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New $[(D-terpyridine)-Ru-(D \text{ or } A-terpyridine)][4-EtPhCO_2]_2$ complexes (D = electron donor group; A = electron acceptor group) as active second-order non linear optical chromophores

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The dipolar and octupolar contributions of the second order nonlinear optical properties of $[(4'-(C_6H_4-p-D)-2,2':6',2''-terpyridine)-Ru-(4'-(C_6H_4-p-A)-2,2':6',2''-terpyridine)]Y_2$ heteroleptic complexes (D and A are donor and acceptor groups, respectively), and related free terpyridines and homoleptic complexes, have been obtained by means of a comprehensive combination of Electric Field Induced Second Harmonic generation, Third Harmonic Generation, and Harmonic Light Scattering measurements. These results evidence how a metal can act as a bridge between two π -delocalized terpyridine moieties bearing a D and an A group, respectively, leading to a large quadratic hyperpolarizability hugely dominated by the octupolar contribution.

Introduction

For π -delocalized nitrogen donor ligands, such as push-pull pyridines, bipyridines, and terpyridines, it is now well known that the dipolar contribution to the quadratic hyperpolarizability β_{EFISH} , which is measured by the solution-phase dc Electric Field Induced Second Harmonic generation (EFISH) method,¹ increases significantly upon coordination to a metal center, which, according to its oxidation state, may display an ambivalent acceptor or donor key role.² This enhancement of β_{EFISH} is due either to a red shift of the intraligand charge transfer (ILCT) transition upon coordination (when the π -delocalized nitrogen donor ligand bears a strong electron-donor substituent) or to a significant contribution to β_{EFISH} of metal-to-ligand (MLCT) or ligand-to-metal (LMCT) charge transfer transitions.² In these latter cases, β_{EFISH} may assume a negative sign, as a consequence of a negative value of $\Delta \mu_{eg}$, which is the difference between the dipole moment in the excited and ground state.^{2,3} In other words, a negative $\Delta \mu_{eg}$ value reflects a decrease of the dipole moment upon excitation, in contrast with the more frequent case of the acceptor group acquiring charge, or the donor

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group releasing charge, upon charge transfer. Such a situation is sometimes referred to as one whereby there is more charge transfer in the ground than in the excited state. Therefore, in the design of organometallic compounds with relevant nonlinear optical (NLO) properties, a metal center, due to its ambivalent acceptor or donor role, appears as an interesting bridge between two π -delocalized nitrogen ligands bearing an electron donor and an electron acceptor substituent, respectively. Ambivalence between the donor and acceptor natures had been pointed-out already at an early stage of molecular nonlinear optics, in the case of para-substituted pyridine-1-oxide derivatives. In this case, following a route by Katrizky et al.,4 the N-oxide group was shown to act either as a donor or as an acceptor, as triggered by the reciprocal acceptor or donor nature of the substituent group in the para position of the pyridine ring. This approach led to the investigation of the 3-methyl-4-nitropyridine-1-oxide (POM) as second order NLO molecular crystals.

We have now tried to follow a new approach, by studying the second order NLO features of cationic complexes of the type $[(D-terpyridine)-Ru-(A-terpyridine)]^{2+}$ (D and A are electron donor and acceptor groups, respectively) that would combine the peculiar characteristics of traditional push–pull organic chromophores (presence of a donor and an acceptor group linked by a bridge) with those of organometallic complexes (introduction of possible low energy metal to ligand or ligand to metal charge transfer transitions). Here, we report findings on the second order NLO properties of push–pull heteroleptic ($[T_{D1}RuT_A]$ -[EtPhCO₂]₂, $[T_{D2}RuT_A]$ [EtPhCO₂]₂, $[T_{D2}RuT_A]$ [EtPhCO₂]₂ and $[T_{D2}RuT_{D2}]$ -[EtPhCO₂]₂) cationic Ru(II) complexes (where T_{D1}, T_{D2} and T_{D3} are 4'-(C₆H₄-*p*-D)-2,2':6',2''-terpyridine with D=N(C₁₆H₃₃)₂, N(C₁₆H₃₃)₂PhCH=CH, and CH₃, respectively, whereas T_A

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Chart 1

Table 1 Electronic spectra, $\mu\beta_{1,907 \text{ EFISH}}$, μ , $\gamma_{1,907 \text{ EFISH}}$ and $\gamma_{1,907 \text{ THG}}$ of the free terpyridine ligands and their related Ru(II) complexes, working in CHCl₃ with an incident radiation wavelength of 1.907 µm

Compound ^{<i>a</i>}	λ_{\max} (nm)	$\begin{array}{l}\mu\beta_{1.907 \text{ EFISH}}\\(\times 10^{-48} \text{ esu})\end{array}$	$\mu_{\exp} \left(\mu_{\text{theo}} \right) (\text{D})$	$\beta_{1.907 \text{ EFISH}}^{b}$ (×10 ⁻³⁰ esu)	$\beta_{0,\text{EFISH}} (\beta_{0,\text{EFISH, theo}})$ (×10 ⁻³⁰ esu)	$\gamma_{1.907 \text{ EFISH}}$ (×10 ⁻³³ esu)	$\gamma_{1.907 \text{ THG}}$ (×10 ⁻³³ esu)
T _{D1}	362 ^c	247	$3.6 (2.1^d, 2.4^e)$	69	57 (29)	1.2	0.27
T _{D2}	397 ^c	350	5.1	69	54	1.7	0.22
T _{D3}	280 ^f	80	1.8	44	39	0.4	0.04
T _A	280 ^f	-17	1.7	-10	-9	-0.08	0.07
$[T_{D1}RuT_A]Y_2$	525 ^g	525	10	52	33 (118)	2.6	0.44
$[T_{D1}RuT_{D1}]Y_2$	547 ^g	_	Ca 0	_		0.9	0.50
$[T_{D1}RuT_{D3}]Y_2$	529 ^g	520	7.8	68	43 (96)	2.6	0.14
			$(7.5^{d,h}, 9.2^{e,h})$				
$[T_{D2}RuT_A]Y_2$	507 ^g	793	10.3	77	51	3.7	0.38
$[T_{D2}RuT_{D2}]Y_2$	528 ^g	_	Ca 0	_		1.5	1.62
$[T_{D2}RuT_{D3}]Y_2$	500 ^g	540	10.2	53	36	2.8	0.32

^{*a*} Y = 4-EtPhCO₂. ^{*b*} The experimental value of μ was used to calculate $\beta_{1.907 \text{ EFISH}}$. ^{*c*} ILCT transition. ^{*d*} Calculated *in vacuo* with 3-21g* basis set. ^{*e*} Calculated in CHCl₃ solution with 3-21g* basis set. ^{*f*} $\pi \to \pi^*$ transition. ^{*g*} There is superposition of the MLCT and ILCT transitions. ^{*h*} Calculated with N(*n*-butyl)₂ instead of N(*n*-hexadecyl)₂.

is 4'-(C₆H₄-p-NO₂)-2,2':6',2"-terpyridine; see Chart 1). Their second order NLO response, along with that of the free terpyridines, was measured in solution by means of a comprehensive combination of EFISH, THG (Third Harmonic Generation), and HLS (Harmonic Light Scattering) methods in order to evaluate both the dipolar and octupolar contributions to the quadratic hyperpolarizability.^{6,7} An incident wavelength of 1907 nm was used, whose second harmonic 2ω and third harmonic 3ω lie at 953 and 636 nm, respectively, which means they are in a transparent region with respect to the absorption electronic spectra of all the ruthenium cationic complexes and terpyridines investigated. To gain insight into the electronic structure and optical properties of the investigated complexes we also performed Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT) calculations. Since in CHCl₃ solutions all the investigated cationic complexes generate strong ion-pairing, we were able to measure the dipole moments of the ion pairs by the Guggenheim method.⁸

Results and discussion

Synthesis and spectroscopic characterization

The terpyridines ligands were prepared as previously described,^{9,10} whereas the heteroleptic and homoleptic Ru(II)

complexes were prepared following the method reported in the literature for related compounds.^{11*a*} 4'-(C₆H₄-*p*-D)-2,2':6',2''-terpyridine (T_{D1} or T_{D2}) was reacted with a stoichiometric amount of RuCl₃·*n*H₂O, in ethanol under reflux, to give [RuCl₃(4'-(C₆H₄-*p*-D)-2,2':6',2''-terpyridine)]. This was followed by treatment, in methanol under reflux, with the other terpyridine (T_{D1}, T_{D2}, T_{D3} or T_A), in the presence of a catalytic amount of *N*-ethylmorpholine as a reducing agent. The cationic complexes were finally purified and crystallized by addition of 4-EtPhCO₂T was chosen as the counterion because it gives a good solubility to all the cationic species investigated in CHCl₃, a relatively low polar solvent that allows, by strong ion-pairing, EFISH measurements to be carried out even for ionic species.¹²

All ligands and complexes were characterized by ¹H NMR, electronic absorption spectroscopy, mass spectrometry (Fast Atom Bombardment, FAB⁺), and elemental analysis (see Experimental section).

Electronic absorption spectra (Table 1) of the free terpyridine ligands T_{D1} and T_{D2} , in addition to $\pi - \pi^*$ transitions at *ca.* 280 nm, show one strong absorption band at 362 and 397 nm, respectively, which can be attributed to the intraligand charge transfer (ILCT) transition that emanates from the dialky-lamino group. Upon coordination to a Ru(II) center, this band is significantly red-shifted (λ_{max} is shifted to *ca.* 500–547 nm) and

becomes broader due to superposition of the ILCT and $MLCT^{11,13,14}$ transitions, see below.

EFISH and THG investigation

In order to investigate their nonlinear optical properties, the various free terpyridines and complexes were first investigated by EFISH and THG (see Table 1). It is known that the EFISH technique¹ can provide direct information on the intrinsic molecular second order NLO properties through eqn (1):

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

where $\mu\beta_{\text{EFISH}}/5kT$ is the dipolar orientational contribution, β_{EFISH} is the projection along the dipole moment axis of the vectorial component of the tensor of the quadratic hyperpolarizability, and $\gamma(-2\omega; \omega, \omega, 0)$, which is a third order term at frequency ω of the incident light, is a purely electronic cubic contribution to γ_{EFISH} . The cubic contribution is usually negligible when studying (with the EFISH technique) the second order NLO properties of push-pull dipolar compounds such as terpyridines.^{2,9} Therefore, for the terpyridine ligands and related heteroleptic complexes investigated here, the cubic contribution can be reasonably neglected, also because the cubic γ_{THG} values are less than 5–20% of the $\gamma_{\rm EFISH}$ values, allowing therefore the determination of $\mu\beta_{1.907}$ EFISH (Table 1). On the contrary, the γ_{THG} values of the homoleptic complexes $[T_{D1}RuT_{D1}]$ - $[EtPhCO_2]_2$ and $[T_{D2}RuT_{D2}][EtPhCO_2]_2$ are quite similar to those of the related γ_{EFISH} values, in agreement with a negligible dipolar contribution and a relevant role of $\gamma(-2\omega; \omega, \omega, 0)$, which is the cubic contribution.

In order to obtain β_{EFISH} from EFISH measurements, it is necessary to know the value of the dipole moments. These were measured for the terpyridines and their complexes using the Guggenheim method,⁸ working in chloroform solution. It should be pointed out that the dipole moments measured in the case of the cationic complexes could be overestimated, since we measured the dipole moment of strong ion-pairs.¹⁵ Although this can lead to an underestimation of the value of the $\beta_{1.907}$ EFISH values of the ionic complexes, it is not problematic in the present study, as the dipolar contribution is expected to be much lower than the octupolar one in these π -delocalized systems, as described below.

As evidenced in Table 1, we applied the two-level model¹ to calculate the zero-frequency static quadratic hyperpolarizability β_0 from β_{EFISH} , measured at 1.907 µm, using the following expression:

$$\beta_0 = \beta_{\text{EFISH}} (1 - (2\lambda_{\text{max}}/\lambda)^2) (1 - (\lambda_{\text{max}}/\lambda)^2)$$
(2)

where λ is the fundamental wavelength of the incident photon (1907 nm) and λ_{max} is the maximum absorption value of the charge transfer transition that is mainly responsible for the second order NLO response (Table 1).

For the terpyridine ligands bearing a donor substituent, where the second order NLO response can be ascribed mainly to the ILCT transition,⁹ the $\mu\beta_{1.907}$ _{EFISH} value of T_{D3} is lower than that of the related T_{D1}, due to both a lower value of the dipole moment and a lower $\beta_{1.907}$ _{EFISH}, since a methyl group is not a strong donor when compared to a dialkylamino group. Besides, the $\mu\beta_{1.907\ EFISH}$ value of the more π -delocalized terpyridine T_{D2} is higher than that of T_{D1} due to a higher value of the dipole moment. The terpyridine T_A , bearing a withdrawing NO₂ group, is characterized by a small and negative $\mu\beta_{1.907\ EFISH}$ value, as previously reported.⁹

The significant red shift of the ILCT transitions that is produced upon coordination of the terpyridines T_{D1} and T_{D2} (see Table 1) is consistent with the perturbation due to the acidic character of the Ru(II) center, which enhances the strength of the pyridine acceptor part of the ligands and so induces an increase of their second order NLO response.^{2,9} Heteroleptic complexes $[T_{D1}RuT_A][EtPhCO_2]_2$ and $[T_{D2}RuT_A][EtPhCO_2]_2$ show a $\mu\beta_{1.907 \text{ EFISH}}$ value that is higher (enhancement factor = 2.1–2.3) than that of free T_{D1} and T_{D2} , respectively, but this enhancement is mainly due to an increase of the dipole moment. The $\mu\beta_{1.907 \text{ EFISH}}$ value of $[T_{D2}RuT_A][EtPhCO_2]_2$ is higher (by a factor of 1.5) than that of [T_{D2}RuT_{D3}][EtPhCO₂]₂, which has a similar dipole moment. This shows that the presence of a strong electron-withdrawing group on the second terpyridine may exalt the second order NLO response, like in traditional push-pull organic chromophores. However, this enhancement is relatively small and not observed for the couple [T_{D1}RuT_A][EtPhCO₂]₂/ $[T_{D1}RuT_{D3}][EtPhCO_2]_2$.

HLS investigation

In order to have a complete understanding of the second order NLO properties of the terpyridines and the related cationic ruthenium(II) complexes investigated, and in particular to evaluate also the octupolar contribution to the quadratic hyperpolarizability, we completed our EFISH and THG measurements using an HLS study, working at 1907 nm. The results are presented in Table 2. The dipolar (J = 1) and octupolar (J = 3) contributions and the modulus of the quadratic hyperpolarizability ($\|\vec{\beta}_{1.907}\|$) have been calculated using the following equations, ^{6,7,16} assuming that all the compounds, in good approximation, have a C_{2v} symmetry.

$$\|\overline{\beta}\|^{2} = \|\overline{\beta}^{I=1}\|^{2} + \|\overline{\beta}^{I=3}\|^{2}$$
(3)

$$\gamma_{0,C_{2(\mathrm{or}\infty)\nu}} = \frac{\mu^{(0)}}{\sqrt{15}k_{\mathrm{B}}T} \left\| \overline{\beta}^{J=1} \right\| \tag{4}$$

$$\langle \beta_{\text{HLS}}^2 \rangle = \langle |\beta_{\text{XXX}}|^2 \rangle + \langle |\beta_{\text{ZXX}}|^2 \rangle = \frac{2}{9} \left\| \overline{\beta}^{J=1} \right\|^2 + \frac{2}{21} \left\| \overline{\beta}^{J=3} \right\|^2 \tag{5}$$

As evidenced in Table 2, all of the terpyridines and related cationic complexes investigated are characterized by a remarkably high value of $\|\vec{\beta}^0\|$. This is due to a very high contribution of the octupolar component, as expected for very rich electron systems. For the free terpyridines bearing an electron donor group, the octupolar contribution $(\|\vec{\beta}_{1.907}^{J=3}\|)$ is 10 to 15 times higher than the dipolar contribution $(\|\vec{\beta}_{1.907}^{J=1}\|)$, whereas for the heteroleptic complexes the enhancement is even higher (by a factor of 20 to 66). This result is of particular relevance because it confirms that the quadratic hyperpolarizability of a dipolar compound can be largely dominated by the octupolar component, as recently observed in the case of cyclometallated neutral $Ln(m)^{17}$ or cationic $Ir(m)^{18}$ complexes.

Compound	$\langle \beta_{1.907 \text{ HLS}} \rangle$ (×10 ⁻³⁰ esu)	$\langle \boldsymbol{\beta}^{0}_{\rm HLS} \rangle$ (×10 ⁻³⁰ esu)	$\ \bar{\beta}_{1.907}^{J=1}\ $ (×10 ⁻³⁰ esu)	$\ \bar{\beta}_{1.907}^{J=3}\ $ (×10 ⁻³⁰ esu)	$\ \bar{\beta}_{1.907}\ _{(\times 10^{-30} \text{ esu})}$	$\ \bar{\beta}^{0}\ $ (×10 ⁻³⁰ esu)
T _{D1}	178	147	53	571	573	473
T _{D2}	215	170	53	692	694	549
T _{D3}	162	145	34	522	523	468
TA	260	232	-8	842	842	751
$[T_{D1}RuT_A]Y_2$	511	330	41	1655	1655	1068
$[T_{D1}RuT_{D1}]Y_2$	427	263	<i>ca.</i> 0	<i>ca</i> . 1384	ca. 1384	854
$[T_{D1}RuT_{D3}]Y_2$	320	205	53	1034	1035	662
$[T_{D2}RuT_A]Y_2$	1201	801	59	3890	3890	2594
$[T_{D2}RuT_{D2}]Y_2$	846	542	Ca 0	2741	2741	1756

Table 2 $\langle \beta_{1.907 \text{ HLS}} \rangle$, $\langle \beta^0_{\text{HLS}} \rangle$, dipolar and octupolar contributions and the modulus of the quadratic hyperpolarizability of some free terpyridine ligands and their related Ru(II) complexes, working in CHCl₃ with an incident radiation wavelength of 1.907 µm

It is worth pointing out that the $\|\bar{\beta}_{1.907}^{J=3}\|$ value of $[T_{D1}RuT_{D3}]$ [EtPhCO₂]₂ is similar to the sum of those of the two free terpyridines $(T_{D1} + T_{D3})$, and that the $\|\bar{\beta}_{1.907}\|^{J=3}$ values of [T_{D1}RuT_{D1}][EtPhCO₂]₂ and [T_{D1}RuT_A][EtPhCO₂]₂ are slightly higher (by a factor of 1.2 times) than the sum of the two terpyridines $(T_{D1} + T_{D1} \text{ and } T_{D1} + T_A$, respectively). This suggests the absence of an effect on the second order NLO response due to a charge transfer through the ruthenium center, so that a simple additive model could be used to give approximately the octupolar contribution of the quadratic hyperpolarizability of these Ru (II) complexes. However, the $\|\bar{\beta}_{1.907}^{J=3}\|$ value of $[T_{D2}RuT_{D2}]$ -[EtPhCO₂]₂ is 1.6 times higher than the sum of the value of the two terpyridines, whereas the $\|\bar{\beta}_{1,907}^{J=3}\|$ value of $[T_{D2}RuT_A]$ -[EtPhCO₂]₂ is 2.5 times higher than the sum of the value of the two terpyridines (T_{D2} and T_A). This suggests that, with the terpyridine T_{D2}, the metal plays a role in the second order NLO response. Similarly, an increase (although much lower, a factor of 1.3 times) of the dipolar contribution value, $\|\bar{\beta}_{1.907}^{J=1}\|$, of $[T_{D2}RuT_A]$ [EtPhCO₂]₂ is observed with respect to the sum of the two terpyridines (T_{D2} and T_A), but this is not the case for $[T_{D1}RuT_A]$ [EtPhCO₂]₂. Clearly, the role of the metal as a transmitter seems to be relevant only with complexes bearing a ligand with a more π -delocalized push-pull system, such as terpyridine T_{D2}.

Computational analyses

The representative $[T_{D1}RuT_A]^{2+}$, $[T_{D1}RuT_{D3}]^{2+}$ and $[T_{D2}RuT_A]^{2+}$ complexes have been investigated by means of Density Functional Theory (DFT) and Time Dependent DFT (TDDFT) to gain insight into their electronic and optical properties.

The geometry, electronic structure and TDDFT calculations have been performed with the Gaussian03 program package.¹⁹ Geometry optimizations, performed at the B3LYP/3-21G* level without any symmetry constraint, are in good agreement with the crystallographic data reported in the literature.^{11*a*} For the calculation of the optical absorption spectra by TDDFT we investigated the effect of the exchange-correlations functional and included solvation effects by means of the non-equilibrium C-PCM implementation²⁰ on the geometries optimized *in vacuo*. TDDFT calculations have been performed with the larger DZVP basis set for all atoms; the same B3LYP functional used for geometry optimizations as well as the PBE0 and MPW1K functionals have been tested, to check the effect of the amount of

Hartree–Fock (HF) exchange on the electronic and optical properties of the investigated systems. Indeed, the B3LYP functional²¹ contains 20% HF exchange, the PBE0²² 25% HF exchange and the MPW1K²³ 41.7% of HF exchange. As will be clear in the following, for the more extended and π -delocalized TD₂ system only the MPW1K functional provides reasonable results. Static hyperpolarizabilities were calculated for the related $[T_{D1}RuT_A]^{2+}$ and $[T_{D1}RuT_{D3}]^{2+}$ by a finite field differentiation of analytic polarizabilities, employing the B3LYP functional.²⁴ We only report the *zzz* component of the static hyperpolarizability tensor (β^0_{zzz}), *i.e.* the hyperpolarizability component oriented along the dipole axis, since all the other components are at least one order of magnitude smaller than the *zzz* one, so that β^0_{zzz} can be directly compared with the static hyperpolarizability derived from EFISH experiments.

The optimized geometrical structures for $[T_{D1}RuT_A]^{2+}$ and $[T_{D2}RuT_A]^{2+}$ do not show significant differences in the coordination sphere of the metal center and will not be discussed in detail. A schematic representation of the molecular orbitals obtained by the MPW1K functional in CHCl₃ solution for $[T_{D1}RuT_A]^{2+}$ and $[T_{D2}RuT_A]^{2+}$ is reported in Fig. 1.

In the investigated complexes, the Highest Occupied Molecular Orbital (HOMO) is a π -bonding orbital localized on the terpyridine system of the T_{Dx} (x = 1, 2) ligand bearing the NBu₂ substituent, with substantial contribution from the latter, whereas the Lowest Unoccupied Molecular Orbital (LUMO) is a π^* orbital localized on the T_A ligand, see Fig. 1. A 3.44 eV HOMO–LUMO gap is calculated for $[T_{D1}RuT_A]^{2+}$, which reduces to 2.69 eV in $[T_{D2}RuT_A]^{2+}$, see Fig. 1. This is mainly the result of the strong destabilization of the occupied molecular orbitals found in $[T_{D2}RuT_A]^{2+}$, due to the increased electron richness and π -delocalization of T_{D2} compared to T_{D1} ; the LUMOs lie at essentially the same energy in the two complexes (3.63 *vs.* 3.64 eV in $[T_{D1}RuT_A]^{2+}$ and $[T_{D2}RuT_A]^{2+}$, respectively).

Substantial differences between the $[T_{D1}RuT_A]^{2+}$ and $[T_{D2}RuT_A]^{2+}$ complexes are found also in the lower lying occupied orbitals. Indeed, while in $[T_{D1}RuT_A]^{2+}$ the HOMO – 1/HOMO – 3 have mainly Ru-t_{2g} character, with a small contribution coming from the C and N p orbitals of both terpyridines, in $[T_{D2}RuT_A]^{2+}$ substantial mixing of the Ru-t_{2g} orbitals with T_{D2} π -bonding character takes place, see the HOMO – 1 in Fig. 1. The lower-lying HOMO – 2/HOMO – 4 maintain a similar mixing of metal and ligand character, while no t_{2g} metal character is found in the lower-lying frontier molecular orbitals.



Fig. 1 A schematic representation of the molecular orbitals for the $[T_{D1}RuT_A]^{2+}$ and $[T_{D2}RuT_A]^{2+}$ complexes, calculated in CHCl₃ solution by the MPW1K functional and the DZVP basis set. Also shown are the isodensity plots of selected molecular orbitals for the $[T_{D1}RuT_A]^{2+}$ and $[T_{D2}RuT_A]^{2+}$ complexes.

The LUMO + 1 of $[T_{D1}RuT_A]^{2+}$ is essentially delocalized on the terpyridine of the T_A ligand, with some involvement of the t_{2g} Ru orbitals, reflecting π -back donation from the metal, while in $[T_{D2}RuT_A]^{2+}$ the LUMO + 1 is a π^* orbital localized on the T_{D2} ligand, see Fig. 1.

It is interesting to notice the remarkable effect of solvation and exchange-correlation functional on the calculated electronic structure of $[T_{D2}RuT_A]^{2+}$. As an example of the effect of solvation, we notice that *in vacuo* a substantial reduction of the HOMO–LUMO gap is calculated compared to the system in solution (1.75 *vs.* 2.69 eV, respectively). Comparing the results in solution using the PBE0 and MPW1K exchange-correlation functionals, we notice again a remarkable effect: the HOMO– LUMO gap is calculated to be 1.63 eV with PBE0 *vs.* 2.69 with MPW1K, due to a concomitant HOMO stabilization (0.60 eV) and LUMO destabilization (0.46 eV) taking place with the latter functional.

We then performed TDDFT excited state calculations to gain insight into the optical properties of the investigated systems and to assign their absorption spectra. As found above for the HOMO–LUMO gaps, the excited states are extremely sensitive to solvation and functional effects: as an example, the lowest excitation energy in solution is computed to be 2.25 (1.43) eV with the MPW1K (PBE0) functional. The substantial functional effect is essentially due to the increased amount of HF exchange in MPW1K, which increases the HOMO–LUMO gap and excitation energy. Based on the above results, we now discuss only the results obtained in solution with the MPW1K functional. The lowest excitation energy in $[T_{D2}RuT_A]^{2+}$ is calculated, as mentioned above, at 2.25 eV (550 nm). This is a strong (f = 1.62) Intra Ligand Charge Transfer (ILCT) transition involving the T_{D2} ligand: all the involved orbitals are mainly localized on the T_{D2} ligand, with the main contribution from the HOMO \rightarrow LUMO + 1 excitation and a small but sizable contribution arising from the HOMO $-1 \rightarrow$ LUMO +1 excitation, which is of mixed Ru-T_{D2} character, see above. The HOMO \rightarrow LUMO excitation is calculated to be the second excited state at 2.31 eV (536 nm), this state involving a $T_{\rm D2}$ to $T_{\rm A}$ charge transfer excitation. Due to the orthogonality of the $T_{\rm D2}$ and $T_{\rm A}$ terpyridine ligands, this transition has, however, zero oscillator strength and does not contribute to the absorption spectrum and (dipolar second-order) non-linear optical properties. The lowest transition is essentially the only relevant transition up to 400 nm, where some weak Metal to Ligand Charge Transfer (MLCT) excitations are computed. The calculated transition energy for the first excited state (550 nm, 2.25 eV) nicely compares with the experimental absorption maximum measured for $[T_{D2}RuT_A]^{2+}$ in CHCl₃ solution (507 nm, 2.45 eV), allowing us to assign the experimental feature to an ILCT transition of the T_{D2} ligand, red-shifted compared to that of the free ligand by coordination to the metal. The shift between calculated and experimental data is well within the accuracy of the employed methodology;

differences between calculations and experimental measurements can, however, be also originated because calculations have been performed on the free cationic Ru complexes, while experimental measurements are performed on the corresponding strong ion pair.

We notice that the peculiar electronic structure of the $[T_{D2}RuT_A]^{2+}$ complex, which translates into a substantial mixing of the ligand and metal orbitals also in the excited state, might be responsible of the communication between the donor and acceptor ligands that is evidenced by the non additive non-linear optical response of this system.²⁵ For the "conventional" $[T_{D1}RuT_A]^{2+}$ system, such mixing was not evidenced and a purely additive model of the non-linear optical response was found to hold for this system. Finally, we found that, in agreement with the experimental data, similar $\beta_{0,\text{EFISH}}$ are computed for the couple $[T_{D1}RuT_A][EtPhCO_2]_2/[T_{D1}RuT_{D3}][EtPhCO_2]_2$. Although these values are overestimated, compared to their experimental counterpart, they agree as order of magnitude, which considering the rather simplified level of theory, can be considered more than satisfactory.

Experimental

General comments

RuCl₃·xH₂O was purchased from Engelhard. Terpyridine T_{D3} was purchased from Sigma Aldrich and used without further purification, while ligands T_{D1},¹⁰ T_{D2},¹⁰ T_A⁹ and the salt 4-EtPhCOOAg⁹ were prepared as previously reported by some of us. All solvents were used as purchased, without further purification. Products were characterized by ¹H-NMR (Bruker DRX-300 spectrometer) and UV-vis (Jasco V-530 spectrophotometer) spectroscopy, mass spectrometry (Varian VG9090 spectrometer) and elemental analysis. Dipole moments, μ , were measured in CHCl₃ (amylene stabilized) by using a WTW-DM01 dipole meter (dielectric constant) coupled with a RX-5000 ATAGO Digital Refractometer (refractive index) according to the Guggenheim method.⁸ Elemental analyses were carried out at the Dipartimento di Chimica Inorganica, Metallorganica e Analitica "Lamberto Malatesta" of the Università degli Studi di Milano.

EFISH and THG measurements

All EFISH and THG measurements were carried out at the Dipartimento di Chimica Inorganica Metallorganica e Analitica "Lamberto Malatesta" of the Università degli Studi di Milano, in CHCl₃ solutions at a concentration of 1×10^{-3} M, working with a non-resonant incident wavelength of 1.907 µm, obtained by Raman-shifting the fundamental 1.064 µm wavelength produced by a Q-switched, mode-locked Nd³⁺:YAG laser manufactured by Atalaser. The apparatus for the EFISH and THG measurements is a prototype made by SOPRA (France). The $\mu\beta_{\rm EFISH}$ values reported are the mean values of 16 successive measurements performed on the same sample. The sign of $\mu\beta$ is determined by comparison with the reference solvent (CHCl₃).

HLS measurements

The HLS technique^{6,7,26} involves the detection of the incoherently scattered second harmonic generated by a solution of the molecule under irradiation with a laser of wavelength λ , leading to the measurement of the mean value of the $\beta \times \beta$ tensor product, $\langle\beta$ HLS \rangle . All HLS measurements were carried out at the École Normale Supérieure de Cachan in CHCl₃ at a concentration of 1×10^{-3} M, working with a low energy non resonant incident radiation of 1.907 µm.

Preparation of ruthenium complexes

For the numbering used in the attribution of the ¹H-NMR signals see below.



RuCl₃T_{D1} and RuCl₃T_{D2}

A solution of T_{D1} or T_{D2} (1 mmol) in MeOH or absolute EtOH was added to a solution of RuCl₃:xH₂O (1 mmol) in the same solvent. The resulting dark red mixture was refluxed for 4 h and then left at room temperature overnight. The brownish red precipitate thus collected was filtered, washed with a small amount of cold MeOH or absolute EtOH and dried in vacuum, affording the desired product in high yield (82% or 72%, respectively).

RuCl₃T_{D1}. MS-FAB⁺ m/z 943 (M - Cl)⁺ (calcd for C₅₃H₈₀N₄RuCl₃ = 978). Anal. calcd (found): C, 64.90 (64.30); H, 8.22 (7.76); N, 5.68 (5.71).

RuCl₃T_{D2}. MS-FAB⁺ m/z 1047 (M - Cl)⁺ (calcd for C₆₁H₈₆N₄RuCl₃ = 1082). Anal. calcd (found): C, 67.66 (67.85); H, 8.00 (8.14); N, 5.17 (5.66).

Heteroleptic complexes $[T_{D1}RuT_A]$ [4-EtPhCO₂]₂ and $[T_{D2}RuT_A]$ [4-EtPhCO₂]₂

A solution of T_A (1 mmol) in absolute EtOH (5 mL) and 5 drops of *N*-ethylmorpholine were added to a solution of $RuCl_3T_{D1}$ or $RuCl_3T_{D2}$ (1 mmol) in the same solvent (5 mL). The brown mixture was refluxed for 1 h and subsequently hot filtered on celite.

A solution of 4-EtPhCOOAg (2 mmol) in hot EtOH (10 mL) was then added to the filtrate and the mixture was stirred at room temperature overnight. After filtration of AgCl on celite and evaporation of this second filtrate, the desired products were

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obtained as bright dark red powders (70% and 23% yield, respectively).

[**T**_{D1}**RuT**_A][4-EtPhCO₂]₂. ¹H-NMR (300 MHz, CD₃OD, 25 °C, TMS): δ (ppm) 9.35 (s, 2H, H_{c'}, H_{e'}), 9.19 (s, 2H, H_{3'}, H_{5'}), 8.91 (d, 2H, J = 7.9 Hz, H_c, H_{c''}), 8.86 (d, 2H, J = 7.7 Hz, H₃, H_{3''}), 8.61 (d, 2H, J = 8.7 Hz, H_h, H_{h'}), 8.53 (d, 2H, J = 8.7 Hz, H_g, H_{g'}), 8.20 (d, 2H, J = 8.4 Hz, H₇, H_{7'}), 8.03 (m, 6H, H_d, H_{d''}, H₄, H_{4''}, H₅, H_{5''}), 7.91 (d, 4H, J = 8.1 Hz, H_x, H_x'), 7.62 (d, 2H, J = 5.0 Hz, H_f, H_{f''}), 7.52 (d, 2H, J = 5.2 Hz, H₆, H_{6''}), 7.33 (m, 2H, H_e, H_{e''}), 7.26 (d, 4H, J = 8.0 Hz, H_y, H_y'), 6.99 (d, 2H, J = 8.7 Hz, H₈, H₈'), 3.51 (t, 4H, J = 7.2 Hz, N–CH₂), 2.70 (q, 4H, J = 7.6 Hz, CH₃–CH₂ of 4-EtPhCO₂⁻), 0.88 (t, 6H, J = 7.2 Hz, CH₃). Anal. calcd (found): C, 72.36 (69.53); H, 7.39 (7.21); N, 7.33 (6.30).

[**T**_{D2}**RuT**_A][4-**EtPhCO**₂]₂. ¹H-NMR (300 MHz, CD₃OD, 25 °C, TMS): δ (ppm) 9.36 (s, 2H, H_{c'}, H_{e'}), 9.30 (s, 2H, H_{3'}, H_{5'}), 8.92 (dd, 4H, J = 7.9 Hz, J = 3.5 Hz, H_c, H_{c''}, H₃, H_{3''}), 8.59 (d, 2H, J = 8.9 Hz, H_h, H_{h'}), 8.53 (d, 2H, J = 8.7 Hz, H_g, H_{g'}), 8.29 (d, 2H, J = 8.4 Hz, H₁₂, H_{12'}), 8.04 (m, 4H, H_d, H_{d''}, H₄, H_{4''}), 7.92 (d, 4H, J = 8.1 Hz, H_x, H_{x'}), 7.86 (d, 2H, J = 8.4Hz, H₇, H_{7'}), 7.61 (d, 2H, J = 5.0 Hz, H_f, H_{f''}), 7.56 (d, 2H, J = 8.4Hz, H₇, H_{7'}), 7.61 (d, 2H, J = 5.0 Hz, H₆, H_{6''}), 7.30 (m, 5H, H₉ or H₁₀, H_e, H_{e''}, H₅, H_{5''}), 7.27 (d, 4H, J = 8.1 Hz, H_y, H_{y'}), 7.08 (d, 1H, J = 16.3 Hz, H₁₀ or H₉), 6.72 (d, 2H, J = 8.9Hz, H₁₃, H_{13'}), 3.33 (t, 4H, J = 7.1 Hz, N–CH₂), 2.70 (q, 4H, J = 7.6 Hz, CH₃–*CH*₂ of 4-EtPhCO₂⁻), 1.65 (m, –CH₂–), 1.31 (m, –CH₂– and CH₃ of 4-EtPhCO₂⁻), 0.91 (t, 6H, J = 6.4 Hz, CH₃). Anal. calcd (found): C, 72.36 (69.53); H, 7.39 (7.21); N, 7.33 (6.30).

Heteroleptic complexes $[T_{D1}RuT_{D3}][4\text{-}EtPhCO_2]_2$ and $[T_{D2}RuT_{D3}][4\text{-}EtPhCO_2]_2$

A solution of T_{D3} (1 mmol) in absolute EtOH (10 mL) and 5 drops of *N*-ethylmorpholine were added to a solution of RuCl₃T_{D1} or RuCl₃T_{D2} (1 mmol) in the same solvent (5 mL). The brown mixture was refluxed for 1 h and subsequently hot filtered on celite. A solution of 4-EtPhCOOAg (2 mmol) in hot EtOH (10 mL) was then added to the filtrate and the mixture stirred at room temperature overnight. After filtration of AgCl on celite and evaporation of this second filtrate, the desired products were obtained as dark red powders (96% and 92% yield, respectively).

[**T**_{D1}**RuT**_{D3}][4-EtPhCO₂]₂. ¹H-NMR (300 MHz, CD₃OD, 25 °C, TMS): δ (ppm) 9.24 (s, 2H, H_{c'}, H_{e'}), 9.17 (s, 2H, H_{3'}, H_{5'}), 8.86 (dd, 4H, J = 8.4 Hz, H_c, H_{c''}, H₃, H_{3''}), 8.20 (d, 2H, J = 8.4 Hz, H₇, H_{7'}, H_g, H_{g'}), 8.00 (m, 4H, H_d, H_{d''}, H₄, H_{4''}), 7.89 (d, 4H, J = 8.1 Hz, H_x, H_{x'}), 7.58 (m, 2H, H_f, H_{f'}), 7.52 (d, 2H, J = 5.2 Hz, H₆, H_{6''}), 7.27 (m, 4H, H₅, H_{5''}, H_e, H_{e''}), 7.24 (d, 4H, J = 7.9 Hz, H_y, H_{y'}), 6.99 (d, 2H, J = 8.9 Hz, H₈, H_{8'}), 3.52 (t, 4H, J = 6.8 Hz, N–CH₂), 2.69 (q, 4H, J = 7.5 Hz, CH₃–CH₂ of 4-EtPhCO₂⁻), 2.56 (s, 3H, CH₃ of T_{D3}), 1.74 (m, –CH₂–), 1.44 (m, –CH₂– and *CH*₃–CH₂ of 4-EtPhCO₂⁻), 0.91 (t, 6H, J = 6.2 Hz, CH₃). Anal. calcd (found): C, 74.66 (74.49); H, 7.73 (7.75); N, 6.55 (6.69). [**T**_{D2}**RuT**_{D3}][4-EtPhCO₂]₂. ¹H-NMR (300 MHz, CD₃OD, 25 °C, TMS): δ (ppm) 9.28 (s, 2H, H_{3'}, H_{5'}), 9.25 (s, 2H, H_{c'}, H_{e'}), 8.88 (dd, 4H, J = 8.1 Hz, J = 4.9 Hz, H_c, H_{c''}, H₃, H_{3''}), 8.28 (d, 2H, J = 8.5 Hz, H₁₂, H_{12'}), 8.19 (d, 2H, J = 8.5 Hz, H₇, H₇), 8.02 (m, 4H, H_d, H_{d''}, H₄, H_{4''}), 7.88 (d, 4H, J = 8.5 Hz, H_x, H_x), 7.85 (d, 2H, J = 8.9 Hz, H₇, H₇), 7.56 (m, 4H, H₆, H_{6''}, H_f, H_{f'}), 7.48 (d, 2H, J = 8.9 Hz, H₈, H₈'), 7.28 (m, 5H, H₉ or H₁₀, H_e, H_{e''}, H₅, H_{5''}), 7.23 (d, 4H, J = 8.5 Hz, H_y, H_y'), 7.10 (d, 1H, J = 15.9 Hz, H₁₀ or H₉), 6.70 (d, 2H, J = 8.5 Hz, H₁₃, H_{13'}), 3.30 (t, 4H, J = 7.1 Hz, N–CH₂), 2.68 (q, 4H, J = 7.7 Hz, CH₃–CH₂ of 4-EtPhCO₂⁻), 1.65 (m, –CH₂–), 1.31 (m, –CH₂–), 1.23 (t, 6H, J = 7.7 Hz, CH₃ of 4-EtPhCO₂⁻), 0.90 (t, 6H, J =6.9 Hz, CH₃). Anal. calcd (found): C, 73.73 (72.91); H, 7.57 (7.56); N, 7.15 (7.36).

Homoleptic complexes $[T_{D1}RuT_{D1}]$ [4-EtPhCO₂]₂ and $[T_{D2}RuT_{D2}]$ [4-EtPhCO₂]₂

A solution of T_{D1} or T_{D2} (1 mmol) in absolute EtOH (5 mL) and 5 drops of *N*-ethylmorpholine were added to a solution of RuCl₃T_{D1} or RuCl₃T_{D2} (1 mmol) in the same solvent (5 mL). The brown mixture was refluxed for 1 h and subsequently hot filtered on celite.

A solution of 4-EtPhCOOAg (2 mmol) in hot EtOH (10 mL) was then added to the filtrate and the mixture stirred at room temperature overnight. After filtration of AgCl on celite and evaporation of this second filtrate, the desired products were obtained as bright dark red powders (78% and 35% yield respectively).

 $[\mathbf{T}_{D1}\mathbf{RuT}_{D1}][4-EtPhCO_2]_2. ^{1}H-NMR (300 MHz, CD_3OD, 25 °C, TMS): <math>\delta$ (ppm) 9.14 (s, 4H, H_{3'}, H_{5'}), 8.81 (d, 4H, J = 7.7 Hz, H₃, H_{3''}), 8.17 (d, 4H, J = 8.3 Hz, H₇, H_{7'}), 7.97 (dd, 4H, J = 7.7 Hz, H₄, H_{4''}), 7.90 (d, 4H, J = 8.4 Hz, H_x, H_x'), 7.51 (d, 4H, J = 5.2 Hz, H₆, H_{6''}), 7.25 (d, 4H, J = 7.7 Hz, H_y, H_{y'}), 7.24 (m, 4H, H₅, H_{5''}), 6.96 (d, 4H, J = 9.0 Hz, H₈, H_{8'}), 3.49 (t, 8H, J = 7.1 Hz, N–CH₂), 2.69 (q, 4H, J = 7.7 Hz, CH₃–*CH*₂ of 4-EtPhCO₂⁻), 1.72 (m, –CH₂–), 1.42 (m, –CH₂–), 1.27 (m, –CH₂–), 1.24 (t, 6H, J = 7.7 Hz, CH₃ of 4-EtPhCO₂⁻), 0.87 (t, 12H, J = 7.0 Hz, CH₃). Anal. calcd (found): C, 76.54 (76.34); H, 9.22 (9.20); N, 5.76 (5.71).

 $[T_{D2}RuT_{D2}][4-EtPhCO_2]_2$. ¹H-NMR (300 MHz, CD₃OD, 25 °C, TMS): δ (ppm) 9.29 (s, 4H, H_{3'}, H_{5'}), 8.90 (d, 4H, J =8.3 Hz, H₃, H_{3"}), 8.29 (d, 4H, J = 8.4 Hz, H₁₂, H₁₂'), 8.04 (dd, 4H, J = 7.8 Hz, H₄, H_{4"}), 7.92 (d, 4H, J = 8.1 Hz, H_x, H_x'), 7.86 (d, 4H, J = 8.4 Hz, H₇, H₇'), 7.56 (d, 4H, J = 5.4 Hz, H₆, H_{6"}), 7.49 (d, 4H, J = 8.9 Hz, H₈, H₈'), 7.30 (m, 6H, H₉ or H₁₀, H₅, H_{5"}), 7.27 (d, 4H, J = 8.0 Hz, Hy, Hy'), 7.08 (d, 2H, J = 16.2 Hz, H₁₀ or H₉), 6.73 (d, 4H, J = 8.7 Hz, H₁₃, H₁₃'), 3.32 (m, 8H, J = 7.1 Hz, N–CH₂), 2.70 (q, 4H, J = 7.6 Hz, CH₃–*CH*₂ of 4-EtPhCO₂⁻), 1.41 (m, –CH₂–), 1.26 (t, 6H, J = 7.6 Hz, CH₃ of 4-EtPhCO₂⁻), 0.92 (t, 12H, J = 7.0 Hz, CH₃). Anal. calcd (found): C, 78.20 (77.67); H, 8.91 (9.05); N, 5.21 (5.35).

Conclusions

In conclusion, the $[T_{D1}RuT_A][4\text{-EtPhCO}_2]_2$ and $[T_{D2}RuT_A]-[4\text{-EtPhCO}_2]_2$ heteroleptic complexes investigated in this work

represent a nice example of push-pull systems where a metal, instead of an organic fragment, acts as a bridge between the two π -delocalized organic moieties bearing a donor and an acceptor group, respectively. Their quadratic hyperpolarizability, along with that of free terpyridines and related homoleptic [T_{D1}RuT_{D1}]-[4-EtPhCO₂]₂ and [T_{D2}RuT_{D2}][4-EtPhCO₂]₂ complexes with two terpyridines bearing a donor substituent, is remarkably high and largely dominated by the octupolar contribution, even in the case of the push-pull asymmetric cations. Interestingly, it appears that, in the highly π -delocalized push-pull heteroleptic $[T_{D2}RuT_A]$ [4-EtPhCO₂]₂ complex, the efficiency of the ruthenium bridge on the octupolar contribution to the quadratic hyperpolarizability is particularly high, while such a bridging effect is not so relevant for the less π delocalized system $[T_{D1}RuT_A]$ -[4-EtPhCO₂]₂. In this latter case the octupolar contribution is just the sum of the contribution of the two terpyridines.

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