

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

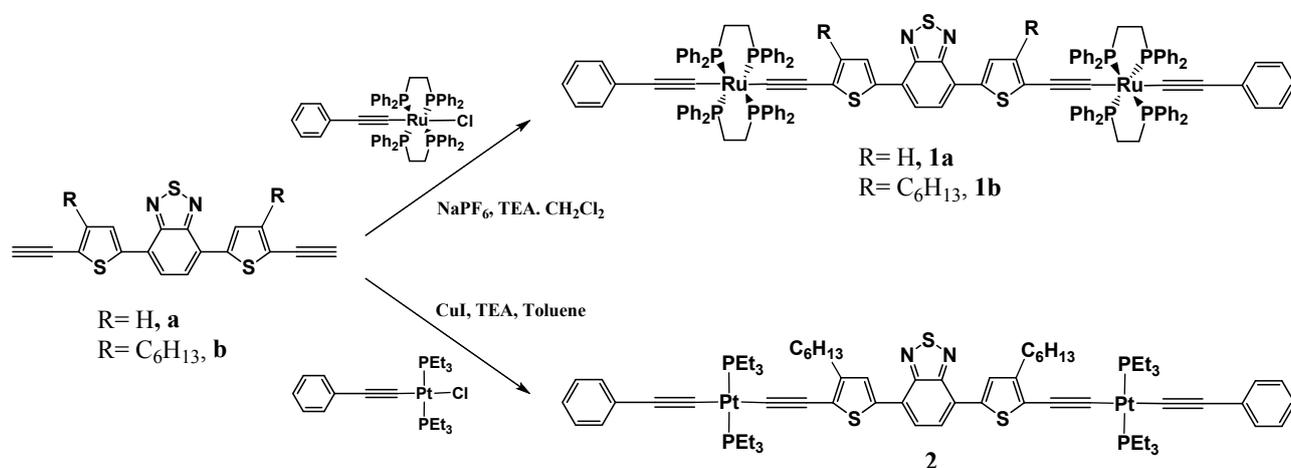
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## Supporting Information

### Synthesis of complexes 1a, 1b and 2.

Complex **1a** and the new complex **1b** were obtained using an adaptation of the method of Humphrey *et al* as previously reported<sup>1</sup>, by reaction of the known  $[\text{ClRu}(\text{L}_2)\equiv\text{Ph}]^2$  with  $\text{H}\equiv\text{Th-BTDTh}\equiv\text{H}^3$  or with its dihexyl derivative<sup>4</sup>. The new complex **2** was synthesized in a similar manner by Frechet methodology<sup>5</sup>.



**Table 1.** UV/Vis spectra in CH<sub>2</sub>Cl<sub>2</sub>

SAMPLE	$\lambda(\text{nm})$ [ $\epsilon$ ( $\text{M}^{-1} \text{cm}^{-1}$ )]
Complex 1a	393 [35011], 633 [35340]
Complex 1b	398 [39664], 656 [36018]
Complex2	378 [34462], 561 [26254]

## Synthesis of Ruthenium complexes 1a and 1b : General procedure

A mixture of dialkyne (0.07 mmol), ruthenium complex (152 mg, 0.15 mmol) and NaPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> (46 mL) was stirred in the dark for 18 h, triethylamine (99 μL) was added and stirring was maintained for 3h. The solvent was removed under reduced pressure and the residue was taken up in CH<sub>2</sub>Cl<sub>2</sub> and purified by column chromatography on neutral alumina. Elution with Hexane: CH<sub>2</sub>Cl<sub>2</sub> 8:2 gave a dark blue band that was collected and dried in vacuo. The dark blue product was obtained in 85-90% yields.

Characterization data for **complex 1a**: IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 2924 (w), 2855 (w), 2392 (vw), 2338 (vw), 2042 (vs, v C≡C), 1605 (m), 1482 (m), 1366 (vw), 1097 (w); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ (ppm)) 7.53-7.26 (m, 60H, 54H<sub>m,p</sub> of 18Ph and 6H spacer), 7.17-7.08 (m, 36 H,H of 18Ph), 2.80-2.65 (m, 16H, PCH<sub>2</sub>CH<sub>2</sub>P); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ (ppm)) 136.56, 134.63, 134.40, 134.07, 133.87, 129.10, 128.92, 128.81, 128.50, 127.46, 127.30, 127.03, 126.33, 110.01, 93.26, 67.91, 66.56, 38.81, 29.67; <sup>31</sup>P NMR (161.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ (ppm)) 52.47; MS (MALDI-TOF, 2-[(2E)-3-(4-tert-butylphenyl)-2 methylprop-2-enylidene]malonitrile as the matrix) calcd for C<sub>138</sub>H<sub>112</sub>N<sub>2</sub>-P<sub>8</sub>Ru<sub>2</sub>S<sub>3</sub> m/z 2344.5, found 2345.9. Anal. Calcd: C, 70.70; H, 4.82; N, 1.19. Found: C, 71.00; H, 4.83; N, 1.19.

Characterization data for **complex 1b**: IR (cm<sup>-1</sup>, CH<sub>2</sub>Cl<sub>2</sub>) 2986 (w), 2685 (w), 2361 (vw), 2337 (vw), 2042 (vs, v C≡C), 2072 (vw), 2032 (vs, v C≡C), 1605 (m); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ (ppm)) 7.50-7.28 (m, 58H, 54H<sub>m,p</sub> of 18Ph and 4H spacer), 7.15-7.05 (m, 36 H,H of 18Ph), 2.80-2.65 (m, 16H, PCH<sub>2</sub>CH<sub>2</sub>P), 2.64-2.62 (m, 20 H<sub>hexyl</sub>), 1.32 (t, 6H<sub>hexyl</sub>); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ (ppm)) 135.30, 134.49, 134.09, 129.58, 128.28, 128.81, 128.50, 127.46, 127.30, 127.03, 126.33, 110.01, 93.26, 67.91, 66.56, 38.81, 29.67; <sup>31</sup>P NMR (161.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>, δ (ppm)) 54.21; MS (MALDI-TOF, 2-[(2E)-3-(4-tert-butylphenyl)-2 methylprop-2-enylidene]malonitrile as the matrix) calcd for C<sub>150</sub>H<sub>136</sub>N<sub>2</sub>P<sub>8</sub>Ru<sub>2</sub>S<sub>3</sub> m/z 2512.59, found 2515.1. Anal. Calcd: C, 71.70; H, 5.46; N, 1.11. Found: C, 71.28; H, 5.39; N, 1.12.

## Synthesis of Platinum complex 2:

A mixture of dialkyne (25 mg, 0.045 mmol), platinum complex (56 mg, 0.09 mmol) and CuI (2.45 mg, 0.013 mmol) in triethylamine / toluene (8 mL/15 mL) was stirred at room temperature for 12 h. The mixture was filtered and the solvent was removed, the purple residue was loaded on an a neutral alumina column and eluted with hexane/ethyl acetate 97:3. The purple band was collected affording the compound as a purple solid (31.6 mg, 45%).

Characterization data for **complex 2**:

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) ppm: 7.98 (s, 2H), 7.77 (s, 2H), 7.30-7.22 (m, 8H), 7.17-7.15 (m, 2H) 2.63-2.61 (m, 20H), 2.24-2.18 (m, 24 H), 1.34-1.24 (m, 42H). (MALDI-TOF, 2-[(2E)-3-(4-tert-butylphenyl)-2 methylprop-2-enylidene]malonitrile as the matrix) calcd for C<sub>70</sub>H<sub>100</sub>N<sub>2</sub>P<sub>4</sub>Pt<sub>2</sub>S<sub>3</sub> m/z 1578.5, found 1579.3 Anal. Calcd: C, 53.22; H, 6.38; N, 1.77. Found: C, 54.31; H, 6.30 N, 1.68.

## Corona poling setup.

The fundamental incident light was generated by a 1064 nm Q-switched Nd:YAG (Quanta System Giant G790-20) laser with a pulse of 7 ns and 20 Hz repetition rate. The output pulse was attenuated to 0.55 mJ and was focused with a lens ( $f = 600$  mm) on the sample, placed over the hot stage. Corona poling process was performed inside a drybox in a  $N_2$  atmosphere. The fundamental beam was polarized in the incidence plane (so-called p-polarized) with an angle of about  $55^\circ$  with respect to the sample in order to optimize the second harmonic generation (SHG) signal. The hot stage temperature was controlled by a GEFTRAN 800 controller, while the corona-wire voltage (up to 9.5 kV across a 10 mm gap) was applied by a TREK 610E high voltage supply. After rejection of the fundamental beam by an interference filter and a glass cutoff filter, the p-polarized SHG signal at 532 nm was detected with a UV-vis photomultiplier (PT) Hamamatsu C3830. The output signal from the PT was set to a digital store oscilloscope and then processed by a computer with dedicated software.

## Maker measurements.

The absolute value  $d_{33}$  of the second order NLO coefficient of the composite polymeric material was obtained by following the standard Maker fringe technique.<sup>6,7</sup> In order to determine the nonzero independent components of the susceptibility tensor for films with  $C_{\infty v}$  symmetry measurements were conducted with different polarizations:  $p \rightarrow p$ ,  $s \rightarrow p$ , and  $45 \rightarrow s$ . second harmonic signal was normalized with respect to that of a calibrated quartz crystal wafer (X-cut) 1mm thick whose  $d_{11}$  is 0.46 pm/V.

## Computational details.

All the calculations have been performed by the GAUSSIAN09 program package.<sup>8</sup> Geometry optimizations of 1a, 1b and 2 compounds were performed in vacuo, using the B3LYP<sup>9</sup> exchange-correlation functional and using a LANL2DZ basis set<sup>10</sup> for all atoms along with the corresponding pseudopotentials for Ru and Pt.

The geometries have been optimized by DFT, and dipole moments have been calculated according to the optimized geometries.

The single point were performed in  $CH_2Cl_2$  solution using a LANL2DZ basis set. Solvation effects were included in the geometry optimizations by means of the conductor-like polarizable continuum model (C-PCM),<sup>11,12</sup> as implemented in G09.

**Table 2.** Energies of the lowest unoccupied and highest occupied Kohn-Sham orbitals of 1a, 1b and 2 complexes in  $CH_2Cl_2$  solution. Energy in eV.

	<b>1a</b>	<b>1b</b>	<b>2</b>
H-2	-4.88	-4.88	-5.82
H-1	-4.82	-4.82	-5.30
H	-4.48	-4.42	-4.75
L	-3.04	-2.99	-3.15
L+1	-1.48	-1.46	-1.72
L+2	-1.33	-1.34	-1.33
$\Delta E_{H \rightarrow L}$	1.44	1.43	1.60

## Dipole moments.

The DFT methods can provide accurate polarizabilities and hyperpolarizabilities not only for atoms and small molecules but also for large system. Several groups have investigated the dipole moment using different theoretical approach (HF, MP2 and DFT methods).<sup>13-18</sup> For the DFT schemes they have tried either increase  $\mu$  or do not alter it significantly from the Hartree-Fock value.

We also tested a series of hybrid functional, B3LYP,<sup>19</sup> PBE0<sup>20</sup> that use 20 and 25% exchange, respectively, and a hybrid meta GGA functional, M06-L.<sup>21</sup>

In Table 1 we report the computed dipole moment and the related  $\beta_{\text{EFISH}}$ .

For the hybrid functional the dipole moments calculated using B3LYP are only 0.1-0.2  $\times 10^{-18}$  esu higher respect to the PBE0 values. The computed  $\beta_{\text{EFISH}}$  using  $\mu_{\text{B3LYP}}$  is 21-6  $\times 10^{-30}$  esu higher respect to the computed  $\beta_{\text{EFISH}}$  using PBE0. The dipole moments computed with the M06-L are slightly lower that the  $\mu$  computed with hybrid functional, while the  $\beta_{\text{EFISH}}$  are higher.

In general the dipole moment computed with B3LYP functional represents a good result in terms of prediction of NLO properties and computational cost.

SAMPLE	$\mu\beta_{\text{EFISH}}$ ( $\times 10^{-48}$ esu) <sup>a,b,13</sup>	B3LYP		PBE0		M06-L	
		$\mu(\times 10^{-18}$ esu) <sup>c</sup>	$\beta_{\text{EFISH}}$ ( $\times 10^{-30}$ esu)	$\mu(\times 10^{-18}$ esu) <sup>c</sup>	$\beta_{\text{EFISH}}$ ( $\times 10^{-30}$ esu)	$\mu(\times 10^{-18}$ esu) <sup>c</sup>	$\beta_{\text{EFISH}}$ ( $\times 10^{-30}$ esu)
1a	-900	1.6	-566	1.7	-545	1.4	-662
1b	-1370	2.8	-498	2.9	-479	2.4	-561
2	-520	3.4	-151	3.6	-145	3.3	-156

<sup>a</sup>In anhydrous  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup>the error on EFISH measurements is 10%. <sup>c</sup> Computed dipole moments in vacuo.

## References

1. A. Colombo, C. Dragonetti, D. Roberto, R. Ugo, L. Falciola, S. Luzzati, D. Kotowski, *Organometallics* **2011**, *30*, 1279.
2. D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, *Organometallics* **1997**, *16*, 3640.
3. J. Mei, K. Ogawa, Y.-G. Kim, N.C. Neston, D.J. Arenas, Z. Nasrollahi, T.D. McCarley, D.B. Tanner, J.R. Reynolds, K.S. Schanze, *Appl. Mater. Interfaces* **2009**, *1*, 150.
4. F.C. Krebs, H. Spanggaard, H. *Sol. Energy Mater. Sol. Cells* **2005**, *88*, 363.
5. J.M.J. Frechet, B. Kim, B. Ma, C. Piliago, D.A. Poulsen, D.A. Unruh, X. Zhao, *Chemistry of Materials*, **2010**, *22*, 2325.
6. P. D. Maker, R. W. Terhune, M. Nisenoff and C. M. Savage, *Phys. Rev. Lett.*, **1962**, *8*, 21.
7. W. N. Herman and L. M. Hayden, *J. Opt. Soc. Am. B*, **1995**, *12*, 416.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.

- Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09, Revision A.1*, Gaussian, Inc.: Wallingford CT, **2009**.
9. A.D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
  10. J.S. Binkley, J.A. Pople, W.J. Hehre, *J. Am. Chem. Soc.* **1980**, *102*, 939.
  11. M. Cossi, V. Barone, R. Cammi, J. Tomasi, *Chem. Phys. Lett.* **1996**, *255*, 327.
  12. S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117.
  13. A.J. Cohen, Y. Tantirungrotechai, *Chem. Phys. Lett.*, **1999**, *299*, 465.
  14. D. Jacquemin, J.-M. André, E.A. Perpète, *J. Chem. Phys.*, **2004**, *121*, 4389.
  15. D. Jacquemin, E.A. Perpète, M. Medved', G. Scalmani, M.J. Frisch, R. Kobayashi, C. Adamo, *J. Chem. Phys.*, **2007**, *126*, 191108.
  16. B. Champagne, E.A. Perpète, D. Jacquemin, S.J.A. van Gisbergen, E.-J. Baerends, C. Soubra-Ghaoui, K.A. Robins, B. Kirtman, *J. Phys. Chem. A*, **2000**, *104*, 4755.
  17. N.N. Ma, G.C. Yang, S.L. Sun, C.G. Liu, Y.Q. Qiu, *J. Organomet. Chem.*, **2011**, *696*, 2380.
  18. M. Kamiya, H. Sekino, T. Tsuneda, K. Hirao, *J. Chem. Phys.*, **2005**, *122*.
  19. A.D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648.
  20. C. Adamo, V. Barone, *J. Chem. Phys.*, **1999**, *110*, 6158.
  21. Y. Zhao, D.G. Truhlar, *J. Chem. Phys.*, **2006**, *125*, 194101.