ChemComm

COMMUNICATION



View Article Online

PPh

Ph₂E

PEt₃

PEt₃

Cite this: Chem. Commun., 2014, **50**. 7986

Received 2nd April 2014, Accepted 3rd June 2014

DOI: 10.1039/c4cc02432j

www.rsc.org/chemcomm

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

Alessia Colombo,^{ab} Filippo Nisic,^{ab} Claudia Dragonetti,*^{abc} Daniele Marinotto,^{abc} Ivan Pietro Oliveri,^a Stefania Righetto,^{ab} Maria Grazia Lobello^d and Filippo De Angelis*d

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(π) 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=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 multimetallic 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



(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 ${trans-[Ru(C \equiv CPh)(dppe)_2]}_2(\mu-4,4'-C \equiv CC_6H_4C \equiv CC \equiv CC_6 H_4C \equiv C$) 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

^a Dipartimento di Chimica dell'Università degli Studi di Milano, Italy.

E-mail: claudia.dragonetti@unimi.it

^b UdR INSTM and Centro di Eccellenza CIMAINA dell'Università degli Studi di Milano, Italy

^c ISTM-CNR, via Golgi 19, 20133 Milano, Italy

^d Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), ISTM-CNR, Via Elce di Sotto 8, 06213 Perugia, Italy. E-mail: filippo@thch.unipg.it

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cc02432j

ChemComm

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):

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

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 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 CH₂Cl₂ at a concentration of 10⁻³ M with a non resonant incident wavelength of 1.907 µm, obtained by Raman-shifting under high H₂ pressure at the fundamental wavelength of 1.064 µm produced by using a Q-switched, mode-locked Nd³⁺: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

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

Sample	$rac{\lambda \ (nm)}{\left[\epsilon \ (M^{-1} \ cm^{-1}) ight]^a}$	$\begin{array}{l} \mu\beta_{\rm EFISH} \\ (\times 10^{-48} \ {\rm esu})^{a,b} \\ ({\rm ref.} \ 15) \end{array}$	$(\times 10^{-18} \text{ esu})^c$	$egin{smallmatrix} eta_{ ext{EFISH}}\ (imes 10^{-30} ext{ esu}) \end{split}$
1a	393 [35 011],	-900	1.6	-566
1b	633 [35 340] 398 [39 664],	-1370	2.8	-498
2	656 [36 018] 378 [34 462], 561 [26 254]	-520	3.4	-151

^{*a*} In anhydrous CH₂Cl₂. ^{*b*} The error in EFISH measurements is 10%. ^{*c*} Computed dipole moments *in vacuo*, also see ESI.



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-bridgeacceptor complexes of the type *trans*-[Ru(4,4,4"-C \equiv CC₆H₄X₂C₆H₄⁻ Y₂C₆H₄NO₂)Cl(dppe)₂] with high μ (13.34–14.68 \times 10⁻¹⁸ esu) and fair β_{EFISH} values (55–89 \times 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 nonclassical 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 µm (see UV-Vis characterization in the ESI†).

In Fig. 2 the isodensity plots of the main molecular orbitals are shown (see the ESI^{\dagger} 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 noncentrosymmetric 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. 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 $^{\circ}$ 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 $\chi_{33}^{(2)} = 3.28 \text{ pm V}^{-1}$) 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.

This work was financially supported by MIUR (FIRB 2003: RBNE033KMA and FIRB 2004: RBPR05JH2P) and CNR.

Notes and references

 See for instance (a) J. Zyss, Molecular Nonlinear Optics: Materials, Physics and Devices, Academic Press, Boston, 1994; (b) B. J. Coe, Acc. Chem. Res., 2006, 39, 383; (c) S. Di Bella, C. Dragonetti, M. Pizzotti, D. Roberto, F. Tessore and R. Ugo, Top. Organomet. Chem., 2010, 28, 1; (d) O. Maury

and H. Le Bozec, in Molecular Materials, ed. D. W. Bruce, D. O'Hare and R. I. Walton, Wiley, Chichester, 2010, pp. 1-59; (e) F. Tessore, D. Roberto, R. Ugo, P. Mussini, S. Quici, I. Ledoux-Rak and J. Zyss, Angew. Chem., Int. Ed., 2003, 42, 456; (f) C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, A. Valore, F. Demartin, F. De Angelis, A. Sgamellotti and S. Fantacci, Inorg. Chim. Acta, 2008, 361, 4070; (g) A. Valore, M. Balordi, A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, T. Benincori, G. Rampinini, F. Sannicolò and F. Demartin, Dalton Trans., 2010, 39, 10314; (h) A. Valore, E. Cariati, S. Righetto, D. Roberto, F. Tessore, R. Ugo, I. L. Fragalà, M. E. Fragalà, G. Malandrino, F. De Angelis, L. Belpassi, I. Ledoux-Rak, K. H. Thi and J. Zyss, J. Am. Chem. Soc., 2010, 132, 4966; (i) A. Valore, E. Cariati, C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, F. De Angelis, S. Fantacci, A. Sgamellotti, A. Macchioni and D. Zuccaccia, Chem. -Eur. J., 2010, 16, 4814; (j) V. Aubert, L. Ordronneau, M. Escadeillas. J. A. G. Williams, A. Boucekkine, E. Coulaud, C. Dragonetti, S. Righetto, D. Roberto, R. Ugo, A. Valore, A. Singh, J. Zyss, I. Ledoux, H. Le Bozec and V. Guerchais, Inorg. Chem., 2011, 50, 5027; (k) F. Todescato, I. Fortunati, S. Carlotto, C. Ferrante, L. Grisanti, C. Sissa, A. Painelli, A. Colombo, C. Dragonetti and D. Roberto, Phys. Chem. Chem. Phys., 2011, 13, 11099; (l) M. Pizzotti, R. Ugo, D. Roberto, S. Bruni, P. Fantucci and C. Rovizzi, Organometallics, 2002, 21, 5830; (m) A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, A. Valore, T. Benincori, F. Colombo and F. Sannicolò, J. Mater. Chem., 2012, 37, 19761; (n) S. Di Bella, I. P. Oliveri, A. Colombo, C. Dragonetti, S. Righetto and D. Roberto, Dalton Trans., 2012, 41, 7013.

- (a) C. E. Powell and M. G. Humphrey, *Coord. Chem. Rev.*, 2004, 248, 725; (b) M. G. Humphrey and M. Samoc, *Adv. Organomet. Chem.*, 2008, 55, 61; (c) M. P. Cifuentes and M. G. Humphrey, *J. Organomet. Chem.*, 2004, 689, 3968; (d) G. Guillaume, M. P. Cifuentes, F. Paul and M. G. Humphrey, *J. Organomet. Chem.*, 2014, 751, 181.
- 3 (a) G.-J. Zhou and W.-Y. Wong, *Chem. Soc. Rev.*, 2011, 40, 2541;
 (b) G.-J. Zhou, W.-Y. Wong, Z. Lin and C. Ye, *Angew. Chem., Int. Ed.*, 2006, 45, 6189; (c) G.-J. Zhou, W.-Y. Wong, C. Ye and Z. Lin, *Adv. Funct. Mater.*, 2007, 17, 963; (d) G. Zhou, W.-Y. Wong, S.-Y. Poon, C. Ye and Z. Lin, *Adv. Funct. Mater.*, 2009, 19, 531; (e) G.-J. Zhou, W.-Y. Wong, D. Cui and C. Ye, *Chem. Mater.*, 2005, 17, 5209.
- 4 (a) W.-Y. Wong, X.-Z. Wang, Z. He, A. B. Djurišić, C.-T. Yip, K.-Y. Cheung, H. Wang, C. S. K. Mak and W.-K. Chan, Nat. Mater., 2007, 6, 521; (b) W.-Y. Wong and C.-L. Ho, Acc. Chem. Res., 2010, 43, 1246; (c) F.-R. Dai, H.-M. Zhan, Q. Liu, Y.-Y. Fu, J.-H. Li, Q.-W. Wang, Z. Xie, L. Wang, F. Yan and W.-Y. Wong, Chem. Eur. J., 2012, 18, 1502; (d) Q. Wang and W.-Y. Wong, Polym. Chem., 2011, 2, 432; (e) F.-R. Dai, Y.-C. Chen, L.-F. Lai, W.-J. Wu, C.-H. Cui, G.-P. Tan, X.-Z. Wang, J.-T. Lin, H. Tian and W.-Y. Wong, Chem. Asian J., 2012, 7, 1426; (f) A. Ng, C.-L. Ho, M. K. Fung, Y. C. Sun, S.-Y. Shao, Y.-Y. Fu, A. M. C. Ng, C. H. Li, W. K. Cheung, Y. H. Leung, A. B. Djurišić, Q. Wang, Z. He, X. Wang, W.-K. Chan, Z.-Y. Xie, J. A. Zapien, C. H. To and W.-Y. Wong, Macromol. Chem. Phys., 2012, 213, 1300.
- (a) A. M. McDonagh, I. R. Whittall, M. G. Humphrey, D. C. R. Hockless, B. W. Skelton and A. H. White, *J. Organomet. Chem.*, 1996, 523, 33;
 (b) A. M. McDonagh, M. P. Cifuentes, I. R. Whittall, M. G. Humphrey, M. Samoc, B. Luther-Davies and D. C. R. Hockless, *J. Organomet. Chem.*, 1996, 526, 99.
- 6 (a) R. H. Naulty, A. M. McDonagh, I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, S. Houbrechts, J. Maes, A. Persoons, G. A. Heath and D. C. R. Hockless, *J. Organomet. Chem.*, 1998, **563**, 137; (b) S. K. Hurst, M. G. Humphrey, J. P. Morrall, M. P. Cifuentes, M. Samoc, B. Luther-Davies, G. A. Heath and A. C. Willis, *J. Organomet. Chem.*, 2003, **670**, 56.
- 7 K. A. Green, M. P. Cifuentes, M. Samoc and M. G. Humphrey, *Coord. Chem. Rev.*, 2011, 255, 2025.
- 8 K. A. Green, M. P. Cifuentes, M. Samoc and M. G. Humphrey, *Coord. Chem. Rev.*, 2011, 255, 2530.
- 9 L. Rigamonti, B. Babgi, M. P. Cifuentes, R. L. Roberts, S. Petrie, R. Stranger, S. Righetto, A. Teshome, I. Asselberghs, K. Clays and M. G. Humphrey, *Inorg. Chem.*, 2009, 48, 3562.
- 10 A. Colombo, C. Dragonetti, D. Roberto, R. Ugo, L. Falciola, S. Luzzati and D. Kotowski, *Organometallics*, 2011, **30**, 1279.
- 11 C. E. Powell, M. P. Cifuentes, J. P. Morrall, R. Stranger, M. G. Humphrey, M. Samoc, B. Luther-Davies and G. A. Heath, *J. Am. Chem. Soc.*, 2003, 125, 602.
- 12 S. K. Hurst, M. P. Cifuentes, A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs and A. Persoons, *J. Organomet. Chem.*, 2003, 670, 56.

- (a) B. F. Levine and C. G. Bethea, J. Chem. Phys., 1975, 63, 2666;
 (b) I. Ledoux and J. Zyss, Chem. Phys., 1982, 73, 203.
- (a) P. D. Maker, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1970, 1, 923;
 (b) K. Clays and A. Persoons, *Phys. Rev. Lett.*, 1991, 66, 2980;
 (c) J. Zyss and I. Ledoux, *Chem. Rev.*, 1994, 94, 77.
- 15 In order to calculate the $\mu\beta_{\rm EFISH}$ values, the purely electronic cubic contribution to $\gamma_{\rm EFISH}$ was neglected.
- 16 As examples, (a) E. Cariati, R. Macchi, D. Roberto, R. Ugo, S. Galli, N. Masciocchi and A. Sironi, *Chem. Mater.*, 2007, **19**, 3704;
 (b) L. R. Dalton, P. A. Sullivan and D. H. Bale, *Chem. Rev.*, 2010, **110**, 25 and references therein.
- 17 J. L. Fillaut, J. Perruchon, P. Blanchard, J. Roncali, S. Golhen, M. Allain, A. Migalsaka-Zalas, I. V. Kityk and B. Sahraoui, *Organometallics*, 2005, 24, 687.
- 18 (a) D. Marinotto, S. Proutiere, C. Dragonetti, A. Colombo, P. Ferruti, D. Pedron, M. C. Ubaldi and S. Pietralunga, J. Non-Cryst. Solids, 2011, 357, 2075; (b) D. Marinotto, R. Castagna, S. Righetto, C. Dragonetti, A. Colombo, C. Bertarelli, M. Garbugli and G. Lanzani, J. Phys. Chem. C, 2011, 115, 20425; (c) D. Roberto, A. Colombo, C. Dragonetti, D. Marinotto, S. Righetto, S. Tavazzi, M. Escadeillas, V. Guerchais, H. Le Bozec, A. Boucekkine and C. Latouche, Organometallics, 2013, 32, 3890; (d) C. Dragonetti, A. Colombo, D. Marinotto, S. Righetto, D. Roberto, A. Valore, M. Escadeillas, V. Guerchais, H. Le Bozec, A. Boucekkine and C. Latouche, J. Organomet. Chem., 2014, 751, 568; (e) J. Boixel, V. Guerchais, H. Le Bozec, D. Jacquemin, A. Amar, A. Boucekkine, A. Colombo, C. Dragonetti, D. Marinotto, D. Roberto, S. Righetto and R. De Angelis, J. Am. Chem. Soc., 2014, 136, 5367.