7.38 (d, 2H, J_{ortho} = 8.5 Hz, H_{15}, $H_{15'}$), 7.37 (m, 2H, H_5, $H_{5''}$), 7.07 (dd, 1H, J_{trans} = 15.4 Hz, $J_{12,11}$ = 10.2 Hz, H_{12}), 6.86 (d, 1H, J_{trans} = 15.3 Hz, H_{10}), 6.72 (d, 2H, J_{ortho} = 8.5 Hz, H_{16}, $H_{16'}$), 6.67 (m, 2H, H_{11}, H_{13}), 3.01 (s, 6H, N(CH_3)$_2$).

^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C, TMS): δ (ppm) 8.86 (s, 2H, $H_{3'}$, $H_{5'}$), 8.77 (m, 4H, H_6, $H_{6''}$, H_3, $H_{3''}$), 8.01 (ddd, 2H, $J_{4,3}$ = 7.5 Hz, $J_{4,5}$ = 5.8 Hz, J = 1.7 Hz, H_4, $H_{4''}$), 7.96 (d, 2H, J_{ortho} = 8.3 Hz, H_7, $H_{7'}$), 7.74 (d, 2H, J_{ortho} = 8.3 Hz, H_8, $H_{8'}$), 7.50 (m, 2H, H_5, $H_{5''}$), 7.41 (d, 2H, J_{ortho} = 8.8 Hz, H_{15}, $H_{15'}$), 7.23 (dd, 1H, J_{trans} = 15.6 Hz, $J_{12,11}$ = 10.4 Hz, H_{12}), 6.94 (dd, 1H, J_{trans} = 15.2 Hz, $J_{11,12}$ = 10.4 Hz, H_{11}), 6.74 (m, 4H, H_{16}, $H_{16'}$, H_{10}, H_{13}), 3.01 (s, 6H, N(CH_3)$_2$). MS-EI: *m*/*e* 480 (calcd for $C_{33}H_{28}N_4$ *m*/*e* 480). Anal. Calcd (found): C, 82.47 (82.51); H, 5.87 (5.69); N, 11.66 (11.80).

(*E*)-3-(4″-Nitrophenyl)-1-(pyrid-2′-yl)prop-2-enone (4). A 10% aqueous NaOH solution (0.5 mL) was added to a suspension of 4-nitrobenzaldehyde (1.26 g, 8.34 mmol) in EtOH (10 mL). To the resulting mixture, cooled at 0 °C, 2-acetylpyridine (0.93 mL, 8.30 mmol) was added dropwise in 2.5 h. The solution was stirred at 0 °C for 2 h, allowing the formation of a precipitate, which was collected by filtration and washed with a small amount of EtOH, affording 1.43 g of **4** (67%) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.78 (d, 2H, $J_{6,5}$ = 4.7 Hz, H_6), 8.46 (d, 2H, J_{trans} = 16.0 Hz, H_7), 8.30 (d,

2H, J_{ortho} = 8.7 Hz, H_{10}, $H_{10'}$), 8.23 (d, 2H, $J_{3,4}$ = 7.9 Hz, H_3), 7.94 (m, 1H, H_4), 7.94 (d, 2H, J_{trans} = 16.1 Hz, H_8), 7.89 (d, 2H, J_{ortho} = 8.6 Hz, H_9, $H_{9'}$), 7.55 (m, 1H, H_5). Anal. Calcd (found): C, 66.14 (66.54); H, 3.96 (3.67); N, 11.02 (11.09).

4′-(Phenyl-*p*-nitro)-2,2′:6′,2″-terpyridine (T_3). A solution of **5** (0.633 g, 1.94 mmol) in MeOH (10 mL) was added to a solution of **4** (0.491 g, 1.94 mmol) in MeOH (10 mL) and the resulting mixture was refluxed for 24 h. The brown solid formed was collected by filtration, washed with a small amount of cold MeOH, and finally crystallized from EtOH, affording 0.531 g of T_3 (78%) as a pale violet solid.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.77 (s, 2H, $H_{3'}$, $H_{5'}$), 8.75 (d, 2H, $J_{6,5}$ = 4.1 Hz, H_6, $H_{6''}$), 8.70 (d, 2H, $J_{3,4}$ = 8.0 Hz, H_3, $H_{3''}$), 8.38 (d, 2H, J_{ortho} = 8.6 Hz, H_8, $H_{8'}$), 8.06 (d, 2H, J_{ortho} = 8.6 Hz, H_7, $H_{7'}$), 7.91 (ddd, 2H, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 6.3 Hz, J = 1.7 Hz, H_4, $H_{4''}$), 7.39 (dd, 2H, $J_{5,4}$ = 6.3 Hz, $J_{5,6}$ = 4.6 Hz, H_5, $H_{5''}$).

^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ (ppm) 8.79 (s, 2H, $H_{3'}$, $H_{5'}$), 8.73 (d, 2H, $J_{6,5}$ = 4.1 Hz, H_6, $H_{6''}$), 8.71 (d, 2H, $J_{3,4}$ = 8.0 Hz, H_3, $H_{3''}$), 8.39 (d, 2H, J_{ortho} = 9.0 Hz, H_8, $H_{8'}$), 8.01 (d, 2H, J_{ortho} = 9.0 Hz, H_7, $H_{7'}$), 7.98 (ddd, 2H, $J_{4,3}$ = 8.0 Hz, $J_{4,5}$ = 6.3 Hz, J = 1.7 Hz, H_4, $H_{4''}$), 7.46 (dd, 2H, $J_{5,4}$ = 6.3 Hz, $J_{5,6}$ = 4.6 Hz, H_5, $H_{5''}$). MS-EI: *m*/*e* 354 (calcd for $C_{21}H_{14}N_4O_2$ *m*/*e* 354). Anal. Calcd (found): C, 71.18 (71.32); H, 3.98 (4.16); N, 15.81 (15.56).

Silver 4-Ethylbenzoate. A solution of 4-ethylbenzoic acid (0.312 g, 2.08 mmol) in CH_3CN (20 mL) was added dropwise to a suspension of Ag_2CO_3 (0.287 g, 1.04 mmol) in CH_3CN (20 mL) at room temperature and under vigorous stirring. The reaction mixture was refluxed for 7 h, and then after it cooled at room temperature, a light brown precipitate was collected by filtration. This solid was suspended in H_2O (100 mL) and the suspension was refluxed until the major part of the solid was dissolved. After hot filtration and evaporation to dryness, 0.120 g of 4-Et$C_6H_4CO_2$Ag (45%) was obtained as a pale yellow powder.

^{1}H NMR (300 MHz, CD_3OD, 25 °C, TMS): δ (ppm) 7.93 (d, 2H, J_{ortho} = 7.7 Hz, H_2, $H_{2'}$), 7.28 (d, 2H, J_{ortho} = 7.7 Hz, H_3, $H_{3'}$), 2.70 (q, 2H, $J_{vic.}$ = 7.8 Hz, $-CH_2-$), 1.26 (t, 3H, $J_{vic.}$ = 7.6 Hz, $-CH_3$). MS-EI *m*/*e* 149 (M − Ag) (calcd for $C_9H_9O_2$Ag *m*/*e* 256). Anal. Calcd (found): C, 42.05 (42.06); H, 3.53 (3.51).

(i) Synthesis of the Complexes. *[$ZnCl_2T_0$] and [$Zn(CF_3CO_2)_2T_0$]*. A solution of T_0 (0.200 g, 0.46 mmol) in EtOH (20 mL) was added to a solution of the Zn(II) salt (0.46 mmol) in EtOH (10 mL). The reaction mixture was vigorously stirred at room temperature for 1 h. Removal of the solvent under vacuum afforded an orange−yellow solid, which was dissolved in CH_2Cl_2 and precipitated by the addition of *n*-pentane at room temperature, giving the desired product as a bright yellow powder (80%).

[$ZnCl_2T_0$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.87 (d, 2H, $J_{6,5}$ = 4.1 Hz, H_6, $H_{6''}$), 7.78 (d, 2H, $J_{3,4}$ = 8.0 Hz, H_3, $H_{3''}$), 7.74 (s, 2H, $H_{3'}$, $H_{5'}$), 7.49 (dt, 2H, $J_{4,3}$ = $J_{4,5}$ = 7.7 Hz, H_4, $H_{4''}$), 7.47 (d, 2H, J_{ortho} = 8.9 Hz, H_7, $H_{7'}$), 7.27 (dd, 2H, $J_{5,4}$ = 7.4 Hz, $J_{5,6}$ = 4.1 Hz, H_5, $H_{5''}$), 6.73 (d, 2H, J_{ortho} = 8.9 Hz, H_8, $H_{8'}$), 3.22 (t, 4H, J = 7.3 Hz, N$CH_2$$CH_2CH_2CH_3$), 1.56 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.40 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.03 (t, 6H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$). MS−FAB$^+$ *m*/*e* 535 (M − Cl)$^+$ (calcd for $C_{29}H_{32}N_4Cl_2Zn$ *m*/*e* 570). Anal. Calcd (found): C, 60.80 (60.51); H, 5.63 (5.81); N, 9.78 (9.88).

[$Zn(CF_3CO_2)_2T_0$]. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 8.89 (d, 2H, $J_{6,5}$ = 5.1 Hz, H_6, $H_{6''}$), 8.06 (s, 2H, $H_{3'}$, $H_{5'}$), 7.94 (d, 2H, $J_{3,4}$ = 8.0 Hz, H_3, $H_{3''}$), 7.75 (t, 2H, $J_{4,3}$ = $J_{4,5}$ = 7.5 Hz, H_4, $H_{4''}$), 7.52 (d, 2H, J_{ortho} = 8.9 Hz, H_7, $H_{7'}$), 7.47 (dd, 2H, $J_{5,4}$ = 7.5 Hz, $J_{5,6}$ = 5.2 Hz, H_5, $H_{5''}$), 6.48 (d, 2H, J_{ortho} = 8.8 Hz, H_8, $H_{8'}$), 3.28 (t, 4H, J = 7.2 Hz, N$CH_2$$CH_2CH_2CH_3$), 1.56 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.41 (m, 4H, $NCH_2CH_2CH_2CH_3$), 1.02 (t, 6H, J = 7.2 Hz, $NCH_2CH_2CH_2CH_3$). MS−FAB$^+$: *m*/*e* 613 (M − CF_3CO_2)$^+$ (calcd for $C_{33}H_{32}N_4O_4F_6Zn$ *m*/*e* 726). Anal. Calcd (found): C, 54.44 (54.70); H, 4.43 (4.43); N, 7.69 (7.51).

[$Zn(CF_3CO_2)_2T_1$]. A solution of T_1 (0.539 g, 0.216 mmol) in EtOH (50 mL) was added to a solution of $Zn(CF_3CO_2)_2 \cdot xH_2O$ (0.291 g, 0.216 mmol) in EtOH (25 mL). The reaction mixture was stirred at room temperature in the dark (aluminum foil) for 2 h. Removal of the solvent under vacuum afforded a red powder, which was dissolved in CH_2Cl_2 and precipitated by addition of *n*-pentane at room temperature, giving 0.145 g of [$Zn(CF_3CO_2)_2T_1$] (81%) as a yellow powder.

^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C, TMS): δ (ppm) 8.96 (d, 2H, $J_{6,5}$ = 4.2 Hz, H_6, $H_{6''}$), 8.90 (s, 2H, $H_{3'}$, $H_{5'}$), 8.71 (m, 2H, H_3, $H_{3''}$), 8.21 (m, 2H, H_4, $H_{4''}$), 8.10 (d, 2H, J_{ortho} = 8.0 Hz, H_7, $H_{7'}$), 7.85 (m, 2H, H_5, $H_{5''}$), 7.65 (d, 2H, J_{ortho} = 7.8 Hz, H_8, $H_{8'}$), 7.50 (d, 2H, J_{ortho} = 8.8 Hz, H_{13}, $H_{13'}$), 7.29 (d, 1H, J_{trans} = 16.4 Hz, H_{10} or H_{11}), 7.02 (d, 1H, J_{trans} = 16.0 Hz, H_{10} o H_{11}), 6.75 (d, 2H, J_{ortho} = 8.8 Hz, H_{14}, $H_{14'}$). MS−FAB$^+$: *m*/*e* 715 (M − CF_3CO_2)$^+$ (calcd for $C_{41}H_{38}N_4O_4F_6Zn$ *m*/*e* 828). Anal. Calcd (found): C, 59.32 (59.71); H, 4.61 (4.59); N, 6.74 (6.43).

[$Zn(CF_3CO_2)_2T_2$]. A solution of T_2 (66 mg, 0.138 mmol) in EtOH (65 mL) was added to a solution of $Zn(CF_3CO_2)_2 \cdot xH_2O$ (40 mg, 0.138 mmol) in EtOH (5 mL). The reaction mixture was refluxed in the dark (aluminum foil) for 3 h. Removal of the solvent in vacuo afforded a red powder, which was dissolved in CH_2Cl_2 and precipitated by *n*-hexane at room temperature, giving 72 mg of [$Zn(CF_3CO_2)_2T_2$] (68%) as a dark orange powder.

^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C, TMS): δ (ppm) 9.01 (m, 4H, $H_{3'}$, $H_{5'}$, H_6, $H_{6''}$), 8.86 (m, 2H, H_3, $H_{3''}$), 8.32 (m, 2H, H_4, $H_{4'}$), 8.19 (d, 2H, J = 7.5 Hz, H_7, $H_{7'}$), 7.88 (m, 2H, H_5, $H_{5''}$), 7.73 (d, 2H, H_8, $H_{8'}$), 7.41 (d, 2H, J_{ortho} = 8.6 Hz, H_{15}, $H_{15'}$), 7.26 (dd, 1H, J_{trans} = 15.2 Hz, $J_{12,11}$ = 10.4 Hz, H_{12}), 6.94 (dd, 1H, J_{trans} = 15.6 Hz, $J_{11,12}$ = 10.6 Hz, H_{11}), 6.76 (d, 2H, J_{ortho} = 8.8 Hz, H_{16}, $H_{16'}$), 6.76 (m, 2H, H_{10}, H_{13}), 3.01 (s, 6H, N(CH_3)$_2$). MS−FAB$^+$: *m*/*e* 657 (M − CF_3CO_2)$^+$ (calcd for $C_{37}H_{28}N_4O_4F_6Zn$ *m*/*e* 770). Anal. Calcd (found): C, 57.56 (57.47); H, 3.63 (3.86); N, 7.26 (6.99).

[$RuCl_3T_0$]. A solution of T_0 (0.317 g, 0.726 mmol) in EtOH (50 mL) was added to a solution of $RuCl_3 \cdot xH_2O$ (% Ru = 42.68%) (0.172 g, 0.726 mmol) in EtOH (30 mL). The dark brown reaction mixture was refluxed under vigorous stirring for 6 h, then left at room temperature overnight, affording a brown precipitate which was collected by filtration. It was then dissolved in CH_2Cl_2 (50 mL) and the small insoluble residue was filtered off. The filtrate was evaporated to dryness, leading to 0.281 g of [$RuCl_3T_0$] (60%) as a dark brown powder.

MS−FAB$^+$: *m*/*e* 608 (M − Cl)$^+$ (calcd for $C_{29}H_{32}N_4RuCl_3$ *m*/*e* 643). Anal. Calcd (found): C, 54.08 (54.25); H, 5.01 (5.11); N, 8.69 (8.44).

[$Ru(CF_3CO_2)_3T_0$]. $Ag(CF_3CO_2)$ (63.4 mg, 0.287 mmol) was added at room temperature to a solution of [$RuCl_3T_0$] (51.7 mg, 0.0803 mmol) in CH_3CN (7 mL). The dark red mixture was vigorously stirred at room temperature for 24 h, then the solvent was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (100 mL) and the insoluble part filtered off. The filtrate was evaporated to dryness, affording 41.7 mg of [$Ru(CF_3CO_2)_3T_0$] (59%) as a dark red solid.

MS−FAB$^+$: *m*/*e* 764 (M − CF_3CO_2)$^+$ (calcd for $C_{35}H_{32}N_4O_6F_9Ru$ *m*/*e* 877). Anal. Calcd (found): C, 47.95 (47.74); H, 3.68 (3.59); N, 6.39 (6.16).

[$RuCl_3T_1$]. A solution of T_1 (46.2 mg, 0.0858 mmol) in EtOH (3 mL) was added to a solution of $RuCl_3 \cdot xH_2O$ (%Ru = 39.95%) (22 mg, 0.0866 mmol) in EtOH (2 mL). The dark red solution was refluxed for 4 h, then stirred at room temperature overnight, leading to 43.2 mg of [$RuCl_3T_1$] (67%) as a a dark red powder.

MS−FAB$^+$: *m*/*e* 710 $(M - Cl)^+$ (calcd for $C_{37}H_{38}N_4RuCl_3$ *m*/*e* 745). Anal. Calcd (found): C, 59.56 (59.35); H, 5.13 (5.59); N, 7.15 (7.26).

[$Ru(CF_3CO_2)_3 \cdot 2CH_3CN \cdot H_2O$]. $Ag(CF_3CO_2)$ (0.252 g, 1.14 mmol) was added at room temperature to a solution of $RuCl_3 \cdot xH_2O$ (%Ru = 39.95%) (0.096 mg, 0.38 mmol) in CH_3CN (15 mL). The dark green reaction mixture was vigorously stirred for 1 h, then AgCl was filtered off and the filtrate evaporated to dryness. The dark brown residue was triturated several times with small amounts of *n*-hexane, affording in almost quantitative yield [$Ru(CF_3CO_2)_3 \cdot 2CH_3CN \cdot H_2O$] as a dark brown powder.

Anal. Calcd (found): C, 22.20 (22.10); H, 1.49 (1.60); N, 5.18 (5.18).

[$Ru(CF_3CO_2)_3T_3$]. A suspension of [$Ru(CF_3CO_2)_3 \cdot 2CH_3CN \cdot H_2O$] (0.103 g, 0.191 mmol) in EtOH (25 mL) was added to a suspension of T_3 (0.074 g, 0.210 mmol) in EtOH (25 mL). The dark brown reaction mixture was refluxed for 7 h. Removal of the solvent under vacuum afforded a thick oily residue, which was triturated with a small amount of *n*-hexane, giving 0.090 g of [$Ru(CF_3CO_2)_3$ T_3] (59%) as a dark brown powder.

^{1}H NMR (300 MHz, CD_3CN, 25 °C, TMS): δ (ppm) 9.09 (s, 2H, $H_{3'}$, $H_{5'}$), 8.69 (d, 2H, $J_{3,4}$ = 7.6 Hz, H_3, $H_{3''}$), 8.59 (d, 2H, J_{ortho} = 8.8 Hz, H_8, $H_{8'}$), 8.42 (d, 2H, J_{ortho} = 8.8 Hz, H_7, $H_{7'}$), 7.97 (dt, 2H, $J_{4,3} = J_{4,5}$ = 8.0 Hz, J = 1.7 Hz, H_4, $H_{4''}$), 7.43 (d, 2H, $J_{6,5}$ = 4.8 Hz, H_6, $H_{6''}$), 7.19 (ddd, 2H, $J_{5,4}$ = 7.6 Hz, $J_{5,6}$ = 4.02 Hz, J = 1.6 Hz, H_5, $H_{5''}$). MS-EI: *m*/*e* 795 (calcd for $C_{27}H_{14}N_4O_8F_9Ru$ *m*/*e* 795). Anal. Calcd (found): C, 41.70 (41.71); H, 2.98 (2.81); N, 8.15 (8.38).

[$IrCl_3T_0$]. A solution of T_0 (0.357 g, 0.818 mmol) in EtOH (50 mL) was added to a solution of $IrCl_3 \cdot xH_2O$ (% Ir = 53.57%) (0.293 g, 0.818 mmol) in EtOH (50 mL). The dark brown reaction mixture was refluxed under vigorous stirring for 6 h, then stirred at room temperature overnight, affording a brown precipitate. It was then dissolved in CH_2Cl_2 (100 mL) and the small insoluble residue was filtered off. The filtrate was evaporated to dryness, leading to 212 mg of [$IrCl_3T_0$] (35%) as a red powder.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 9.58 (d, 2H, $J_{6,5}$ = 4.3 Hz, H_6, $H_{6''}$), 8.12 (s, 2H, $H_{3'}$, $H_{5'}$), 8.06 (d, 2H, $J_{3,4}$ = 7.5 Hz, H_3, $H_{3''}$), 7.86 (t, 2H, $J_{4,3} = J_{4,5}$ = 7.6 Hz, H_4, $H_{4''}$), 7.63 (m, 4H, H_7, $H_{7'}$, H_5, $H_{5''}$), 6.73 (d, 2H, J_{ortho} = 7.9 Hz, H_8, $H_{8'}$), 3.39 (t, broad, N*CH*$_2$), 1.43 (m, 8H, *CH*$_2$), 1.03 (t, 6H, J = 7.3 Hz, *CH*$_3$). MS−FAB$^+$: *m*/*e* 699 $(M - Cl)^+$ (calcd for $C_{29}H_{32}N_4IrCl_3$ *m*/*e* 734). Anal. Calcd (found): C, 47.38 (47.32); H, 4.39 (4.44); N, 7.62 (7.52).

[Ir(4-Et$C_6H_4CO_2$)$_3T_0$]. 4-Et$C_6H_4CO_2Ag$ (52.9 mg, 0.206 mmol) was added to a solution of [$IrCl_3T_0$] (50.4 mg, 0.0686 mmol) in $CHCl_3$ (80 mL). The red reaction mixture was stirred at room temperature for 24 h. AgCl was filtered off and the filtrate evaporated to dryness, affording 62 mg of [Ir(4-Et$C_6H_4CO_2$)$_3T_0$] (84%) as a red powder.

^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) 9.59 (d, broad, 2H, H_6, $H_{6''}$), 8.13 (s, 2H, $H_{3'}$, $H_{5'}$), 8.05 (m, 8H, H_3, $H_{3''}$, CH benzoate), 7.94 (t, 2H, $J_{4,3} = J_{4,5}$ = 7.3 Hz, H_4, $H_{4''}$), 7.67 (m, 4H, H_7, $H_{7'}$, H_5, $H_{5''}$), 7.29 (d, 6H, CH benzoate), 6.76 (d, 2H, J_{ortho} = 8.5 Hz, H_8, $H_{8'}$), 3.40 (t, broad, 4H, N*CH*$_2$), 2.75 (q, broad, 6H, $CH_3CH_2C_6H_4$), 1.43 (m, 8H, *CH*$_2$), 1.03 (t, 6H, J = 7.3 Hz, *CH*$_3$), 0.87 (t, 9H, J = 7.5 Hz, CH_3CH_2Ph). MS−FAB$^+$: *m*/*e* 926 $(M - (4\text{-Et}C_6H_4CO_2)_2)^+$ (calcd for $C_{56}H_{59}N_4O_6Ir$ *m*/*e* 1075). Anal. Calcd (found): C, 62.49 (62.30); H, 5.52 (5.67); N, 5.20 (5.13).

[$IrCl_3T_1$]. A solution of T_1 (0.101 g, 0.188 mmol) in EtOH (100 mL) was added to a solution of $IrCl_3 \cdot xH_2O$ (%Ir = 52.15%) (0.069 g, 0.188 mmol) in EtOH (100 mL). The resulting mixture was refluxed for 6 h and the red precipitate formed was collected and dissolved in CH_2Cl_2 (100 mL). The insoluble residue was filtered off and the filtrate evaporated to dryness, affording 35.5 mg of [$IrCl_3T_1$] (22.6%) as a dark red powder.

^{1}H NMR (300 MHz, CD_3COCD_3, 25 °C, TMS): δ (ppm) 9.42 (d, 2H, $J_{6,5}$ = 5.04 Hz, H_6, $H_{6''}$), 8.95 (s, 2H, $H_{3'}$, $H_{5'}$), 8.78 (d, 2H, $J_{3,4}$ = 8.1 Hz, H_3, $H_{3''}$), 8.26 (t, 2H, $J_{4,3} = J_{4,5}$ = 7.6 Hz, H_4, $H_{4''}$), 8.15 (d, 2H, J_{ortho} = 8.3 Hz, H_7, $H_{7'}$), 7.94 (dd, 2H, $J_{5,6}$ = 5.2 Hz, $J_{5,4}$ = 7.4 Hz, H_5, $H_{5''}$), 7.79 (d, 2H, J_{ortho} = 7.7 Hz, H_8, $H_{8'}$), 7.50 (m, 2H, H_{13}, $H_{13'}$), 7.34 (d, 1H, J_{trans} = 16.5 Hz, H_{10} or H_{11}), 7.10 (d, 1H, J_{trans} = 15.9 Hz, H_{10} or H_{11}), 6.78 (m, 2H, H_{14}, $H_{14'}$). MS−FAB$^+$: *m*/*e* 800 $(M - Cl)^+$ (calcd for $C_{37}H_{38}N_4IrCl_3$ *m*/*e* 835). Anal. Calcd (found): C, 53.07 (53.55); H, 4.57 (4.35); N, 6.69 (6.49).

[$IrCl_3 \cdot 3CH_3CN$]. A solution of $IrCl_3 \cdot xH_2O$ (%Ir = 52.15%) (0.252 g, 0.684 mmol) in CH_3CN (40 mL) was refluxed under nitrogen atmosphere for 6 h. The solvent was then removed, affording in almost quantitative yield [$IrCl_3 \cdot 3CH_3CN$] as a yellow powder, stored under nitrogen and in the dark (aluminum foil).

MS−FAB$^+$: *m*/*e* 421 $(M + H)^+$, 386 $(M - Cl)^+$, 380 $(M - CH_3CN)^+$ (calcd for $C_6H_9N_3IrCl_3$ *m*/*e* 420). Anal. Calcd (found): C, 17.07 (17.26); H, 2.13 (2.26); N, 9.96 (9.93).

[$IrCl_3T_3$]. A solution of [$IrCl_3 \cdot 3CH_3CN$] (0.146 g, 0.347 mmol) in *N*,*N*-dimethylacetamide (20 mL) was added to a solution of T_3 (0.123 g, 0.347 mmol) in *N*,*N*-dimethylacetamide (5 mL). The reaction mixture was stirred at 100 °C in the dark (aluminum foil) for 4 h. The resulting suspension was filtered and the filtrate evaporated to dryness. The resulting oily product was triturated with a small amount of *n*-pentane, affording 0.080 mg of [$IrCl_3T_3$] (35.3%) as a dark brown powder.

^{1}H NMR (300 MHz, DMSO-d_6, 25 °C, TMS): δ (ppm) 9.23 (m, 4H, $H_{3'}$, $H_{5'}$, H_6, $H_{6''}$), 8.93 (d, 2H, $J_{3,4}$ = 8.1 Hz, H_3, $H_{3''}$), 8.52 (m, 4H, H_7, $H_{7'}$, H_8, $H_{8'}$), 8.34 (t, 2H, $J_{4,3}$ = 8.0 Hz, H_4, $H_{4''}$), 8.01 (m, 2H, H_5, $H_{5''}$). MS−FAB$^+$: *m*/*e* 617 $(M - Cl)^+$ (calcd for $C_{21}H_{14}N_4O_2IrCl_3$ *m*/*e* 652). Anal. Calcd (found): C, 38.62 (38.97); H, 2.16 (2.27); N, 8.58 (8.42).

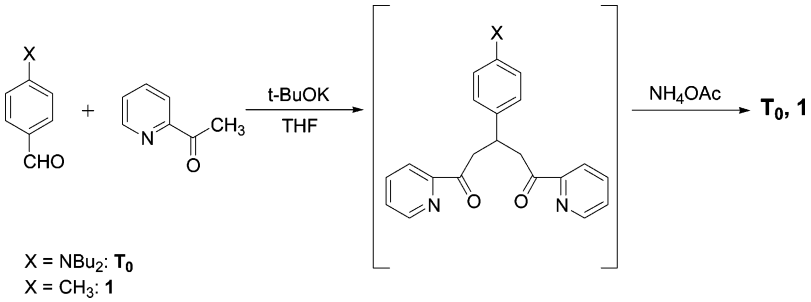
[Ir(4-Et$C_6H_4CO_2$)$_3T_3$]. [$IrCl_3T_3$] (80 mg, 0.122 mmol) was added to a solution of 4-Et$C_6H_4CO_2Ag$ (94.5 mg, 0.366 mmol) in *N*,*N*-dimethylacetamide (100 mL). The resulting mixture was stirred in the dark and under nitrogen atmosphere at 120 °C for 4 days. The suspension was filtered and the red filtrate evaporated to dryness, affording an oily product, which was triturated with a small amount of *n*-pentane, giving an orange powder. This powder was dissolved in $CHCl_3$ (50 mL). After filtration of the insoluble residue and evaporation of the filtrate, 43.3 mg of [Ir(4-Et$C_6H_4CO_2$)$_3T_3$] (35.7%) was obtained as a dark orange powder.

MS−FAB$^+$: *m*/*e* 844 $(M - (4\text{-Et}C_6H_4CO_2))^+$ (calcd for $C_{48}H_{41}N_4O_8Ir$ *m*/*e* 993). Anal. Calcd (found): C, 57.99 (58.43); H, 4.16 (4.20); N, 5.63 (5.64).

Results and Discussion

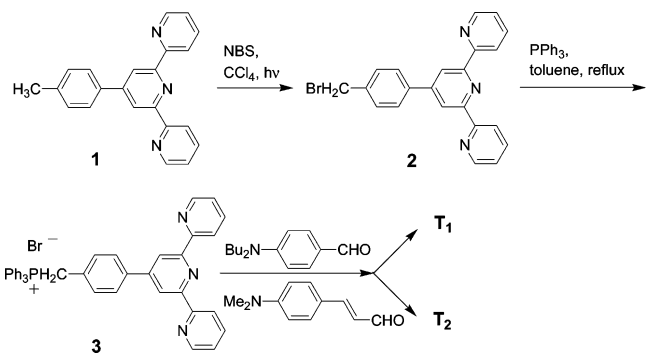
1. Synthesis of Ligands and Complexes. A series of 4′-(C_6H_4-*p*-X)-2,2′:6′,2″-terpyridines (X = NBu_2 (T_0), (*E*)-CH=CH−C_6H_4-*p*-NBu_2 (T_1), (*E*,*E*)-(CH=CH)$_2$−C_6H_4-*p*-NMe_2 (T_2), NO_2 (T_3)) (see Figure 1) and their complexes with Zn(II), Ru(III), and Ir(III) ions carrying various ancillary ligands were synthesized and characterized.

Scheme 1

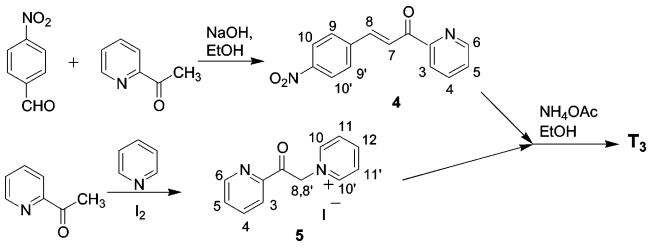


Terpyridine **1**, used as starting material for the synthesis of T_1 and T_2, was synthesized by the Kröhnke methodology (see Scheme 1),[11a] the most convenient way to prepare aromatic substituted terpyridines, by condensation of *p*-tolualdehyde with 2 equiv of 2-acetylpyridine, in the presence of potassium *tert*-butoxide as a base and in anhydrous THF. The corresponding 1,5-diketone, not isolated, was then reacted with NH_4OAc to afford **1** (40% yield). This procedure was followed, as previously reported,[8a] for the synthesis of T_0 (60% yield). Terpyridine **1** was then brominated, following a methodology described in the literature,[11b] with *N*-bromosuccinimide in CCl_4 and a catalytic amount of dibenzoylperoxide as radical starter. Quaternization of compound **2** with triphenylphosphine in refluxing toluene afforded the salt **3** (over 80% yield). Wittig condensation of **3** was carried out with *p*-(dibutylamino)benzaldehyde in anhydrous *N*,*N*-dimethylformamide, using potassium *tert*-butoxide as a base, and afforded terpyridine T_1 (53% yield), while the reaction carried out under the same conditions between **3** and *p*-(dimethylamino)cinnamaldehyde afforded terpyridine T_2 (64% yield) (see Scheme 2).Terpyridine T_3, with the strong electron-withdrawing nitro group, was obtained by a convergent synthesis (see Scheme 3), as reported in the literature,[11c] starting from *p*-nitrobenzaldehyde, which was condensed with 1 equiv of 2-acetylpyridine, in the presence of a 10% aqueous solution of NaOH, affording the corresponding enone **4** in good yields. By reaction of 2-acetylpyridine with pyridine and iodine, the pyridinium salt **5** was obtained.[11a] Finally, stoichiometric amounts of compounds **4** and **5** were condensed with ammonium acetate to obtain T_3 (78% yield). To study the role of the ancillary ligand on the second-order NLO response, Zn(II) complexes of terpyridine T_0 with chlorine and trifluoroacetate ancillary ligands were prepared in good

Scheme 2



Scheme 3



yield (80%) by reaction of stoichiometric amounts of the Zn(II) salt and of the ligand T_0 with terpyridines T_1 and T_2; only Zn(II) complexes with the trifluoroacetate as ancillary ligand were prepared, following the procedure above. According to the known structure of [$ZnCl_2$(2,2′:6′,2″-terpyridine)],[21] in these Zn(II) complexes the terpyridines T_0, T_1, and T_2, which, when free, are in *transoid* geometry, as confirmed by experimental and theoretical dipole moments (see later), assume the cis-like configuration expected for a metal chelated terdentate ligand, while the Zn(II) ion assumes a trigonal bipyramidal geometry of the coordination sphere.

Ru(III) and Ir(III) complexes of T_0 and T_1 with chlorine as an ancillary ligand were synthesized by mixing terpyridine and stoichiometric amounts of $RuCl_3 \cdot xH_2O$ or $IrCl_3 \cdot xH_2O$ respectively, followed by refluxing in absolute ethanol. However, the complex [$RuCl_3T_0$] is not soluble enough in $CHCl_3$ for dipole moments and EFISH measurements, so that in its reaction with silver trifluoroacetate in CH_3CN, the more soluble complex [$Ru(CF_3CO_2)_3T_0$] was synthesized.

The complex [$Ru(CF_3CO_2)_3T_3$] was prepared by reacting $RuCl_3 \cdot xH_2O$ with the stoichiometric amount of silver trifluoroacetate in refluxing acetonitrile. This afforded, in almost quantitative yield, the compound [$Ru(CF_3CO_2)_3 \cdot 2CH_3CN \cdot H_2O$], which was then reacted with the stoichiometric amount of terpyridine T_3 under refluxing ethanol (59% yield).

Finally, we prepared the complex [$Ir(4\text{-}EtC_6H_4CO_2)_3T_3$], which is soluble enough for dipole moments and EFISH measurements since both [$IrCl_3T_3$] and [$Ir(CF_3CO_2)_3T_3$] are not sufficiently soluble. Its synthesis first required the preparation of [$IrCl_3 \cdot 3CH_3CN$], by reaction of $IrCl_3 \cdot xH_2O$ with excess CH_3CN, followed by an exchange reaction with terpyridine T_3 in *N*,*N*-dimethylacetamide to give [$IrCl_3T_3$] (35.3% yield). The ancillary ligand exchange was made by

(21) (a) Einstein, F. W. B.; Penfold, B. R. *Acta Crystallogr.* **1966**, *20*, 924−926. (b) Douglas, J. E.; Wilkins, C. J. *Inorg. Chim. Acta* **1969**, 635−638.

the reaction of this latter complex with 4-$EtC_6H_4CO_2Ag$. In the same way, a reaction of $[IrCl_3T_0]$ with 4-$EtC_6H_4CO_2Ag$ in $CHCl_3$ afforded $[Ir(4\text{-}EtC_6H_4CO_2)_3T_0]$ (35.7% yield), a reference compound to be compared with $[Ir(4\text{-}EtC_6H_4\text{-}CO_2)_3T_3]$.

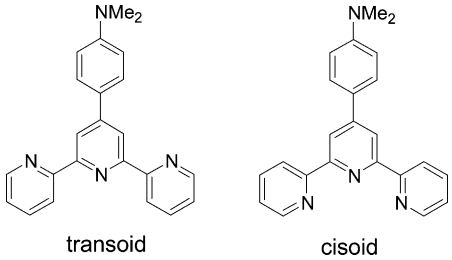
2. Characterization of Some Electronic Properties of terpyridines and Their Zn(II), Ir(III), and Ru(III) Complexes. ^{1}H NMR Spectra. In the ^{1}H NMR spectra (see Experimental Section) of terpyridines T_0, T_1, and T_2 coordinated to Zn(II) and Ir(III) metal centers, the signals of hydrogens in α position to the terpyridine nitrogen atoms are shifted to lower fields with respect to those of the ligand, as already observed for other Zn(II) complexes with similar nitrogen donor ligands such as phenanthrolines and stilbazoles[3f] (for example, $\Delta\delta$ in $CDCl_3$ 0.15−0.17 ppm for $[ZnCl_2T_0]$ and $[Zn(CF_3CO_2)_2T_0]$ respectively; $\Delta\delta$ in CD_3COCD_3 0.09−0.15 ppm for $[Zn(CF_3CO_2)_2T_1]$ and $[Zn(CF_3CO_2)_2T_2]$ respectively; and $\Delta\delta$ in CD_3COCD_3 0.55 ppm for $[IrCl_3T_1]$). This shift is related to the electron transfer from the nitrogen donor atoms to the metal center, which appears to be, in agreement with the Lewis acidity of the metal center, more relevant for the Ir(III) ion than the Zn(II) ion. The coupling constant between the trans olefinic hydrogens in terpyridines T_1 (J_{trans} = 16.2 Hz) and T_2 (J_{trans} = 15.4 Hz) is maintained in their metal complexes (see Experimental Section).

The Ru(III) ion is a d^5 low-spin ($^5t_{2g}$) paramagnetic metal center, but in the case of the $[Ru(CF_3CO_2)_3T_3]$ complex, a well-defined ^{1}H NMR spectrum in CD_3CN was obtained, which showed the expected "Fermi contact shift" of the hydrogen atoms of the terpyridine ligand closer to the paramagnetic metal center.[22a,b] The spectrum of $[Ru(CF_3\text{-}CO_2)_3T_3]$, when compared, for example, to that of $[IrCl_3T_3]$, shows that the signals of the hydrogens in α position of the central pyridinic ring are shifted, not to lower fields with respect to those of the free terpyridine (δ = 8.43 ppm in CD_3CN), but to higher fields, with a significant shielding effect (δ = 7.43 ppm in CD_3CN). This observation would suggest that, in the Ru(III) complex, the electron spin density is shifted from the metal to the terpyridine ligand.

Dipole Moments. Dipole moments of terpyridines and complexes, when sufficiently soluble, were measured in $CHCl_3$ by the Guggenheim method (see Table 1).[13]

Dipole moments of terpyridines T_1 and T_2 are low, comparable to each other, and only slightly higher than that of the less π-delocalized ligand T_0. In addition, dipole moments of T_0 and T_3 are similar, although they bear a strong donor and a strong acceptor substituent respectively (Table 1). This result would suggest, as confirmed by DFT geometry optimizations (see below), that the phenyl group in position 4 of the central pyridine ring of these terpyridines is not coplanar with the pyridine ring itself, thus reducing the π interactions between the two rings and therefore the significant electronic transitions.

Scheme 4



The molecular geometry of the model 4′-(C_6H_4-*p*-NMe_2)-2,2′:6′,2″-terpyridine of T_0 was optimized taking into account two isomers, labeled as "up" (or *transoid*) and "down" (or *cisoid*), which differ for the orientation of the terpyridyl nitrogen atoms (see Scheme 4). For the up isomer the three terpyridine aromatic rings are essentially planar, while the substituted phenyl ring bearing the donor group is twisted with respect to the terpyridine plane by 30.4°. The NMe_2 group is essentially coplanar with the phenyl ring to which it is bound. The down isomer is instead characterized by a twisting of the terminal terpyridine rings with respect to the central one of ca. 30° to minimize the repulsion between the two nitrogen lone pairs.

We calculate the up isomer to be more stable than the corresponding down isomer by 14.5 kcal/mol when including solvation effects. Therefore, the very low experimental dipole moment of all the terpyridines investigated is obviously related to the presence in solution of only the up isomer, with a *transoid* configuration about the interannular carbon−carbon bonds, as it occurs for 2,2′:6′,2″-terpyridines.[23] As a matter of fact, we obtained a fairly good agreement between the calculated dipole moment (1.69 D) of the reduced model of T_0 with two methyl groups at the nitrogen atom and the experimental dipole moment of T_0 (2.1 D).

The shift of the terpyridine geometry from *transoid* to *cisoid* configuration upon coordination also justifies the unusually strong increase of the dipole moment (Table 1) occurring upon coordination (μ enhancement factor = $\mu_{complex}/\mu_{terpyridine}$), an increase much stronger than that of other chelating nitrogen donor π-delocalized ligands, such as phenanthrolines and bypyridines.[3f,4b] However, the enhancement factor is slightly higher for terpyridine T_0 (μ enhancement factor 3.8−4.8) than for the more delocalized terpyridines T_1 and T_2 (μ enhancement factor 2.3−3), which is in agreement with what was reported for some Zn(II) and Cd(II) complexes with substituted phenanthrolines.[3f] For Zn(II) complexes of T_0, the dipole moment increased with the increased electron-withdrawing strength of the ancillary ligand (see Table 1; μ enhancement factor = 3.8 for $[ZnCl_2T_0]$ and 4.7 for $[Zn(CF_3CO_2)_2T_0]$).

Given its very low dipole moment, coordination of terpyridine T_3 to Ir(III) leads to a very high enhancement factor (5.3). In the case of $[Ru(CF_3CO_2)_3T_3]$, which was not soluble enough in $CHCl_3$ to obtain reproducible dipole moment measurements, the dipole moment calculated by DFT in $CHCl_3$ solution (see Table 1) confirms a significant enhancement factor (4.8).

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UV−Visible Spectra. The UV−visible spectra in $CHCl_3$ of terpyridines carrying a NR_2 electron donor substituent show one strong absorption band around 360−399 nm, attributed to the $n \rightarrow \pi^*$ ILCT transition, which emanates from the donor group.[3d,e,6] As in chelating nitrogen donor ligands, such as phenanthrolines,[3f] the absorption band of the ILCT transition is located at lower energy by increasing the length of the π-delocalized spacer between the electron donor group and the chelating system (see Table 1). For the reduced model of T_0, the calculated TDDFT absorption maximum in solution for the ILCT transition (368 nm) is in excellent agreement with the experimental value of 360 nm and confirms the assignment of the main spectral feature as a ILCT single transition involving the HOMO and LUMO as starting and arriving orbitals, respectively.

Upon coordination of T_0, T_1, and T_2 to Zn(II), Ru(III), or Ir(III) metal centers, this ILCT transition is red-shifted with respect to the free terpyridine (0.46−0.77 eV for T_0; 0.41−0.54 eV for T_1; 0.31 eV for T_2; see Table 1), according to the increased acceptor properties of the π^* orbitals of the terpyridine due to coordination.[3d−f] In the case of T_0 and T_1, the shift of the ILCT transition is higher by coordination to Ir(III) and Ru(III) centers than to Zn(II) centers, in agreement with the increased Lewis acidity.[3e] In addition to the ILCT transition, terpyridines T_0, T_1, and T_2 show absorption bands at higher energy, which can be attributed mainly to $\pi \rightarrow \pi^*$ transitions, involving their π core only, much less solvatochromic, as expected for transitions centered on the ligand (LC) of low charge-transfer character.

In accordance with the absence of ILCT transitions, the UV−visible spectrum of terpyridine T_3, bearing an electron−withdrawing NO_2 group instead of an electron−donating NR_2 group, shows only one absorption band at higher energy (λ = 280 nm), as expected for a $\pi \rightarrow \pi^*$ transition centered on the ligand (LC).

In addition to the red-shifted ILCT absorption band, in the spectra of $[Ru(CF_3CO_2)_3T_0]$, $[RuCl_3T_0]$, and $[RuCl_3T_1]$ one relatively weak absorption band appears at 911, 795, and 866 nm respectively. The latter can be tentatively assigned to a LMCT transition,[8a] on the basis of the positive value of $\Delta\mu_{eg}$ (difference between excited- and ground-state dipole moments) obtained by a solvatochromic investigation (see Table 1) and according to the literature.[9,10] In addition this assignment is in agreement with the sensitivity of the energy of the transition to the nature of the anionic ancillary ligand and in particular with the absence of such a band in the spectrum of the complex $[Ru(CF_3CO_2)_3T_3]$ (see Table 1), where the terpyridine is lacking the donor group, which is involved in the LMCT transition. A recent, theoretical time-dependent DFT investigation on the electronic transitions of $[Ru(CF_3CO_2)_3T_0]$ has confimed our assignment.[24]

The electronic spectra of Ir(III) complexes show two major absorption bands (see Table 1). For the complexes with T_0 and T_1 ligands, the band at higher energy (465, 463, and 476 nm respectively) cannot be due only to an ILCT transition (red-shifted, as expected, by 105, 103, and 81 nm respectively, with respect to the ILCT transition of the free ligands), but also to another charge-transfer contribution located under the ILCT, probably a MLCT transition.[7f,g] This latter hypothesis is evidenced by both the high intensity of the band and the slightly negative value of $\Delta\mu_{eg}$ obtained by a solvatocromic investigation, which would suggest the presence of a MLCT transition under the ILCT transition, which, if alone, should produce a positive $\Delta\mu_{eg}$ contribution.

This hypothesis is also supported by the larger negative value of $\Delta\mu_{eg}$ for $[IrCl_3T_1]$ than for $[IrCl_3T_0]$ and by the very large negative value of $\Delta\mu_{eg}$ of the absorption band at 413 nm for the complex $[Ir(4\text{-}EtC_6H_4CO_2)_3T_3]$, with a terpyridine that bears an electron acceptor NO_2 instead of an electron donor NR_2 group. Therefore, the ILCT transition is lacking, being originated by the NR_2 group, and the absorption band is related only to a MLCT transition, in agreement with the large negative value of $\Delta\mu_{eg}$ favored by the presence of the electron-withdrawing NO_2 group (see Table 1).

All Ir(III) complexes show a second weaker band at 520−540 nm, which can be tentatively assigned to another MLCT transition according to the literature[7f,g] and is in agreement with its significant negative $\Delta\mu_{eg}$ value (obtained by a solvatocromic investigation), which increases by going from the T_0 and T_1 complexes to $[Ir(4\text{-}EtC_6H_4CO_2)_3T_3]$, as expected for a MLCT transition (see Table 1).

3. EFISH and Solvatochromic Investigation of Second-Order NLO Properties. The EFISH technique[5] was used to investigate the effect of the different metal centers studied in this work on the quadratic hyperpolarizability β_λ of terpyridines T_0, T_1, T_2, and T_3. Measurements were performed in $CHCl_3$, working mainly with a fundamental incident wavelength of 1.34 μm, chosen to have a second harmonic (at 670 nm) far enough from the absorption bands of all the complexes investigated. In this way the quadratic hyperpolarizability is not overestimated due to resonance effects, as it could occur, for instance, in the case of Ru(III) complexes if working with a fundamental incident wavelength of 1.907 μm, which is usually considered off resonance, but which in these complexes could produce a second harmonic resonant with the weak absorption around 795−911 nm (see Table 1).

However, for Ir(III) complexes, EFISH measurements were carried out working with both 1.34 and 1.907 μm incident wavelengths, with the exception of $[Ir(4\text{-}EtC_6H_4\text{-}CO_2)_3T_0]$. In this case, the quadratic hyperpolarizability was measured only with an incident wavelength of 1.907 μm.

The investigation on the second-order NLO properties was also supported by a solvatocromic investigation, carried out to define the contributions of the various absorption bands to the second-order NLO response.[6,8a]

The static hyperpolarizability value calculated for the reduced model of T_0, essentially due to the zzz component, is in good agreement with the experimental frequency-dependent values (19×10^{-30} and 22×10^{-30} esu respectively). Clearly, the calculated value is smaller due to the effect of frequency dispersion.

(24) De Angelis, F.; Fantacci, S.; Sgamelotti, A.; Cariati, F.; Roberto, D.; Tessore, F.; Ugo, R. manuscript submitted to *Dalton Transactions*.

The latter result is more evidence that, in the terpyridines investigated in this work carrying a NR_2 donor group, the quadratic hyperpolarizability value is dominated by the ILCT transition, as confirmed by solvatochromic investigation (Table 1).

We have shown that, for terpyridines carrying a NR_2 group (T_0, T_1, T_2), increasing the length of the π-conjugated spacer between the NR_2 group and the chelated system of the terpyridine, a significant increase of $\beta_{1.34}$ occurs (from 22 $\times$ 10^{-30} esu for T_0 to 52 $\times$ 10^{-30} esu for T_1 and finally to 95 $\times$ 10^{-30} esu for T_2). A similar enhancement was reported for planar ligands such as stilbazoles,[3e] or 5-X-1,10-phenanthrolines (X = NMe_2, X = *trans*-CH=CHC_6H_4-4′-NMe_2, X = *trans,trans*-$(CH=CH)_2C_6H_4$-4′-NMe_2).[3f] As in the case of pyridines para substituted with an electron-withdrawing group,[3e] the $\beta_{1.34}$ value of T_3, carrying an electron-withdrawing NO_2 group, is small and negative (see Table 1).

In agreement with the significant red shift of the ILCT (see Table 1), upon coordination of terpyridines T_0, T_1, and T_2 to Zn(II), the quadratic hyperpolarizability value shows a relevant enhancement and has still a positive sign. The enhancement factor EF (given by $\beta_{1.34,complex}/\beta_{1.34,terpyridine}$), a useful parameter to evaluate the coordination effectiveness,[3e,f] increases with the increasing electron-withdrawing character of the ancillary ligand (EF = 3.0 for $[ZnCl_2T_0]$; EF = 4.0 for $[Zn(CF_3CO_2)_2T_0]$). Some of us[3e,f] have already shown that, given the same metal center and the same ancillary ligands, the EF decreases when the length of the π-conjugated system of the linker connecting the donor NR_2 group is increased. (EF = 4.0 for $[Zn(CF_3CO_2)_2T_0]$; EF = 3.5 for $[Zn(CF_3CO_2)_2T_1]$; EF = 1.4 for $[Zn(CF_3CO_2)_2T_2]$).

However, such relevant enhancement factors cannot be attributed only to the red-shift of the ligand ILCT transition, but also to the stabilization of the *cisoid* conformation of the terpyridine due to chelation. The significant role of chelation in increasing the quadratic hyperpolarizability of chelating ligands was already discussed by some of us for bypyridines carrying NR_2 strong electron donor groups.[4b]

The negative value of $\beta_{1.34}$ of $[Ru(CF_3CO_2)_3T_0]$, as shown by the solvatochromic investigation (Table 1), is due to the significant contribution to the second-order NLO response of the band at 911 nm. This band must produce a negative contribution since it is located at a wavelength higher than the second harmonic. The ILCT transition of the ligand, red-shifted as expected, gives a significant positive contribution to $\beta_{1.34}$ as it occurs in Zn(II) complexes. Also, the absorption band at 508 nm, which we attributed to a LMCT transition, gives a positive contribution to $\beta_{1.34}$, but, in this case, $\beta_{1.34}$ remains dominated by the negative contribution of the band at 911 nm (Table 1). In fact, the negative contribution of this LMCT band becomes much less relevant in the specific case of the related complex $[RuCl_3T_1]$, thus giving rise to a positive value of $\beta_{1.34}$.

The complex $[IrCl_3T_0]$ shows a significant enhancement of the absolute value of the quadratic hyperpolarizability (EF = 5.0) which, however, becomes negative. As suggested in our preliminary communication,[8a] this is due to the large and negative contribution to the quadratic hyperpolarizability of the band at 533 nm, attributed to a MLCT transition (see Table 1). Interestingly, in this complex, the positive contribution of the red-shifted ligand ILCT transition is not so relevant, due to the negative contribution of a MLCT transition. Both transitions are probably under the absorption band of 465 nm, as discussed in the section devoted to UV−visible spectra, so that the contribution of this band is finally slightly negative.

The negative value of the quadratic hyperpolarizability of this kind of terpyridinic complexes of Ir(III) was confirmed by the second-order NLO response of $[IrCl_3T_1]$ and $[Ir(4\text{-}EtC_6H_4CO_2)_3T_0]$ (Table 1).

In agreement with the significant role of the MLCT transition at about 520−540 nm in Ir(III) complexes, the $\beta_{1.34}$ value for the complex $[Ir(4\text{-}EtC_6H_4CO_2)_3T_3]$ is relevant and negative (see Table 1). In this latter case the $\beta_{1.34}$ enhancement factor is very high (EF = 19), and, as confimed by the solvatochromic investigation, is mainly due to the strong negative contribution of the MLCT transition at 521 nm, enhanced by the presence of the electron-withdrawing NO_2 substituent and of the negative contribution of the absorption band at 413 nm, which becomes significant due to the lack of the positive contribution of the ILCT transition (Table 1).

The comparison of $\beta_{1.907}$ of $[Ir(4\text{-}EtC_6H_4CO_2)_3T_0]$ (−70 $\times$ 10^{-30} esu) and $[Ir(4\text{-}EtC_6H_4CO_2)_3T_3]$ (−126 $\times$ 10^{-30} esu) is in support of the aforementioned statement.

In this work the solvatochromic investigation has confirmed its useful role for the study at least qualitatively of the electronic origin of the second-order NLO response.

For terpyridines T_0, T_1, and T_2 and their Zn(II) complexes we have shown that the major contribution to β_{CT} is given by the absorption band due to an ILCT transition at about 360−399 nm for the ligands and at about 425−454 nm for the complexes (see Table 1). EFISH $\beta_{1.34}$ and β_{CT} at 1.34 μm incident wavelength are comparable for the three terpyridines and for the Zn(II) complex with T_0, while β_{CT} is definitively lower than EFISH $\beta_{1.34}$ in the case of Zn(II) complexes with the more π delocalized terpyridines T_1 and T_2 (see Table 1).

Interestingly, there is good agreement, in sign and absolute value, between EFISH $\beta_{1.34}$ and β_{CT} , working with a 1.34 μm incident wavelength for the Ru(III) complex of T_0 and for the Ir(III) complexes of T_0 and T_1 (Table 1). The agreement is less satisfactory for the Ir(III) complex of T_3, although the sign is negative and the absolute value quite high in both cases. Such an excellent agreement would suggest that many charge-transfer transitions, which contribute to the overall second-order NLO response in Ir(III) and Ru(III), are located along the dipole moment axis. In fact, β_{CT} can be compared to EFISH β_λ only when the charge-transfer processes controlling the second-order NLO response are located close in direction to the dipole moment axis. This location was proved by a theoretical investigation carried out on the complex $[Ru(CF_3CO_2)_3T_0]$.[24]

The solvatochromic investigation has proved to be helpful in getting the necessary information to explain the positive

sign of EFISH $\beta_{1.34}$ and β_{CT} of [$RuCl_3T_1$] when compared to the negative sign of EFISH $\beta_{1.34}$ and β_{CT} of [$Ru(CF_3CO_2)_3T_0$].

In [$RuCl_3T_1$] the positive value of β_{CT} is due to a very weak absorption band at higher wavelengths (866 nm), thus giving only a small negative contribution to the overall β_{CT}, and is then dominated by the positive contribution of the band at 469 nm, which is probably the sum of a ILCT and an LMCT transition.[24] This latter observation confirms the important role played by ancillary ligands in tuning the second-order NLO response of these terpyridinic complexes, as shown when comparing the values of the quadratic hyperpolarizabilities of [$ZnCl_2T_0$] and [$Zn(CF_3CO_2)_2T_0$] and of [$IrCl_3T_0$] and [$Ir(4\text{-}EtC_6H_4CO_2)_3T_0$] (see Table 1).

Conclusions

In this work we have confirmed our preliminary findings[8a] about the relevant role of the nature of the metal ion in tuning the absolute value and sign of the second-order NLO response of Zn(II), Ru(III), and Ir(III) complexes with terdentate chelating push−pull π delocalized nitrogen donor ligands such as 4′-(1-C_6H_4-*p*-X)-2,2′:6′,2″-terpyridines (X = NBu_2, *trans*-CH=CH−C_6H_4-*p*-NBu_2, *trans,trans*-(CH=CH)$_2$−C_6H_4-*p*-NMe_2, NO_2).

While the second-order NLO response of other π-delocalized nitrogen donor ligand complexes (stilbazoles, phenanthrolines, etc.), carrying a NR_2 donor group with low oxidation state soft metal centers such as Rh(I) ($4d^8$), Ir(I) ($5d^8$), Os(II) ($5d^6$), W(0) ($5d^6$),[3c−e] or "$Os_3(CO)_{11}$" cluster core[25] or relatively hard Zn(II) ($3d^{10}$) centers,[3f,4] is dictated mainly by the red-shift of the ligand ILCT transition, we have shown that coordination of π-delocalized nitrogen donor ligands, such as terpyridines, to higher oxidation d open metal centers such as Ir(III) ($5d^6$) or Ru(III) ($4d^5$) produces a second-order NLO response strongly influenced also by LMCT or MLCT transitions, in such a way that they can even change the sign of the quadratic hyperpolarizability. A change of sign was reported for low oxidation state metal complexes only when the push−pull π-delocalized nitrogen donor ligand carries an electron withdrawing group, due to the significant role of the MLCT transition.[3b,d,e] We have shown that this effect is strongly enhanced in an Ir(III) complex with a terpyridine carrying an electron withdrawing NO_2 group. We have also confirmed that an important role is also played by chelation and by ancillary ligands; the ligands can tune the acceptor properties of the metal center, acting on the contribution of various transitions, to the overall second-order NLO response, either by perturbation of the π^* level of the push−pull π delocalized nitrogen donor ligand (ILCT) or by controlling the energy of LMCT or MLCT processes.

It is also noteworthy that the terpyridines investigated in this work, which can be considered as 4-substituted pyridines but with the phenyl ring twisted about the interannular bond,[24,26] show a much higher second-order NLO response when free or coordinated to a metal center with respect to simple 4-substituted pyridines, for example 4-$NMe_2C_5H_4N$ ($\beta_{1.34} = 0.06 \times 10^{-30}$ esu)[3e] or 4-CNC_5H_4N ($\beta_{1.06}$ computed value $= 0.33 \times 10^{-30}$ esu).[3e] It seems that the nonplanarity of the two fused rings and therefore their poor π-conjugation do not decrease the quadratic hyperpolarizability, but, on the contrary, introduce a significant enhancement. This is an observation which deserves further investigation.

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