

Unexpectedly high second-order nonlinear optical properties of simple Ru and Pt alkynyl complexes as an analytical springboard for NLO-active polymer films†

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The unexpectedly high quadratic hyperpolarizability values of simple Ru and Pt alkynyl complexes have been measured by the EFISH technique, and this prompted us to investigate their potential as molecular building blocks for composite films with second harmonic generation properties.

Organotransition metal complexes with second-order nonlinear optical (NLO) properties are important as molecular building block materials for the exciting field of molecular photonics, in particular for optical communications, optical data processing and storage and electro-optical devices.¹ In particular, metal σ -acetylides represent a widely investigated class of second-order NLO chromophores, mainly developed by Humphrey *et al.*,² where the metal acts as the donor group of a donor-acceptor system connected by a π -linker. Pt(II) alkynyl complexes have been studied by W.-Y. Wong *et al.*, as excellent candidates both for optical power limiting³ and for solar cell applications.⁴ The almost linear M-C \equiv C-R structure allows a good coupling between the d orbitals of the metal and the π^* system of the σ -acetylide bridge affording a significant NLO response controlled by low-energy MLCT excitations. Of particular interest are ruthenium σ -alkynyl complexes, due to their facile high-yielding syntheses,⁵ enhanced NLO coefficients,⁶ easy construction of multi-metallic dendrimers,⁷ and reversible redox properties which afford the possibility of NLO switching.⁸ Ruthenium σ -acetylides have been studied through hyper-Rayleigh scattering (HRS) measurements, but, to our knowledge, only in one case through electric field second harmonic (EFISH) generation measurements.⁹

Recently, some of us reported a new dinuclear Ru(II) complex in which two Ru atoms are separated by a 2,1,3-benzothiadiazole bridge

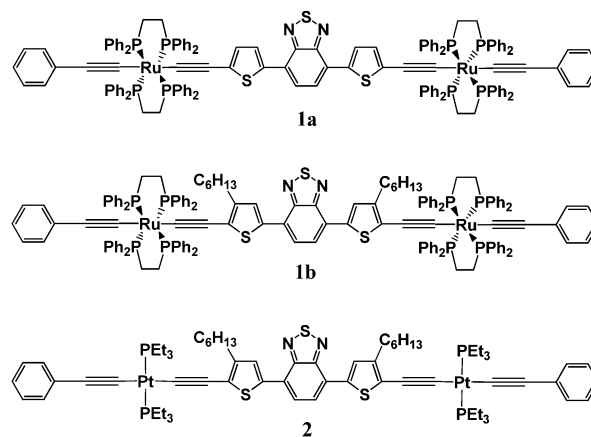


Fig. 1 Simple Ru and Pt alkynyl complexes investigated.

(complex **1a**, see Fig. 1) as a potential donor material to combine with electron-withdrawing fullerides in bulk heterojunction solar cells.¹⁰ Interestingly, the presence of the phenylalkynyl ancillary ligand instead of a chloro ligand should increase the donor properties of the ruthenium center¹¹ in this particular D-A structure where the 2,1,3-benzothiadiazole moiety acts as an acceptor. From the perspective of materials with multifunctional properties, we asked ourselves if these complexes could have interesting second-order NLO properties. In fact, to our knowledge the second-order NLO response of these kinds of diruthenium σ -acetylides have never been investigated. Humphrey studied a diruthenium complex $\{trans-[Ru(C\equiv CPh)(dppe)_2]\}_2(\mu-4,4'-C\equiv CC_6H_4C\equiv CC_6H_4C\equiv C)$ but only for its excellent TPA (two photon absorption) response and not for the second-order nonlinear optical properties because it was centrosymmetric.¹²

In this communication we report the unexpectedly high EFISH values of complex **1a**, and of two new complexes: complex **1b** (analogous to complex **1a**, but with hexyl chains on the thiophenes) and complex **2** (a platinum alkynyl compound analogous to complex **1b**). These complexes have been characterized by UV-vis

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spectroscopy, computed dipole moments, and DFT calculations (see the ESI† for the synthesis details and the chemical and spectroscopical characterization of the three complexes). Complex **1a** was used as molecular building blocks for composite films with second harmonic generation properties.

The use of the EFISH technique¹³ represents in many cases a valuable alternative to HRS¹⁴ which suffers from the limitation of possible overestimation of the value of the quadratic hyperpolarizability due to multiphoton fluorescence. It can provide direct information on the intrinsic molecular NLO properties through eqn (1):

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

where $\mu\beta_{\text{EFISH}}/5kT$ is the dipolar orientational contribution to the molecular nonlinearity, and $\gamma(-2\omega; \omega, \omega, 0)$, the third order polarizability at frequency ω of the incident light, is a purely electronic cubic contribution to γ_{EFISH} .

We found that our complexes are characterized by good to excellent values of $\mu\beta_{\text{EFISH}}$ (-520 – 1370×10^{-48} esu, see Table 1), working in CH_2Cl_2 at a concentration of 10^{-3} M with a non resonant incident wavelength of $1.907 \mu\text{m}$, obtained by Raman-shifting under high H_2 pressure at the fundamental wavelength of $1.064 \mu\text{m}$ produced by using a Q-switched, mode-locked $\text{Nd}^{3+}:\text{YAG}$ laser. To evaluate the quadratic hyperpolarizability of the various complexes it is necessary to have the dipole moment values. We report in Table 1 the total calculated dipole moments (μ) *in vacuo*.

The investigated systems show a bent M-core-M moiety, which is the origin of their non-zero dipole moments. The dipole moments are directed from the two symmetric ligands (negative pole) to the metal (positive pole) (see Fig. 2). A larger dipole moment is associated with the presence of hexyl substituents (compare **1a** and **1b**) and with the use of Pt instead of Ru (compare **1b** and **2**).

As evidenced in Table 1, complexes **1a** and **1b** present a red-shift of the UV-vis absorption maxima with respect to complex **2**, leading to much higher quadratic hyperpolarizability with respect to complex **2** (factor of *ca.* 3.5).

The large β_{EFISH} values observed in the present work are remarkable. In fact, ruthenium σ -alkynyl complexes with good dipolar second-order nonlinear optical properties are expected to be classical push-pull systems with high dipole moments. For example, L. Rigamonti *et al.*⁹ reported the synthesis and NLO

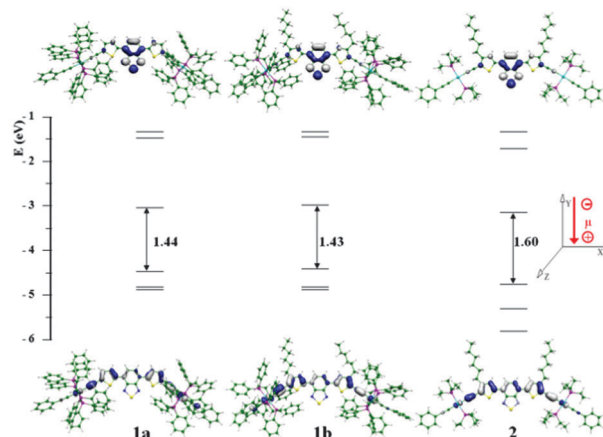


Fig. 2 Schematic representation of the energy levels of complexes **1a**, **1b** and **2**. Isodensity surface plots (isodensity contour: 0.035) of selected molecular orbitals are also shown.

characterization of a series of variously substituted donor-bridge-acceptor complexes of the type *trans*-[Ru(4,4,4'-C \equiv CC₆H₄X₂C₆H₄-Y₂C₆H₄NO₂)Cl(dppe)₂] with high μ (13.34 – 14.68×10^{-18} esu) and fair β_{EFISH} values (55 – 89×10^{-30} esu), as determined by the EFISH technique.

Therefore, the very high β_{EFISH} values (up to -566×10^{-30} esu) observed for our Ru complexes are surprising for such non-classical donor- π delocalized acceptor structures characterized by relatively low dipole moments (Table 1). It is worth pointing out that these β_{EFISH} values are not overestimated by resonance, because we worked with an incident wavelength of $1.907 \mu\text{m}$ (see UV-Vis characterization in the ESI†).

In Fig. 2 the isodensity plots of the main molecular orbitals are shown (see the ESI† for orbital energies). The highest occupied molecular orbitals (HOMOs) of all the investigated complexes are Ru and Pt orbitals combined with the π orbitals of thiophene and benzothiadiazole groups. The lowest unoccupied molecular orbitals (LUMOs) are completely localized on the benzothiadiazole moieties without any contribution from the metal. The HOMO–LUMO gaps for **1a**, **1b** and **2** are 1.44, 1.43 and 1.60 eV, respectively, which nicely parallel the trend in the measured UV-vis absorption maxima showing complex **2** to exhibit a 0.2–0.3 eV blue shift of the lowest transition compared to **1a** and **1b**.

Since the electronic mechanisms which yield the NLO response in molecular systems are well-defined, it is now crucial to face their molecular engineering in order to obtain organized molecular materials showing a temporal, stable and high bulk second-order NLO response.¹⁶ Applications of ruthenium σ -acetylide complexes to produce second-order bulk NLO materials or structured films are very limited.^{1c} In spite of their large molecular quadratic hyperpolarizabilities, they form crystalline materials which exhibit modest bulk second harmonic generation (SHG) efficiency,^{2a} due to the reluctance of acetylide complexes to crystallize in non-centrosymmetric structures. However, a film of a ruthenium oligothiénylacetylide NLO chromophore, incorporated into a polymethylmethacrylate (PMMA) matrix, revealed an acoustically induced SHG signal with a good $\chi^{(2)}$ value (0.80 pm V^{-1}).¹⁷

Table 1 Electronic spectra and $\mu\beta_{\text{EFISH}}$, μ , and β_{EFISH} values of the investigated complexes

Sample	λ (nm) [ϵ ($\text{M}^{-1} \text{cm}^{-1}$)] ^a	$\mu\beta_{\text{EFISH}}$ ($\times 10^{-48}$ esu) ^{a,b}	μ ($\times 10^{-18}$ esu) ^c	β_{EFISH} ($\times 10^{-30}$ esu)
1a	393 [35 011],	−900	1.6	−566
	633 [35 340]			
1b	398 [39 664],	−1370	2.8	−498
	656 [36 018]			
2	378 [34 462],	−520	3.4	−151
	561 [26 254]			

^a In anhydrous CH_2Cl_2 . ^b The error in EFISH measurements is 10%.

^c Computed dipole moments *in vacuo*, also see ESI.

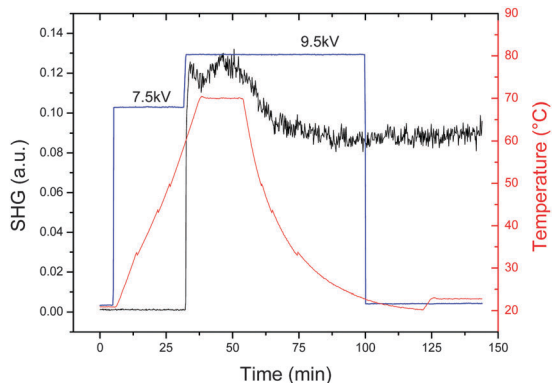


Fig. 3 *In situ* corona-wire poling dynamic of a PMMA film containing complex **1a**.

The unexpectedly high quadratic hyperpolarizability of complex **1a** in solution prompted us to investigate its potential as molecular building blocks for composite films with second harmonic generation properties.¹⁸ Therefore we dispersed and oriented complex **1a** in a PMMA matrix (5% of chromophore with respect to PMMA), as reported in the ESI†. The corona wire poling dynamics of the SHG behaviour of the PMMA composite film was performed using the following parameters: poling temperature of 60–70 °C with an electric field initially of 7.5 kV held for 35 minutes and then of 9.5 kV held for 65 minutes.

As evidenced in Fig. 3, the SHG was negligible at room temperature, but it quickly increased after application of the electric field (7.5 kV) when the temperature reached 60 °C, as expected due to the decrease of the polymeric matrix viscosity, which allows a more facile orientation of the dipolar NLO chromophores. Once the second harmonic signal had stabilized, the sample was cooled and the drybox opened when room temperature was reached. The final switch off of the electric field caused a small drop in the SHG.

The second order NLO coefficient matrix value d_{33} for poled films was obtained by following the standard Maker fringe technique, as previously reported.¹⁸ Remarkably, the d_{33} value (1.64 pm V⁻¹ corresponding to $\chi_{33}^{(2)} = 3.28$ pm V⁻¹) of the composite PMMA film containing the simple complex **1a** is very high and rather stable, the signal remaining even after two months. This particularly high stability, from the perspective of applications, could be attributed to the relatively large size of the NLO chromophore which would hinder its mobility. In conclusion, our work puts in evidence that simple quite symmetrical complexes with a relatively low dipole moment could have remarkably high β_{EFISH} values, and can be the building blocks of active polymeric films characterized by an excellent second-order NLO response. Our ruthenium σ -acetylide complexes will be tested in the near future as third order nonlinear optical chromophores, being surely promising candidates also for two-photon absorption (TPA) applications.

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