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Organometallic Complexes for Nonlinear Optics. 17.[1] Synthesis, Third-Order Optical Nonlinearities, and Two-Photon Absorption Cross Section of an Alkynylruthenium Dendrimer

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Summary: A soluble, oxidatively and thermally very stable alkynylruthenium dendrimer 1,3,5-C_6H_3(4-C≡C-C_6H_4C≡C-trans-[Ru(dppe)$_2$]C≡C-3,5-C_6H_3-{4-C≡CC$_6$-H_4C≡C-trans-[Ru(C≡CPh)(dppe)$_2$]}$_2$)$_3$, containing a large two-dimensional π-delocalized system, has been prepared using an experimentally straightforward convergent synthetic approach. The first third-order nonlinear optical (NLO) measurements of an organometallic dendrimer have been obtained using the Z-scan technique at a wavelength of 800 nm. Progression from 1,3,5-C_6H_3-(4-C≡CC$_6$H$_4$C≡C-trans-[Ru(dppe)$_2$]C≡CPh)$_3$ to the dendrimer results in (i) no loss of optical transparency, (ii) an increase in the second hyperpolarizability, γ, which is proportionately greater than either the increase in the number of phenylethynyl groups or the extinction coefficient for the important MLCT band, and (iii) a dramatic enhancement of two-photon absorption.

Two-photon absorbing materials have been investigated for a range of applications, including multiphoton microscopy, optical limiting, and optical data storage.[2] Recent studies have aimed at uncovering structure/property relationships for the two-photon absorbing characteristics of organic compounds.[3,4] In these studies, molecules with electron-rich π-delocalized systems of varying geometries have been shown to have large two-photon absorption (TPA) cross sections. Dendrimers have excited considerable interest recently as novel materials with uses in medical diagnostics and possible applications in areas such as molecular recognition, catalysis, and photoactive device engineering.[5-7] The physical properties of an array of meta-connected phenylene−acetylene dendrimers have been studied by Moore and co-workers.[8-14] Although previous studies on multiply alkynylated transition metal complexes with

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(2) Bhawalkar, J. D.; He, G. S.; Prasad, P. N. *Rep. Prog. Phys.* **1996**, *59*, 1041−1070.

(3) Reinhardt, B. A.; Lawrence, L. B.; Clarson, S. J.; Dillard, A. G.; Bhatt, J. C.; Kannan, R.; Yuan, L.; He, G. S.; Prasad, P. N. *Chem. Mater.* **1998**, *10*, 1863−1874.

(4) Albota, M.; Beljonne, D.; Bredas, J. L.; Ehrlich, J. E.; Fu, J. Y.; Heikal, A. A.; Hess, S. E.; Kogej, T.; Levin, M. D.; Marder, S. R.; McCordmaughon, D.; Perry, J. W.; Rockel, H.; Rumi, M.; Subramaniam, C.; Webb, W. W.; Wu, I. L.; Xu, C. *Science* **1998**, *281*, 1653−1656.

(5) Fischer, M.; Vogtle, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 885−905.

(6) Archut, A.; Vogtle, F. *Chem. Soc. Rev.* **1998**, *27*, 233−240.

(7) Zeng, F. W.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681−1712.

(8) Xu, Z.; Moore, J. S. *Macromolecules* **1991**, *24*, 5893−5894.

(9) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 246−248.

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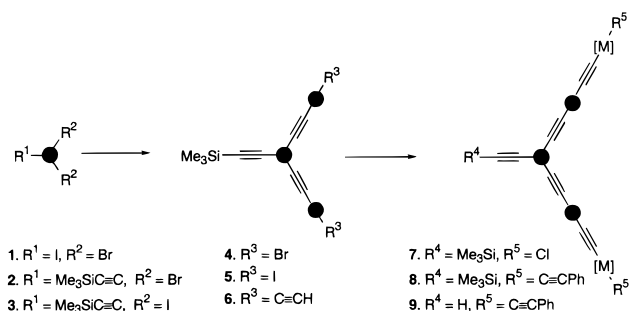† Department of Chemistry.
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extensive systems of π-delocalization have been reported,[15-20][15] th

ere have been no reports thus far on the third-order nonlinear optical (NLO) properties of dendrimers and, in particular, their TPA properties. We present herein the synthesis, cubic NLO, and TPA data for an alkynylruthenium dendrimer containing a large π-delocalized system.

The synthetic procedures employed to prepare the dendrimer are shown in Schemes 1 and 2. A convergent method was used whereby branched dendritic wedges are coupled to a core. The branching is introduced early in the wedge synthesis (Scheme 1) by preparing 1-iodo-3,5-dibromobenzene from 1,3,5-tribromobenzene and then utilizing the palladium(II)-catalyzed coupling method of Sonogashira et al.,[21] where the coupling of a terminal acetylene is much faster to an aryl iodide than to an aryl bromide. The organic component of the wedge may then be built up. The organometallic complex **7** is prepared via a $[PF_6]^-$-stabilized vinylidene intermediate, using adaptations of the method of Dixneuf and co-workers.[22] The complex **8** containing bis-acetylide metal centers is prepared similarly, followed by removal of the trimethylsilyl protecting group to give the wedge, **9**. The synthesis of the complex used for the core, **10**, has been

(10) Xu, Z.; Moore, J. S. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1354−1357.

(11) Xu, Z.; Kahr, M.; Walker, K. L.; Wilkins, C. L.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 4537−4550.

(12) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635−9644.

(13) Shortreed, M. R.; Swallen, S. F.; Shi, Z. Y.; Tan, W.; Xu, Z.; Devadoss, C.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B* **1997**, *101*, 6318−6322.

(14) Pesak, D. J.; Moore, J. S. *Tetrahedron* **1997**, *53*, 15331−15347.

(15) Fink, H.; Long, N. J.; Martin, A. J.; Opromolla, G.; White, A. J. P.; Williams, D. J.; Zanello, P. *Organometallics* **1997**, *16*, 2646−2650.

(16) Bunz, U. H. F.; Enkelmann, V. *Organometallics* **1994**, *13*, 3823−3833.

(17) Müller, T. J. J.; Lindner, H. J. *Chem. Ber.* **1996**, *129*, 607−613.

(18) Constable, E. C.; Eich, O.; Housecroft, C. E.; Johnston, L. A. *Chem. Commun.* **1998**, 2661−2662.

(19) Onitsuka, K.; Fujimoto, M.; Ohshiro, N.; Takahashi, S. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 689−692.

(20) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Maes, J.; Persoons, A.; Schmid, S.; Hockless, D. C. R. *J. Organomet. Chem.* **1997**, *544*, 277−283.

(21) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627−630.

(22) Touchard, D.; Haquette, P.; Pirio, N.; Toupet, L.; Dixneuf, P. H. *Organometallics* **1993**, *12*, 3132−3139.

(23) Gubler, U.; Spreiter, R.; Bosshard, C.; Günter, P.; Tykwinski, R. R.; Diederich, F. *Appl. Phys. Lett.* **1998**, *73*, 2396−2398.

(24) Perry, J. W.; Mansour, K.; Lee, I. Y. S.; Wu, X. L.; Bedworth, P. V.; Chen, C. T.; Ng, D.; Marder, S. R.; Miles, P.; Wada, T.; Tian, M.; Sasabe, H. *Science* **1996**, *273*, 1533−1536.

(25) Naulty, R. H.; McDonagh, A. M.; Whittall, I. R.; Cifuentes, M. P.; Humphrey, M. G.; Houbrechts, S.; Maes, J.; Persoons, A.; Heath, G. A.; Hockless, D. C. R. *J. Organomet. Chem.* **1998**, *563*, 137−146.

(26) Z-scan measurements were performed at 800 nm using 100 fs pulses from a system consisting of a Coherent Mira Ti-sapphire laser pumped with a Verdi cw Nd:YAG laser and a Ti-sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed YAG laser (Spectra Physics GCR) at 30 Hz. The closed-aperture and open-aperture Z-scans were recorded at a few concentrations of each compound in THF, and the real and imaginary part of the nonlinear phase shift determined by numerical fitting using equations given in: Sheik-Bahae, M.; Said, A. A.; Wei, T.; Hagan, D. J.; van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760−769. The real and imaginary part of the hyperpolarizability of the solute were then calculated by linear regression from the concentration dependencies. The nonlinearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1} was assumed.

(27) Sutherland, R. L. *Handbook of Nonlinear Optics*; Marcel Dekker: New York, 1996; Vol. 52.

Scheme 1. Method for the Preparation of Dendritic Wedge Compounds[a]

1. $R^1 = I$, $R^2 = Br$
2. $R^1 = Me_3SiC\equiv C$, $R^2 = Br$
3. $R^1 = Me_3SiC\equiv C$, $R^2 = I$
4. $R^3 = Br$
5. $R^3 = I$
6. $R^3 = C\equiv CH$
7. $R^4 = Me_3Si$, $R^5 = Cl$
8. $R^4 = Me_3Si$, $R^5 = C\equiv CPh$
9. $R^4 = H$, $R^5 = C\equiv CPh$

Preparation of **1**: (a) 1,3,5-tribromobenzene, *n*-BuLi (b) I₂;
Conversion of **1→2**: Me₃SiC≡CH, NEt₃, [PdCl₂(PPh₃)₂], CuI; Conversion of **2→3**: (a) *t*-BuLi (b) I₂;
Conversion of **3→4**: *p*-HC≡CC₆H₄Br, NEt₃, [PdCl₂(PPh₃)₂], CuI;
Conversion of **4→5**: (a) *t*-BuLi (b) I₂; Conversion of **5→6**: MgBrC≡CH, ZnBr₂, [PdCl₂(PPh₃)₂], NEt₃;
Conversion of **6→7**: (a) *cis*-[RuCl₂(dppe)₂], NaPF₆, (b) NEt₃; Conversion of **7→8**: HC≡CPh, NaPF₆, NEt₃;
Conversion of **8→9**: Tetrabutylammonium fluoride

[a]Structural elements: −●−, 1,4-connected phenylene unit.

reported previously.[1] Preparation of the dendrimer (see Scheme 2) again utilizes an adaptation of the Dixneuf coupling method to couple **10** to three of the dendrimer wedges **9**, affording the dendrimer complex **11**. These complexes are two-dimensionally π-delocalized, an important design element influencing third-order NLO properties which has attracted several studies recently.[23,24]

Spectral data for the dendrimer **11** are similar to those of previously reported bis{bis(diphenylphosphino)-ethane}ruthenium bis-acetylide complexes (see the Supporting Information).[1,25] The UV−vis spectrum of **11** and that of the previously reported[1] complex **12** (see Scheme 2) are shown in Figure 1. Complex **11** has an absorption band at 403 nm which may be assigned to an MLCT transition.[25] The UV−vis spectrum of complex **12** has the analogous MLCT band at 411 nm. Significantly, increasing size does not reduce optical transparency. The small blue shift observed in progressing from **12** to **11** may indicate a lack of coplanarity through the dendritic structure of complex **11**. Interestingly, the magnitude of the extinction coefficient, ϵ, increases 4-fold in progressing from the three-metal center containing complex **12** to the nine-metal center containing complex **11**.

Third-order NLO measurements were performed using the Z-scan technique.[26] The results are listed in Table 1 together with UV−vis data. These are the first third-order NLO data for organometallic dendritic complexes. Not unexpectedly, introduction of the ligated metal in proceeding from **6** to **7** and **8** results in a significant increase in γ. The significant γ_{imag} values for the organometallic complexes **7**−**12** are indicative of TPA, which becomes important as the optical frequency at λ_{max} approaches twice the measurement frequency. The negative γ_{real} values for **7**−**12** are therefore likely to result from two-photon dispersion effects, rather than being indicative of zero-frequency negative cubic hyperpolarizabilities. Third-order hyperpolarizabilities for the dendrimer **11** are much bigger than those of its components **9** and **10** or the related complex **12**. In particular, progressing from **12** to **11** results in an increase in γ proportionally greater than either the increase in the number of phenylethynyl groups or the extinction coefficient.

Table 1. Experimental Linear Optical Spectroscopic and Cubic Nonlinear Optical Response Parameters for 4−12[a]

compound	λ_{max} (nm) [ϵ (10^4 M^{-1} cm^{-1})]	γ_{real}[b] (10^{-36} esu)	γ_{imag}[b] (10^{-36} esu)	$\lvert\gamma\rvert$ (10^{-36} esu)	σ_2[c] (10^{-50} cm^4 s)
12[d]	411 [11.6]	-600 ± 200	2900 ± 500	3000 ± 600	700 ± 120
11	402 [42]	-5050 ± 500	20100 ± 2000	20700 ± 2000	4800 ± 500
10[d]	414 [10]	-330 ± 100	2200 ± 500	2200 ± 600	530 ± 120
9	408 [7.3]	-830 ± 100	2200 ± 300	2400 ± 300	530 ± 70
8	407 [6.4]	-700 ± 100	2270 ± 300	2400 ± 300	550 ± 70
7	411 [6.8]	-510 ± 500	4700 ± 1500	4700 ± 2000	1100 ± 360
6	321 [6.3]	67 ± 30	7 ± 5	67 ± 40	2 ± 1
5	314 [6.7]	77 ± 30	4 ± 3	77 ± 40	1 ± 1
4	310 [6.8]	53 ± 20	5 ± 3	53 ± 20	1 ± 1

[a] All measurements in tetrahydrofuran solvent. All complexes are optically transparent at 800 nm. [b] All results are referenced to the nonlinear refractive index of silica $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1}. [c] Calculated using the equation $\sigma_2 = \hbar\omega\beta/N$, where β is the two-photon absorption coefficient.[27] [d] Reference 1.

Scheme 2
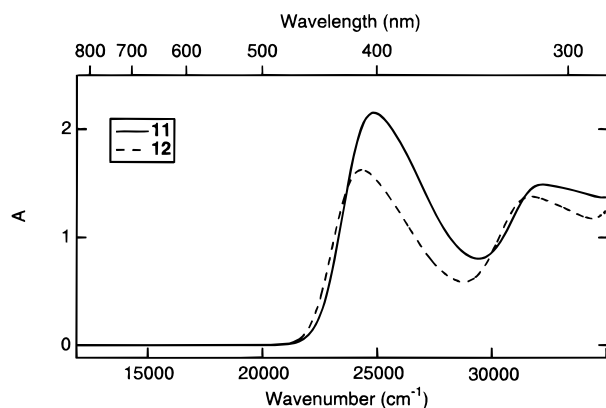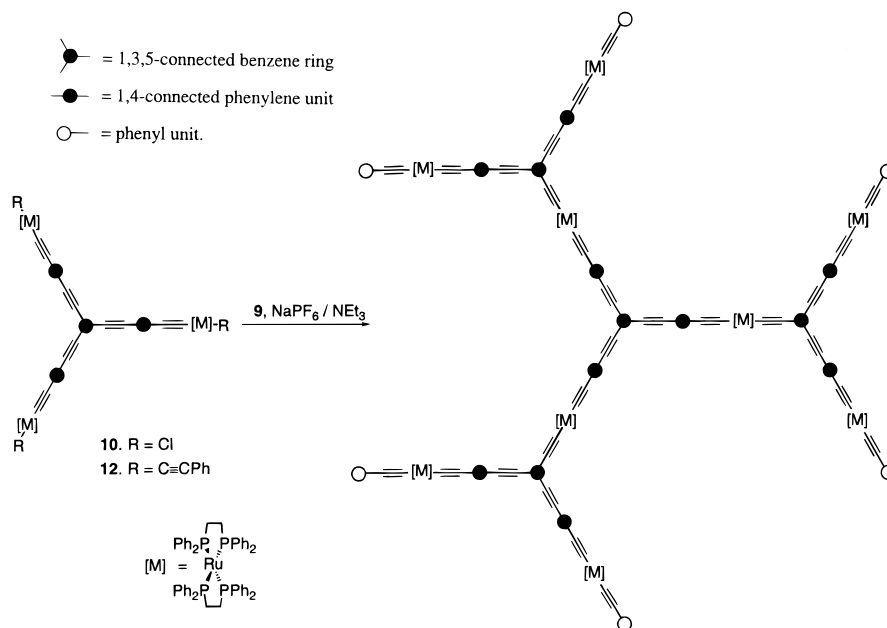
Figure 1. UV−vis spectra for **11** and **12**.

The TPA cross sections, σ_2, calculated from the measured two-photon absorption coefficients, β, are listed in Table 1. The measurements were performed using low repetition rate 100 fs pulses, and excited-state absorption should therefore be negligible. The dendritic complex **11** shows a σ_2 value comparable in magnitude to the σ_2 values of the bis(styryl)benzene derivatives reported by Albota et al.[4] and the heterocyclic compounds reported by Reinhardt et al.[3] In the present case, it is likely that the size and two-dimensional nature of the π-delocalized system combined with the strong MLCT transition all contribute to the large observed σ_2 value. These results suggest that this class of compound deserves further scrutiny in future NLO studies.

In summary, we have prepared a soluble, oxidatively and thermally very stable alkynylruthenium dendrimer containing a large two-dimensional π-delocalized system using an experimentally straightforward convergent synthetic approach. The first third-order NLO measurements for organometallic dendrimers show a significant enhancement of two-photon absorption upon proceeding from the constituent molecules to the dendritic complex.

Supporting Information Available: Experimental procedures for synthesis and nonlinear optical measurements and characterization data for **1−9** and **11**. This material is available free of charge via the Internet at http://pubs.acs.org.