Nonlinear absorption and nonlinear refraction in ruthenium alkynyl complexes

Marek Samoc, Mark G. Humphrey, and Marie P. Cifuentes

Laser Physics Centre and Department of Chemistry, The Australian National University, Canberra, ACT 0200, Australia

The studies of third-order nonlinear optical properties of organometallic compounds containing ruthenium and π-conjugated organic segments (phenylene, ethenylene, and ethynylene) is described. Our special interest has been in trigonal (octupolar) structures and in extending the structures towards dendrimers. The merit of these compounds as nonlinear absorbers and for use in electrically-controlled nonlinear devices is discussed.

OCIS codes: 190.4710, 190.4180, 160.4890, 160.4330.

Organometallic compounds possessing large numbers of delocalized electrons provide an interesting class of substances in the search for new effects and materials for applications in photonics and biophotonics[1,2]. Of special interest is the additional degree of tailorability of material properties provided by the presence of metal centres which can be modified by external stimuli, e.g. electric or magnetic fields.

Our research in this field has been concentrated on cubic nonlinear optical properties of organometallic complexes, mostly involving ruthenium and π-electron ethynyl and ethenyl linkages. The need to maximize the nonlinear optical merit of such structures has led to much attention being placed on π-conjugated organometallic dendrimers providing complex multipolar charge distributions. Figure 1 shows examples of organometallic structures of interest. We used several techniques for the determination of third-order optical nonlinearities of such structures, but most results were obtained by Z-scan carried out at low repetition rates (30—1000 Hz) with $\sim$100–fs laser pulses. The measurements were performed in solutions[3] (the solvent usually being dichloromethane).

The experiments were performed to establish structure-property relations and mechanisms of cubic nonlinear optical response. Table 1 shows examples of the values of the real and imaginary parts of the cubic hyperpolarizability γ determined from Z-scan at 800 nm. Most ruthe-

nium complexes investigated by us are strong two-photon absorbers at this wavelength and show a negative real (refractive) part of the cubic hyperpolarizability. While the numbers are relatively high, the merit of these compounds for NLO applications needs to be taken as the ratio of the molecular parameter (e.g. γ_{real}, γ_{imag} or the two photon absorption cross section σ_2) to the molecular weight or molecular volume. These ratios are in turn related to the macroscopic parameters as the nonlinear refractive index n_2 and the two-photon absorption coefficient β_2. Table 1 lists extrapolated values of these two parameters for examples of the ruthenium complexes. The first two entries in Table 1 are the comparison of molecules with structures corresponding to (b) and (a) in Fig. 1. The second and third entries are two forms of the same ruthenium complex corresponding to structure (a) but differing in the oxidation state of the ruthenium centres.

The early interest of photonics researchers has been in finding materials with minimized two-photon absorption to nonlinear refraction ratio[7] (with the coefficient $T = \beta_2\lambda/n_2 \ll 1$), however materials with strong nonlinear absorption, like the ones investigated by us, are finding many potential applications now. Table 2 shows examples of two-photon absorption properties of the ruthenium complexes expressed as the two-photon absorp-
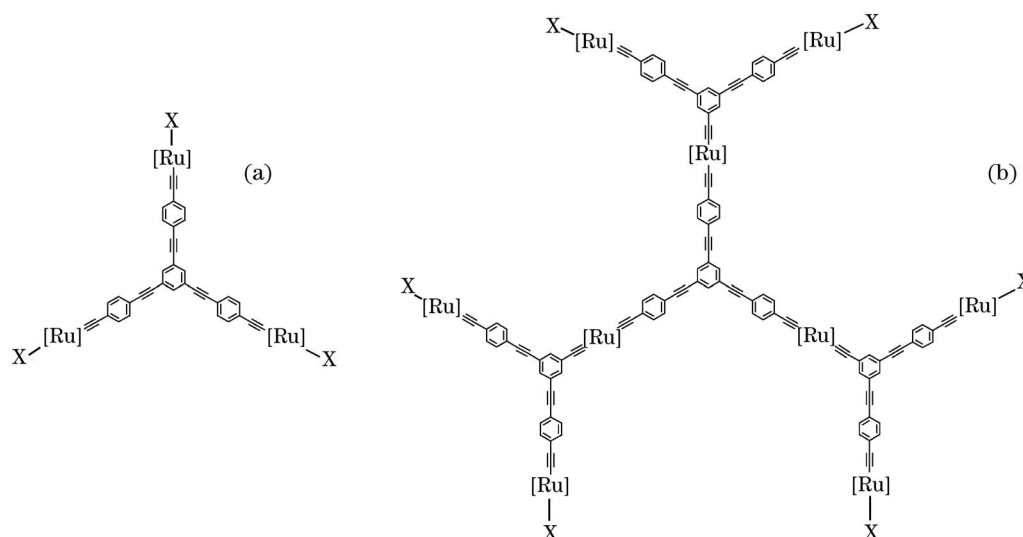

Fig. 1. Examples of trigonally-branched molecular structures explored in our studies.

Table 1. Molecular Third-order NLO Data for Ruthenium Alkynyl and Vinylidene Complexes

Complex	λ_{max} (nm)	γ_{real} ($\times 10^{-36}$ esu)	γ_{imag} ($\times 10^{-36}$ esu)	n_2 Extrapol. ($\times 10^{-14}$ cm^2/W)	β_2 Extrapol. (cm/GW)	Ref.
1,3,5-C$_6$H$_3$(C≡C-4-C$_6$H$_4$C≡C-trans-[Ru(dppe)$_2$]C≡C-3,5-C$_6$H$_3$-{C≡C-4-C$_6$H$_4$C≡C-trans-[Ru(C≡CPh)(dppe)$_2$]}$_2$)$_3$	402	−5050 ±500	20100 ±2000	−1.7	10.6	[4]
[1,3,5-trans-[(dppe)$_2$ClRu(C≡C-4-C$_6$H$_{4m}$C≡C])$_3$C$_6$H$_3$]	414	−330 ± 100	2200 ± 500	−0.46	4.7	[5, 6]
[1,3,5-trans-[(dppe)$_2$ClRu(C≡C-4-C$_6$H$_4$C≡C])$_3$C$_6$H$_3$](PF$_6$)$_3$	893	13500 ± 3000	−4700 ± 500	21	−11.3	[6]

Table 2. Two-photon Absorption Cross-Sections of Selected Alkynylruthenium Complexes

Complex	λ_{max} (nm)	σ_2 (GM = 10^{-50} cm^4·s)	σ_2/M (GM mol/g)	Ref.
[1,3,5-{trans-[Ru(C≡CPh)(C≡C-4-C$_6$H$_4$C≡C)(dppe)$_2$]}$_3$C$_6$H$_3$]	411	700 ± 120	0.2	[5]
[[1-(Me$_3$SiC≡C)C$_6$H$_3$-3,5-{C≡C-4-C$_6$H$_4$C≡C-trans-[Ru(C≡CPh)(dppe)$_2$]}$_2$]]	407	550 ± 70	0.23	[4]
[[1-(HC≡C)C$_6$H$_3$-3,5-{C≡C-4-C$_6$H$_4$C≡C-trans-[Ru(C≡CPh)(dppe)$_2$]}$_2$]]	408	530 ± 70	0.23	[4]
1,3,5-C$_6$H$_3$(C≡C-4-C$_6$H$_4$C≡C-trans-[Ru(dppe)$_2$]C≡C-3,5-C$_6$H$_3$-{C≡C-4-C$_6$H$_4$C≡C-trans-[Ru(C≡CPh)(dppe)$_2$]}$_2$)$_3$]	402	4800 ± 500	0.47	[4]

tion cross-section in Goeppert-Mayer (GM) units and the merit factor σ_2/M where M is the molecular weight. It should be noted that this merit factor is related to the (extrapolated) two-photon absorption coefficient by $\frac{\sigma_2}{M} = \beta_2 \frac{\hbar\omega}{N_0\rho}$ where N_0 is the Avogadro number and ρ is the density.

As indicated in Tables 1 and 2, we found that the two-photon absorption merit factor increases when one moves from simpler molecules towards organometallic dendrimers. The origin of this "dendrimer enhancement" is not clear at this time. We are also finding that competition may exist in some ruthenium dendrimers between absorption saturation and two-photon absorption[8]. This leads to unusual dispersion of the complex cubic hyperpolarizability.

A particularly interesting property of organometallic ruthenium complexes is the facile change in oxidation state of the ruthenium centre and thus the linear and nonlinear optical properties. We have shown that both forms of the ruthenium complexes are characterized by strong nonlinearity with the oxidized forms having an important contribution from absorption saturation within the long wavelength absorption transition[6,8−10]. The transition between the two states can be achieved electrochemically. This electrical switching of the nonlinearities is potentially a useful phenomenon because the signs of both the refractive and the absorptive components of the nonlinear susceptibilities can be reversed by the application of an electrical field leading to electrically controlled nonlinear attenuation or electrically controlled nonlinear

phase shift. Table 1 shows examples of changes in the values of n_2 and β_2 available for such switching at 800 nm.

The conclusion from our studies is that organometallic complexes provide an additional flexibility in the design of nonlinear chromophores for third-order nonlinear optics and thus can be considered interesting candidates for applications.

References

1. I. R. Whittall, A. M. McDonagh, M. G. Humphrey, and M. Samoc, Adv. Organomet. Chem. **42,** 291 (1998).
2. I. R. Whittall, A. M. McDonagh, M. G. Humphrey, and M. Samoc, Adv. Organomet. Chem. **43,** 349 (1999).
3. M. Samoc, A. Samoc, B. Luther-Davies, M. G. Humphrey, and M.-S. Wong, Opt. Mater. **21,** 485 (2003).
4. A. M. McDonagh, M. G. Humphrey, M. Samoc, and B. Luther-Davies, Organometallics **18,** 5195 (1999).
5. A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, T. Wada, H. Sasabe, and A. Persoons, J. Am. Chem. Soc. **121,** 1405 (1999).
6. M. P. Cifuentes, C. E. Powell, M. G. Humphrey, G. A. Heath, M. Samoc, and B. Luther-Davies, J. Phys. Chem. A **105,** 9625 (2001).

7. G. I. Stegeman and W. E. Torruellas, Philos. Trans. R. Soc. London, Ser. A **354,** 745 (1996).

8. C. E. Powell, J. P. Morrall, S. A. Ward, M. P. Cifuentes, E. G. A. Notaras, M. Samoc, and M. G. Humphrey, J. Am. Chem. Soc. **126,** 12234 (2004).

9. C. E. Powell, M. P. Cifuentes, M. G. Humphrey, J. P. Morrall, M. Samoc, and B. Luther-Davies, J. Phys. Chem. A **107,** 11264 (2003).

10. 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. **125,** 602 (2003).