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.,a as excellent candidates both for optical power limiting3 and for solar cell applications.5 The almost linear M–C–R–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.6 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 (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≡CPh)(dppe)2]2[μ-4,4′-C≡CC6H4C≡CLC6H4C≡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...
spectroscopy, computed dipole moments, and DFT calculations (see the ESI† for the synthesis details and the chemical and spectroscopic 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):

\[ \chi_{\text{EFISH}} = \left( \frac{\mu \beta_{\text{EFISH}}}{5kT} \right) + \gamma(-2\omega; \omega, \omega, 0) \tag{1} \]

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 \( \omega \) of the incident light, is a purely electronic cubic contribution to \( \chi_{\text{EFISH}} \).

We found that our complexes are characterized by good to excellent values of \( \mu \beta_{\text{EFISH}} \) (520–1370 \( \times 10^{-48} \) esu, see Table 1), working in \( \text{CH}_2\text{Cl}_2 \) 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 \( \text{H}_2 \) pressure at the fundamental wavelength of 1.064 \( \mu \text{m} \) produced by using a Q-switched, mode-locked Nd\(^{3+}\):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 \( (\mu) \) 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 \( \beta_{\text{EFISH}} \) 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 characterization of a series of variously substituted donor-bridgeacceptor complexes of the type trans-[Ru(4,4,4′-C\(\equiv\text{C}_2\text{H}_4\)X\(\equiv\text{C}_2\text{H}_4\)Y\(\equiv\text{C}_2\text{H}_4\)NO\(\equiv\text{C}_2\text{H}_4\))Cl(dppe)\(_2\)] with high \( \mu \) (13.34–14.68 \( \times 10^{-18} \) esu) and fair \( \beta_{\text{EFISH}} \) values (55–89 \( \times 10^{-30} \) esu), as determined by the EFISH technique.

Therefore, the very high \( \beta_{\text{EFISH}} \) values (up to \( 566 \times 10^{-30} \) 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 \( \beta_{\text{EFISH}} \) 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†).

Fig. 2 shows the isodensity plots of the main molecular orbitals (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.16 In spite of their large molecular quadratic hyperpolarizabilities, they form crystalline materials which exhibit modest bulk second harmonic generation (SHG) efficiency,25 due to the reluctance of acetylide complexes to crystallize in non-centrosymmetric structures. However, a film of a ruthenium oligothienylacetylide 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

![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.](image-url)
optical chromophores, being surely promising candidates also for excellent second-order NLO response. Our ruthenium the building blocks of active polymeric films characterized by an containing the simple complex

Notes and references


In order to calculate the $\mu^\beta_{\text{EFSH}}$ values, the purely electronic cubic contribution to $\gamma_{\text{EFSH}}$ was neglected.


