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Organometallic Complexes for Nonlinear Optics. 39.[1] Syntheses and Third-Order Nonlinear Optical Properties of First-Generation Peripherally Metalated Arylalkynyl Dendrimers

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Steric control of the extent of reaction has been developed to rapidly synthesize ligated metal-containing dendrons that have been employed in arylalkynyl complex dendrimer synthesis. Reaction of 1,3,5-triethynylbenzene with excess *cis*-[RuCl$_2$(dppe)$_2$] affords 1,3-{*trans*-[(dppe)$_2$ClRuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (**1**). Reaction of **1** with 4-RC$_6$H$_4$C≡CH affords 1,3-{*trans*-[(dppe)$_2$(RC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ [R = H (**2a**), NO$_2$ (**2b**), NH$_2$ (**2c**)]. **2a**−**c** are coupled with 4-Me$_3$SiC≡CC$_6$H$_4$I under Sonogashira conditions to give 1,3-{*trans*-[(dppe)$_2$(RC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$-5-(Me$_3$SiC≡CC$_6$H$_4$-4-C≡C)C$_6$H$_3$ [R = H (**3a**), NO$_2$ (**3b**), NH$_2$ (**3c**)], which can be desilylated to afford 1,3-{*trans*-[(dppe)$_2$(RC$_6$H$_4$-4-C≡C)-RuC≡C]}$_2$-5-(HC≡CC$_6$H$_4$-4-C≡C)C$_6$H$_3$ [R = H (**4a**), NO$_2$ (**4b**), NH$_2$ (**4c**)]. Sonogashira coupling of **4a**−**c** with 1,3,5-triiodobenzene gives the systematically varied peripherally metalated arylalkynyl dendrimers 1,3,5-(3,5-{*trans*-[(dppe)$_2$(RC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$C$_6$H$_3$-1-C≡CC$_6$H$_4$-4-C≡C)$_3$C$_6$H$_3$ [R = H (**5a**), NO$_2$ (**5b**), NH$_2$ (**5c**)]. All complexes show two reversible oxidation processes by cyclic voltammetry. Cubic nonlinearities determined using the *Z*-scan technique and low-repetition femtosecond pulses at 660 and 800 nm increase on π-system lengthening and progression from dendron to dendrimer. In contrast to all other complexes in this study, **5b** is a saturable absorber at 800 nm. Dispersion of both the refractive and the absorptive nonlinearities of **5b** has been determined, and the behavior has been modeled for the first time with an inorganic complex.

Introduction

Dendrimers are of significant current interest for a variety of reasons, including applications in medical diagnostics and possible applications in many areas such as molecular recognition, catalysis, and photoactive device engineering.[2,3] Thus far, the vast majority of studies have considered organic dendrimers, but metal-containing dendrimers are also interesting because the metal atoms can potentially impart or modify electronic, optical, and/or magnetic properties;[4−11] efficient synthetic procedures to metal-containing dendrimers are therefore a current challenge. Most existing metal-containing dendrimers contain ligated metals attached to the periphery of saturated organic dendrimers, but examples that are potentially π-delocalizable are also of interest, particularly because the π-system may facilitate the enhancement/modification of the electronic and optical properties mentioned previously. While zero-generation π-delocalizable metal-containing dendrimers have been reported in several publications,[12−24] higher generation examples are significantly scarcer and have largely focused on

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arylalkynylplatinum dendrimers containing 16 electron metal centers;[25−29] electron-rich (18 electron) metal center-containing π-delocalizable dendrimers are restricted to the ruthenium-containing examples we reported previously, available via long-winded multistep syntheses in overall very low yields.[8,30,31] More facile syntheses are needed to fully explore the physical and material properties of these compounds. We report herein straightforward syntheses of first-generation arylethynyl dendrimers peripherally functionalized with (arylethynyl)bis(diphosphine)ruthenium units, including examples bearing donor or acceptor substituents to promote the polarization of electron density, together with their electrochemical and third-order nonlinear optical properties; some of these results have been described in a preliminary fashion.[32,33]

Experimental Procedures

Materials. All reactions were performed under a nitrogen atmosphere with the use of Schlenk techniques unless otherwise stated. Dichloromethane and triethylamine were dried by distilling over calcium hydride; all other solvents were used as received. The petroleum ether had a boiling range of 60−80 °C. Chromatography was performed on silica gel (230−400 mesh ASTM) or ungraded basic alumina. Ammonium hexafluorophosphate, sodium hexafluorophosphate, tetra-*n*-butylammonium fluoride, phenylacetylene (Aldrich), and CuCl (J. T. Baker) were used as received. Pd(PPh$_3$)$_4$ was a gift from Dr. B. L. Flynn, Department of Chemistry, Australian National University. The following were prepared by literature procedures: 1,3,5-triethynylbenzene,[34] 4-Me$_3$SiC≡CC$_6$H$_4$I, 4-HC≡CC$_6$H$_4$NO$_2$, 4-HC≡CC$_6$H$_4$NH$_2$,[35] *cis*-[RuCl$_2$(dppe)$_2$],[36] and 1,3,5-triiodobenzene.[37]

Methods and Instrumentation. Microanalyses were carried out at the Australian National University. UV−vis spectra of solutions in tetrahydrofuran (THF) in 1 cm quartz cells were recorded using a Cary 5 spectrophotometer. Infrared spectra were recorded as dichloromethane solutions using a PerkinElmer System 2000 FT-IR. ^{1}H (300 MHz) and ^{31}P NMR (121 MHz) spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are referenced to residual chloroform (7.24 ppm) or external H$_3$PO$_4$ (0.0 ppm), respectively. Fast atom bombardment mass spectra (FAB MS) were recorded using an AutoSpecC instrument at the University of Western Australia (3-nitrobenzyl alcohol matrix), and secondary ion mass spectra (SI MS) were recorded using a VG ZAB 2SEQ instrument (30 kV Cs$^+$ ions, current 1 mA, accelerating potential 8 kV, and 3-nitrobenzyl alcohol matrix) at the Australian National University; peaks are reported as *m*/*z* (assignment, relative intensity). Cyclic voltammetry measurements were recorded using a MacLab 400 interface and MacLab potentiostat from AD Instruments. The supporting electrolyte was 0.1 M (NBu$^n_4$)PF$_6$ in distilled, deoxygenated CH$_2$Cl$_2$. Solutions containing ca. 1×10^{-3} M complex were maintained under argon. Measurements were carried out at room temperature using Pt disc working, Pt wire auxiliary, and Ag|AgCl reference- electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V (peak separation ca. 0.09 V). Scan rates were typically 100 mV s^{-1}. Transmission electron microscopy (TEM) was carried out using a Philips EM430 microscope (300 kV electron beam). The samples were supported on alumina to reduce particle aggregation (a solution of ca. 2 mg of sample in CH$_2$Cl$_2$ was adsorbed onto ca. 200 mg of alumina, the supernatant was pipetted off, and the sample was air-dried). A MeOH suspension of the supported sample was then dispersed onto a standard copper grid coated with a holey carbon film. Molecular modeling calculations were carried out on a SGI IRIX workstation using the SYBYL forcefield[38] in the program Spartan 5.0.[39]

Synthesis of 1,3-{*trans*-[(dppe)$_2$ClRuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (1). 1,3,5-Triethynylbenzene (70 mg, 0.467 mmol), *cis*-[RuCl$_2$(dppe)$_2$] (1.10 g, 1.14 mmol), and NaPF$_6$ (200 mg, 1.18 mmol) were stirred in CH$_2$Cl$_2$ (25 mL) for 17 h. The solution was filtered into rapidly stirred Et$_2$O (ca. 150 mL). The resultant precipitate was collected, washed with Et$_2$O, and redissolved in CH$_2$Cl$_2$. NEt$_3$ (5 mL) was added, the solution was stirred for 5 min, and the solvent was removed under reduced pressure. The resultant yellow powder was purified by column chromatography on basic alumina, eluting with CH$_2$Cl$_2$, to afford a yellow powder (800 mg, 85%). Anal. Calcd for C$_{116}$H$_{100}$Cl$_2$P$_8$Ru$_2$: C 69.15, H 5.00%. Found: C 69.42, H 5.29%. IR: ν(≡CH) 3302 cm^{-1}, ν(C≡C) 2059 cm^{-1}. UV−vis: λ 334 nm, ϵ 38 300 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.68 (m, 16H, PCH$_2$CH$_2$P), 3.01 (s, 1H, C≡CH), 6.41−7.70 (m, 83H, phenyl). ^{31}P NMR: δ 50.5. SI MS: 2014 ([M]$^+$, 20), 1979 ([M − Cl]$^+$, 15), 933 ([RuCl(dppe)$_2$]$^+$, 15), 898 ([Ru(dppe)$_2$]$^+$, 100).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(PhC≡C)RuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (2a). 1,3-{*trans*-[(dppe)$_2$(ClRuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (**1**) (773 mg, 0.364 mmol), NH$_4$PF$_6$ (92 mg, 0.56 mmol), phenylacetylene (0.4 mL, ca. 3.6 mmol), and NEt$_3$ (2 mL) were stirred in refluxing CH$_2$Cl$_2$ (40 mL) for 17 h. The solution was allowed to cool and dried under reduced pressure. The resultant yellow powder was triturated with diethyl ether, and the residue was purified by column chromatography on alumina. Removal of solvent from the eluate afforded a yellow solid (747 mg, 84%). Anal. Calcd for C$_{132}$H$_{110}$P$_8$Ru$_2$: C 73.87, H 5.17%. Found: C 74.46, H 5.78%. IR: ν(C≡C) 2055 cm^{-1}. UV−vis: λ 335 nm, ϵ 79 700 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.64 (m, 16H, PCH$_2$CH$_2$P), 3.02 (s, 1H, C≡CH), 6.41−7.70 (m, 93H, phenyl). ^{31}P NMR: δ 54.4. SI MS: 2146 ([M]$^+$, 3), 999 ([Ru(C≡CPh)(dppe)$_2$]$^+$, 98), 898 ([Ru(dppe)$_2$]$^+$, 100).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(O$_2$NC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (2b). 1,3-{*trans*-[(dppe)$_2$(ClRuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (**1**) (512 mg, 0.254 mmol), NH$_4$PF$_6$ (55 mg, 0.337 mmol), 4-O$_2$NC$_6$H$_4$C≡CH (153 mg, 1.04 mmol), and NEt$_3$ (1 mL) were stirred in refluxing CH$_2$Cl$_2$ (25 mL) for 22 h. The solution was filtered through a short pad of alumina, and the solvent was removed from the filtrate under reduced pressure. The resultant red residue was triturated with petroleum ether and purified on an alumina column with CH$_2$Cl$_2$ and petroleum ether (11:9) as eluent. The eluant was reduced to dryness, and the red solid was dried under vacuum (218 mg, 38%). Anal. Calcd for C$_{132}$H$_{108}$O$_4$N$_2$P$_8$Ru$_2$: C

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70.90, H 4.87, N 1.25. Found: C 70.24, H 5.16, N 0.91%. IR: ν(C$\equiv$C) 2045 cm^{-1}. UV−vis: λ 475 nm, ϵ 47 800 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.60−2.69 (m, 16H, CH$_2$), 3.06 (s, 1H, C$\equiv$CH), 6.47−7.96 (m, 91H, phenyl). ^{31}P NMR: δ 54.0. FAB MS: 2236 ([M]$^+$, 20), 1044 ([Ru(C$\equiv$CC$_6$H$_4$NO$_2$)(dppe)$_2$]$^+$, 10), 898 ([Ru(dppe)$_2$]$^+$, 100).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(H$_2$NC$_6$H$_4$-4-C$\equiv$C)RuC$\equiv$C]}$_2$-5-HC$\equiv$CC$_6$H$_3$ (2c). A mixture of 1,3-{*trans*-[(dppe)$_2$ClRuC$\equiv$C]}$_2$-5-HC$\equiv$CC$_6$H$_3$ (**1**) (681 mg, 0.356 mmol), NH$_4$PF$_6$ (425 mg, 0.337 mmol), 4-HC$\equiv$CC$_6$H$_4$NH$_2$ (420 mg, 3.59 mmol), and NEt$_3$ (2 mL) was stirred in refluxing CH$_2$Cl$_2$ (50 mL) for 18 h. The solution was allowed to cool and passed through a short pad of alumina with 11:9 CH$_2$Cl$_2$/petroleum ether. The solvent was removed from the eluate under reduced pressure, and the resultant solid was triturated with petroleum ether. The residue was further purified by column chromatography on alumina, eluting with 1:1 CH$_2$Cl$_2$/petroleum ether. Solvent removal from the eluate afforded a mustard-yellow powder (340 mg, 44%). Anal. Calcd for C$_{132}$H$_{112}$N$_2$P$_8$Ru$_2$: C 72.85, H 5.19, N 1.29. Found: C 71.97, H 5.02, N 1.27%. IR: ν(C$\equiv$C) 2054 cm^{-1}. UV−vis: λ 333 nm, ϵ 23 000 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.67 (m, 16H, CH$_2$), 3.03 (s, 1H, C$\equiv$CH), 6.51−7.55 (m, 95H, phenyl). ^{31}P NMR: δ 54.6. FAB MS: 2176 ([M]$^+$, 2), 2060 ([M − C$_2$C$_6$H$_4$NH$_2$]$^+$, 1), 898 ([Ru(dppe)$_2$]$^+$, 100).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(PhC$\equiv$C)RuC$\equiv$C]}$_2$-5-(Me$_3$SiC$\equiv$C-4-C$_6$H$_4$C$\equiv$C)C$_6$H$_3$·CH$_2$Cl$_2$ (3a). 4-Me$_3$SiC$\equiv$CC$_6$H$_4$I (372 mg, 1.24 mmol), 1,3-{*trans*-[(dppe)$_2$(PhC$\equiv$C)RuC$\equiv$C]}$_2$-5-HC$\equiv$CC$_6$H$_3$ (**2a**) (275 mg, 0.13 mmol), and Pd(PPh$_3$)$_4$ (49 mg, 0.042 mmol) were added to a thoroughly deoxygenated mixture of 1:1 CH$_2$Cl$_2$/NEt$_3$ (50 mL) and refluxed for 18 h. The solution was allowed to cool to room temperature, the mixture was filtered through a short pad of alumina, and the solvent was removed from the eluate under reduced pressure. The residue was triturated with petroleum ether, and the resultant yellow product was collected by filtration (226 mg, 76%). Anal. Calcd for C$_{144}$H$_{124}$Cl$_2$P$_8$Ru$_2$Si: C 71.96, H 5.20%. Found: C 72.07, H 5.80%. IR: ν(C$\equiv$CSiMe$_3$) 2157 cm^{-1}, ν(RuC$\equiv$C) 2056 cm^{-1}. UV−vis: λ 335 nm, ϵ 94 900 M^{-1} cm^{-1}. ^{1}H NMR: δ 0.26 (s, 9H, Me), 2.67 (m, 16H, PCH$_2$CH$_2$P), 5.27 (s, 2H, CH$_2$Cl$_2$), 6.41−7.70 (m, 97H, phenyl). ^{31}P NMR: δ 54.4. FAB MS: 2318 ([M]$^+$, 2), 2217 ([M − C$_2$Ph]$^+$, 2), 898 ([Ru(dppe)$_2$]$^+$, l00).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(O$_2$NC$_6$H$_4$-4-C$\equiv$C)RuC$\equiv$C]}$_2$-5-(Me$_3$SiC$\equiv$CC$_6$H$_4$-4-C$\equiv$C)C$_6$H$_3$ (3b). 1,3-{*trans*-[(dppe)$_2$(O$_2$NC$_6$H$_4$-4-C$\equiv$C)RuC$\equiv$C]}$_2$-5-HC$\equiv$CC$_6$H$_3$ (**2b**) (151 mg, 0.067 mmol), 4-Me$_3$SiC$\equiv$CC$_6$H$_4$I (97 mg, 0.32 mmol), and Pd(PPh$_3$)$_4$ (23 mg, 0.020 mmol) were heated in a 1:1 refluxing mixture of CH$_2$Cl$_2$/NEt$_3$ (20 mL) for 21 h. The solution was passed through a short pad of alumina, and the eluate was taken to dryness under reduced pressure. The product was purified by column chromatography on alumina with 3:2 CH$_2$Cl$_2$/petroleum ether as eluent, affording a red solid (82 mg, 50%) after removal of solvent. Anal. Calcd for C$_{143}$H$_{120}$N$_2$O$_4$P$_8$Ru$_2$Si: C 71.31, H 5.02, N 1.16. Found: C 71.24, H 5.41, N 1.19%. IR: ν(C$\equiv$CSiMe$_3$) 2153 cm^{-1}, ν(RuC$\equiv$C) 2045 cm^{-1}. UV−vis: λ 475 nm, ϵ 46 830 M^{-1} cm^{-1}. ^{1}H NMR: δ 0.26 (s, 9H, Me), 2.60−2.69 (m, 16H, CH$_2$), 6.48−7.96 (m, 95H, phenyl). ^{31}P NMR: δ 53.9. FAB MS: 2408 ([M]$^+$, 10), 1044 ([Ru(C$\equiv$CC$_6$H$_4$NO$_2$)(dppe)$_2$]$^+$, 10), 898 ([Ru(dppe)$_2$]$^+$, 100).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(H$_2$NC$_6$H$_4$-4-C$\equiv$C)RuC$\equiv$C]}$_2$-5-(Me$_3$SiC$\equiv$CC$_6$H$_4$-4-C$\equiv$C) C$_6$H$_3$ (3c). A mixture of **2c** (285 mg, 0.138 mmol), 4-Me$_3$SiC$\equiv$CC$_6$H$_4$I (425 mg, 1.42 mmol), Pd(PPh$_3$)$_4$ (6.0 mg, 6.7 μmol), and NEt$_3$ (5 mL) was refluxed in CH$_2$Cl$_2$ (25 mL) for 17 h. The reaction mixture was allowed to cool and was passed through a short pad of alumina with CH$_2$Cl$_2$ as eluent. The eluate was dried and triturated with petroleum ether. The residue was purified by liquid diffusion of MeOH into a solution in CH$_2$Cl$_2$ to afford a brown powder (130 mg, 41%). Anal. Calcd for C$_{143}$H$_{124}$N$_2$P$_8$Ru$_2$Si: C 73.13, H 5.32, N 1.19. Found: C 72.91, H 5.22, N 1.13%. IR: ν(C$\equiv$CSiMe$_3$) 2154 cm^{-1}, ν(RuC$\equiv$C) 2053 cm^{-1}. UV−vis: λ 334 nm, ϵ 55 700 M^{-1} cm^{-1}. ^{1}H NMR: δ 0.22 (s, 9H, Me), 2.69 (m, 16H, CH$_2$), 3.66 (br s, 4H, NH$_2$), 6.93−7.70 (m, 95H, phenyl). ^{31}P NMR: δ 54.5. FAB MS: 2116 ([M − 2H$_2$NC$_6$H$_4$C$_2$)]$^+$, 1), 898 ([Ru(dppe)$_2$]$^+$, 100).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(PhC$\equiv$C)RuC$\equiv$C]}$_2$-5-(HC$\equiv$CC$_6$H$_4$-4-C$\equiv$C)C$_6$H$_3$ (4a). Complex **3a** (185 mg, 0.080 mmol) and NBu$^n{}_4$F (2 mL, 1 M solution in THF) were stirred together in CH$_2$Cl$_2$ (25 mL) for 2 h. The solution was filtered through a short pad of alumina, and the solvent was reduced in volume to yield the yellow product (151 mg, 84%). Anal. Calcd for C$_{140}$H$_{114}$P$_8$Ru$_2$: C 74.86, H 5.12%. Found: C 74.61, H 5.80%. IR: ν(C$\equiv$CH) 3303 cm^{-1}, ν(C$\equiv$C) 2056 cm^{-1}. UV−vis: λ 330 nm, ϵ 99 400 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.66 (m, 16H, PCH$_2$CH$_2$P), 3.18 (s, lH, HC$\equiv$C), 6.40−7.70 (m, 97H, phenyl). ^{31}P NMR: δ 54.4. SI MS: 2246 ([M]$^+$, 5), 2145 ([M − HC$\equiv$CC$_6$H$_4$]$^+$, l0), 999 [Ru(C$\equiv$CPh)(dppe)$_2$]$^+$, 15), 898 ([Ru(dppe)$_2$]$^+$, l00), 500 ([Ru(dppe)]$^+$, 30).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(O$_2$NC$_6$H$_4$-4-C$\equiv$C)RuC$\equiv$C]}$_2$-5-(HC$\equiv$CC$_6$H$_4$-4-C$\equiv$C)C$_6$H$_3$ (4b). A mixture of **3b** (51 mg, 0.021 mmol) and NBu$^n{}_4$F (0.5 mL, 1 M solution in THF) in CH$_2$Cl$_2$ (10 mL) was stirred for 1 h. The resultant solution was passed through a short pad of alumina, and the eluate was dried under reduced pressure to yield a red powder (38 mg, 77%). Anal. Calcd for C$_{140}$H$_{112}$N$_2$O$_4$P$_8$Ru$_2$: C 71.97, H 4.83, N 1.20. Found: C 71.77, H 5.16, N 1.15%. IR: ν(C$\equiv$C) 2045 cm^{-1}. UV−vis: λ 474 nm, ϵ 40 790 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.62−2.66 (m, 16H, CH$_2$), 3.18 (s, 1H, C$\equiv$CH), 6.47−7.96 (m, 95H, phenyl). ^{31}P NMR: δ 53.9. FAB MS: 2289 ([M − NO$_2$ − H]$^+$, 5), 1044 ([Ru(C$\equiv$CC$_6$H$_4$NO$_2$)(dppe)$_2$]$^+$, 10), 898 ([Ru(dppe)$_2$]$^+$, 100).

Synthesis of 1,3-{*trans*-[(dppe)$_2$(H$_2$NC$_6$H$_4$-4-C$\equiv$C)RuC$\equiv$C]}$_2$-5-(HC$\equiv$CC$_6$H$_4$-4-C$\equiv$C)C$_6$H$_3$ (4c). A mixture of **3c** (110 mg, 0.047 mmol) and NBu$^n{}_4$F (1.0 mL, 1 M solution in THF) in CH$_2$Cl$_2$ (40 mL) was stirred for 1 h. The resultant solution was passed through a short pad of alumina, and the eluate was dried under reduced pressure to yield a brown powder. This was further purified by liquid diffusion of MeOH into a solution in CH$_2$Cl$_2$ (95 mg, 89%). Anal. Calcd for C$_{140}$H$_{116}$N$_2$P$_8$Ru$_2$: C 73.87, H 5.14, N 1.23. Found: C 72.81, H 5.10, N 1.17%. IR: ν(C$\equiv$C) 2055 cm^{-1}. UV−vis: λ 328 nm, ϵ 93 200 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.67 (m, 16H, CH$_2$), 3.11 (s, 1H, C$\equiv$CH), 3.72 (br s, 4H, NH$_2$), 6.79−7.85 (m, 95H, phenyl). ^{31}P NMR: δ 54.5.

Synthesis of 1,3,5-(3,5-{*trans*-[(dppe)$_2$(PhC$\equiv$C)RuC$\equiv$C]}$_2$C$_6$H$_3$-1-C$\equiv$CC$_6$H$_4$-4-C$\equiv$C)$_3$C$_6$H$_3$ (5a). 1,3,5-Triiodobenzene (6.8 mg, 0.015 mmol), l,3-{*trans*-[(dppe)$_2$(PhC$\equiv$C)RuC$\equiv$C]}$_2$-5-(HC$\equiv$C-4-C$_6$H$_4$C$\equiv$C)C$_6$H$_3$ (**4a**) (100 mg, 0.045 mmol), and Pd(PPh$_3$)$_4$ (105 mg, 0.091 mmol) were added to a deoxygenated mixture of 1:1 CH$_2$Cl$_2$/NEt$_3$ (50 mL), and the mixture was refluxed for 12 h. The reaction mixture was cooled to room temperature and filtered through a short pad of alumina, and the solvent was removed under reduced pressure. The residue was extracted into CH$_2$Cl$_2$ and was adsorbed onto an alumina column, eluting with diethyl ether (200 mL) to remove any unreacted **4a.** Subsequent elution with CH$_2$Cl$_2$ (200 mL) afforded a yellow solution, which gave a yellow powder on reduction of the solvent volume (57 mg, 56%). Anal. Calcd for C$_{426}$H$_{342}$P$_{24}$Ru$_6$: C 75.12, H 5.06%. Found: C 74.36, H 5.86%. IR: ν(C$\equiv$C) 2057 cm^{-1}. UV−vis: λ 339 nm, ϵ 342 500 M^{-1} cm^{-1}. ^{1}H NMR: δ 2.65 (m, 48H, PCH$_2$CH$_2$P), 6.50−7.75 (m, 294H, phenyl). ^{31}P NMR: δ 54.2. SI MS: 2245 ([l,3-{*trans*-[(dppe)$_2$(PhC$\equiv$C)RuC$\equiv$C]}$_2$-5-(C$\equiv$C-4-C$_6$H$_4$C$\equiv$C)C$_6$H$_3$]$^+$, 7), 2145 (l,3-{*trans*-[(dppe)$_2$(PhC$\equiv$C)RuC$\equiv$C]}$_2$-5-(C$\equiv$C)C$_6$H$_3$]$^+$, 55).

Synthesis of 1,3,5-(3,5-{*trans*-[(dppe)$_2$(O$_2$NC$_6$H$_4$-4-C$\equiv$C)-RuC$\equiv$C]}$_2$C$_6$H$_3$-1-C$\equiv$CC$_6$H$_4$-4-C$\equiv$C)$_3$C$_6$H$_3$ (5b). A mixture of 1,3-{*trans*-[(dppe)$_2$(O$_2$NC$_6$H$_4$-4-C$\equiv$C)RuC$\equiv$C]}$_2$-5-(HC$\equiv$C-4-C$_6$H$_4$C$\equiv$C)C$_6$H$_3$ (**4b**) (26 mg, 0.011 mmol), 1,3,5-triiodobenzene (1.9 mg, 0.004 mmol), and Pd(PPh$_3$)$_4$ (25 mg, 0.022 mmol) was heated for 22 h in refluxing 1:1 CH$_2$Cl$_2$/NEt$_3$ (30 mL). The solution was passed through a short pad of alumina, and the solvent was removed under reduced pressure to yield a red powder

(25 mg, 82%). Anal. Calcd for $C_{426}H_{336}N_6O_{12}P_{24}Ru_6$: C 72.26, H 4.78, N 1.19. Found: C 72.05, H 4.67, N 1.18%. IR: $\nu(C\equiv C)$ 2045 cm^{-1}. UV−vis: λ 475 nm, ϵ 108 660 M^{-1} cm^{-1}. ^1H NMR: δ 2.63−2.66 (m, 48H, CH_2), 6.85−7.96 (m, 288H, phenyl). ^{31}P NMR: δ 53.8. FAB MS: 898 ([Ru(dppe)$_2$]$^+$, 3).

Synthesis of 1,3,5-(3,5-{*trans*-[(dppe)$_2$(H$_2$NC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$C$_6$H$_3$-1-C≡CC$_6$H$_4$-4-C≡C)$_3$C$_6$H$_3$ (5c). A mixture of 1,3-{*trans*-[(dppe)$_2$(H$_2$NC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$-5-(HC≡C-4-C$_6$H$_4$C≡C)C$_6$H$_3$ (**4c**) (88 mg, 0.039 mmol), 1,3,5-triiodobenzene (5.9 mg, 0.013 mmol), and Pd(PPh$_3$)$_4$ (47 mg, 0.053 mmol) was heated for 17 h in refluxing 1:1 CH_2Cl_2/NEt_3 (40 mL). The solution was passed through a short pad of alumina, and the solvent was removed under reduced pressure to yield a brown powder (57 mg, 64%). Anal. Calcd for $C_{426}H_{348}N_6P_{24}Ru_3$: C 74.14, H 5.08, N 1.22. Found: C 73.96, H 5.22, N 1.20%. IR: $\nu(C\equiv C)$ 2052 cm^{-1}. UV−vis: λ 340 nm, ϵ 342 000 M^{-1} cm^{-1}. ^1H NMR: δ 2.63 (m, 48H, CH_2), 3.74 (m, 12H, NH_2), 6.75−7.90 (m, 288H, phenyl). ^{31}P NMR: δ 54.5. FAB MS: 898 ([Ru(dppe)$_2$]$^+$, 100).

***Z*-Scan Measurements.** *Z*-scan measurements[40] were performed using two amplified femtosecond laser systems. The first system was based on a Coherent Mira-900D titanium-sapphire oscillator and included a chirped pulse titanium-sapphire amplifier operating at a repetition rate of 30 Hz. This system was used at a wavelength of 800 nm and provided ca. 150 fs fwhm pulses. The second system was a Clark-MXR CPA-2001 regenerative titanium-sapphire amplifier providing 775 nm femtosecond range pulses pumping a Light Conversion TOPAS traveling wave optical parametric amplifier (OPA). This system was usually operated at a repetition rate of 250 Hz (reduced from the usual default rate of 1 kHz to minimize potential problems with thermal effects and sample photodecomposition[41]). The required wavelengths, which were in the range of 650−1300 nm for measurements of dispersion of nonlinear optical properties, were obtained by using the second harmonic of the signal, the second harmonic of the idler, or the signal, respectively, in three tuning ranges. The OPA pulse duration was ca. 150 fs, and the pulses were attenuated, as needed, to a few microjoules.

The *Z*-scans were performed on solutions placed in 1 mm thick glass cells with ca. 1 mm thick glass walls. We ensured that the Rayleigh lengths, $z_R = \pi w_0^2/\lambda$, where w_0 is the $1/e^2$ radius of the beam at the focal plane, were greater than 3 mm to justify a thin sample approximation. Typically, w_0 was in the range of 40−70 μm. In instances where the beam from the OPA deviated from Gaussian behavior, spatial filtering of the beam was carried out. Occasionally, the truncated Airy pattern beam was used, as described by Rhee et al.[42] This, however, did not influence the accuracy of the results because all measurements were routinely calibrated against *Z*-scans taken on the pure solvent and on silica and glass plates of thicknesses in the range of 1−3 mm; the nonlinearity of silica was taken to be $n_2 = 3 \times 10^{-16}$ cm^2 W^{-1} independent of the wavelength, which is a reasonable approximation within the wavelength range used (see ref 43). In all *Z*-scan experiments, the nonlinear phase shifts $\Delta\Phi_0$ for the measured samples were kept below 1.5 rad. Thus, typically, the pulse energies were on the order of a microjoule per pulse, and the peak light intensities were of the order of 100 GW cm^{-2}.

Results and Discussion

Syntheses and Spectroscopic and Electrochemical Characterization. The two major routes to dendrimers are the original divergent procedure (progressively building away from an initial core) and the more recent convergent approach (preparation of wedges that are coupled to the core at the last step), and both have been applied to the synthesis of π-delocalizable arylalkynylmetal-containing dendrimers. Divergent routes have been exploited to afford platinum-containing dendrimers by Takahashi et al.[26] and Stang et al.[25] and require use of a large excess of reagent at each dendritic growth step to ensure formation of the desired product; while successful, this procedure is difficult to apply to higher generation dendrimers.[27] The convergent procedure to dendrimers, by comparison, usually results in an increased ease of purification of the products. The major difficulty with the convergent route is the need to prepare alkynyl-functionalized 1,3-A$_2$-5-B-trisubstituted arenes, the branching points in dendrimer construction; following preparation of 1,3-dibromo-5-iodobenzene, Takahashi's route requires three steps to afford 1,3-diethynyl-5-triisopropylethynylbenzene,[27] and our route requires five steps to prepare 1,3-bis(4-ethynylphenylethynyl)-5-trimethylsilylethynylbenzene,[30,31] and this is before the metal complexation needed to form the organometallic dendrons. A more facile access to metal-containing 1,3-A$_2$-5-B-substituted arene dendrons is necessary, both for higher generation dendrimer synthesis and to promote physical property investigations.

The tunable steric bulk of a ligated metal center suggests a better approach to dendron synthesis. It has previously been shown that *cis*-[RuCl$_2$(dppm)$_2$] reacts with 1,3,5-triethynylbenzene to afford 1,3-{*trans*-[(dppm)$_2$ClRuC≡C]}$_2$-5-HC≡CC$_6$H$_3$;[12,14] the tris product is not formed, even with excess ruthenium-containing reagent. In the present work, the Ru(dppm)$_2$ unit, which undergoes replacement of the second chloro by alkynyl with difficulty,[44−48] was replaced with the Ru(dppe)$_2$ building block, which undergoes the second substitution with far greater ease[16,47,49−55] and therefore provides a more convenient group to facilitate dendrimer construction. Thus, reacting 1,3,5-triethynylbenzene with *cis*-[RuCl$_2$(dppe)$_2$] immediately affords the peripherally chloro-functionalized dendron 1,3-{*trans*-[(dppe)$_2$ClRuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (**1**) (Scheme 1) under steric control in good yield. Reactions of **1** with alkynes proceed cleanly, again with steric control, to form peripherally arylalkynyl-functionalized dendrons; for example, reactions with 4-RC$_6$H$_4$C≡CH (R = H, NO$_2$, NH$_2$) afford 1,3-{*trans*-[(dppe)$_2$(RC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$-5-HC≡CC$_6$H$_3$ (**2a−c**) in fair to

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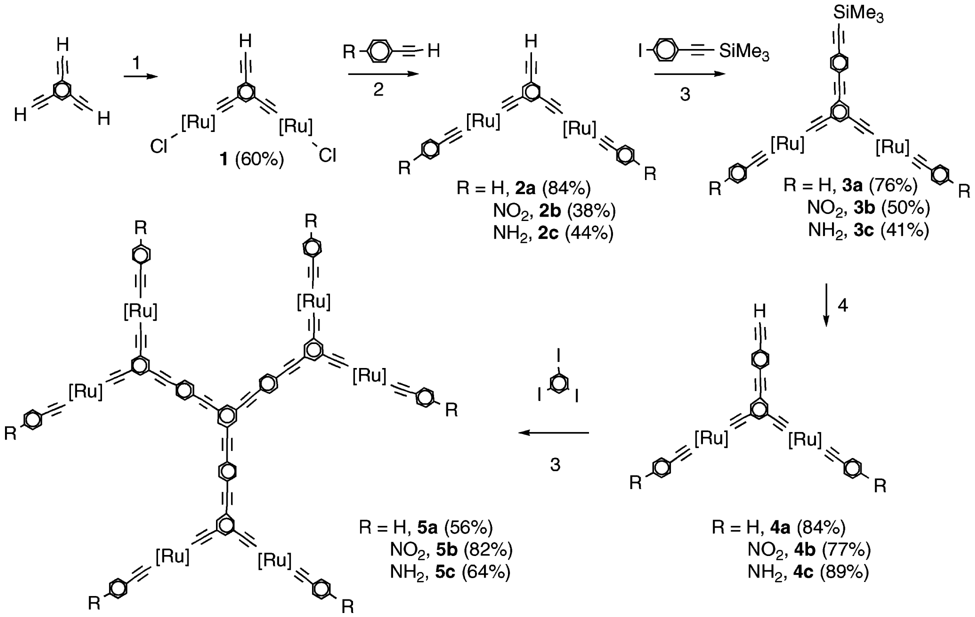
Scheme 1. Syntheses of 1−5[a]



[a] [Ru] = *trans*-[Ru(dppe)$_2$]. (1) a: *cis*-[RuCl$_2$(dppe)$_2$], NH$_4$PF$_6$ and b: NEt$_3$. (2) NH$_4$PF$_6$, NEt$_3$. (3) Pd(PPh$_3$)$_4$, NEt$_3$. (4) Bu$_4$NF.

Table 1. Cyclic Voltammetric Data for Selected Complexes[a]

complex	$E_{1/2}$ Ru$^{II/III}$ (V)	$\Delta E_{1/2}$ (V)
1	0.53, 0.72	0.19
2a	0.47, 0.60	0.13
2b	0.67, 0.81	0.14
3a	0.49, 0.61	0.12
3b	0.68, 0.81	0.13
4a	0.50, 0.62	0.12
4b	0.68, 0.81	0.13
5a	0.48, 0.59	0.11

[a] CH$_2$Cl$_2$ solvent, Ag|AgCl reference electrodes (ferrocene/ferrocenium couple located at 0.56 V).

excellent yield (Scheme 1). While the ethynyl group in **1** is sterically shielded from reacting at a further ruthenium center, this group and those in **2a**−**c** can react with other metal reagents and are therefore available for further derivatization. For example, the ethynyl groups in **2a**−**c** can be coupled with 1-iodo-4-trimethylsilylethynylbenzene to give the trimethylsilylethynyl-terminated dendrons 1,3-{*trans*-[(dppe)$_2$(RC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$-5-(Me$_3$SiC≡C-4-C$_6$H$_4$C≡C)C$_6$H$_3$ (**3a**−**c**) in fair to excellent yield, which can in turn be desilylated with NBu$^n_4$F to afford the ethynyl-terminated dendrons 1,3-{*trans*-[(dppe)$_2$(RC$_6$H$_4$-4-C≡C)RuC≡C]}$_2$-5-(HC≡C-4-C$_6$H$_4$C≡C)-C$_6$H$_3$ (**4a**−**c**) in excellent yield. The terminal ethynyl functionality in the dendrons **4a**−**c** is available for a variety of transformations, including homocoupling to afford tetraruthenium quadrupolar complexes,[32] coupling with a triplatinum zero-generation dendrimer to afford a hexaruthenium−triplatinum dendrimer,[56] and, as in the present study, reaction with 1,3,5-triiodobenzene in a palladium(0)-catalyzed Sonogashira reaction to afford peripherally metalated first-generation arylalkynyl dendrimers (Scheme 1).

Complexes **1**−**5** were characterized by ^{1}H and ^{31}P NMR, IR, and UV−vis spectroscopy. The ^{1}H NMR spectra generally show two major features: a multiplet at approximately 2.6 ppm due to the protons in the dppe bridging unit and a large number of resonances from approximately 6.8−7.5 ppm due to the phenyl groups. ^{1}H NMR spectra of complexes containing an C≡CSiMe$_3$ group (**3a**−**c**) have a strong singlet at ca. 0.2 ppm, while those of complexes containing an ethynyl proton (**1**, **2a**−**c**, and **4a**−**c**) possess singlets at approximately 3 ppm. The ^{31}P NMR spectra contain singlets, consistent with trans ligated metal centers, the mono-alkynyl complex **1** having a chemical shift of 50.5 ppm, and the bisalkynyl complexes (**2a**−**c**, **3a**−**c**, **4a**−**c**, and **5a**−**c**) resonating at ca. 54 ppm. In the IR spectra, RuC≡C stretching bands appear at ca. 2045 cm^{-1} for the nitro-containing complexes (**2b**−**5b**) and in the range of 2060−2055 cm^{-1} for all other complexes, while C≡CSiMe$_3$ stretching bands occur at ca. 2155 cm^{-1} for **3a**−**c**. The UV−vis spectra of all complexes contain an intense metal-to-ligand charge transfer (MLCT) band, in the range of 330−340 nm for the non-nitro-containing complexes and considerably red-shifted to ca. 475 nm for the nitro-containing complexes **2b**−**5b**. The amino-terminated terminal acetylene complexes **2c** and **4c** are significantly less stable than the other complexes prepared in this study, with evidence of oxidation or decomposition being observed upon chromatography or prolonged exposure to air in solution.

While mass spectrometry was useful in characterizing the smaller complexes, larger molecules failed to give a parent ion, an observation noted with other ruthenium alkynyl dendrimers.[31] To further characterize the dendrimers, we employed molecular modeling to calculate the dendrimer dimensions and compared this to transmission electron microscopy (TEM) images (see Figure 1 for the nitro-containing example **5b**); the molecular modeling indicates that the dendrimers are approximately 50 Å in diameter, in agreement with the TEM results (∼50 Å).

Cyclic voltammetry data for selected chloro-, phenyl-, and nitrophenyl-capped complexes **1**−**5** are listed in Table 1. Replacing a chloro substituent by phenylethynyl (proceeding from **1** to **2a**) results in a slight increase in the ease of oxidation. In contrast, the 4-nitrophenylethynyl-substituted complexes are significantly more difficult to oxidize. Peripheral ligand substitution therefore provides a facile method to tune metal electron density. All complexes have two reversible oxidations, which are assigned to Ru$^{II/III}$ processes at the ruthenium atoms separated by 1,3-diethynylbenzene units.

Third-Order NLO Studies. Measurements of third-order molecular nonlinearities were performed on all new complexes

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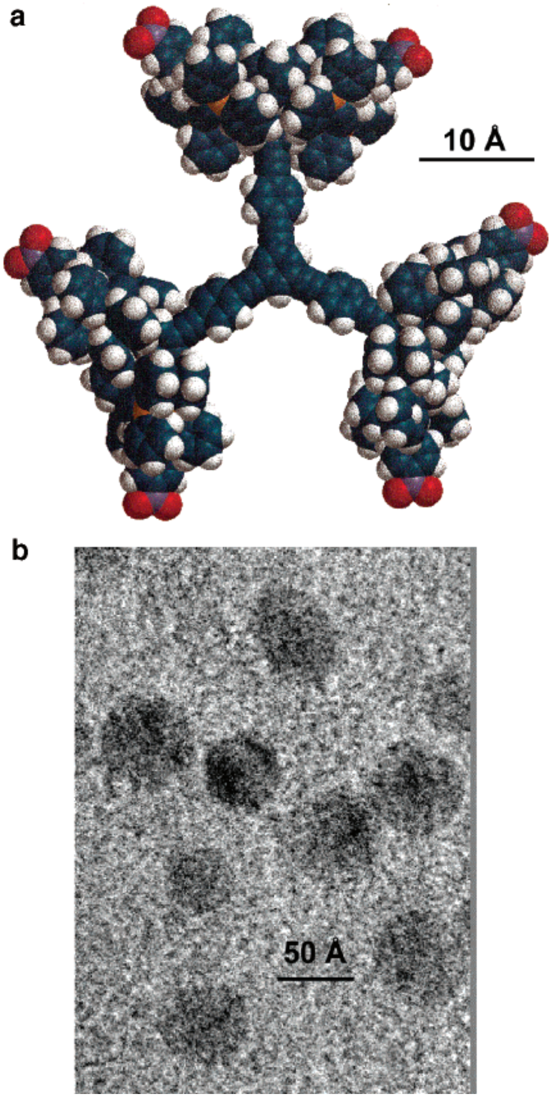

Figure 1. (a) SPARTAN model of **5b**. (b) TEM image of **5b**.

using the *Z*-scan technique at 800 nm; results are presented in Table 2. The nonlinearities for dendrimer **5a** and its wedge constituents **2a**, **3a**, and **4a** in most cases have very large error margins (due to solubility limitations), rendering comparison difficult. The **b** and **c** series of complexes (with the polarizing peripheral substituents NO_2 and NH_2) have considerably higher nonlinearities than the corresponding **a** series. Because of the large uncertainties associated with nonlinearities of these complexes, data for the electron donating wedges and dendrimer (**2c**−**5c**) are indistinguishable from those of their electron withdrawing analogues (**2b**−**5b**).

The cubic nonlinearities for the phenyl-terminated complexes **2a**−**5a** and precursor **1** were also measured at 660 nm, of interest because the second harmonic corresponding to 660 nm (330 nm) is essentially coincident with λ_{max} for these complexes, and hence, two-photon effects may be expected to be enhanced. The similarities in γ_{imag} between the two measurement wavelengths for **1** and **2a** suggest that there is little two-photon enhancement for these complexes. Increasing TPA is noted on progressing from **2a** through **3a**, and **4a** to **5a**, corresponding to an increase in the π-system size.

As can be seen in Table 2, the nitro-containing dendrimer **5b** exhibits surprising behavior at 800 nm. In contrast to the nitro- containing wedges (**2b**, **3b**, and **4b**), which are two-photon absorbers (i.e., possess a positive γ_{imag}), the dendrimer **5b** acts as a saturable absorber (i.e., possesses a negative γ_{imag}). Because of this, a study of the cubic nonlinearities of **5b** over a range of frequencies was undertaken. The dispersion of the real and imaginary parts of the hyperpolarizability γ_{real} and γ_{imag} was found to be approximated relatively well by a simplified, three-term expression for $\gamma = \gamma_{real} + i\gamma_{imag}$ as follows:

$$\gamma = \left[\frac{A}{\nu_a - 2\nu - i\Gamma_1} + \frac{B}{\nu_b - 2\nu - i\Gamma_2} - \frac{C}{\nu_a - \nu - i\Gamma_1}\right]\frac{1}{(\nu_a - \nu - i\Gamma_1)^2}$$

where *A*, *B*, and *C* are adjustable constants. This expression was optimized to fit simultaneously the experimental data for both the real and the imaginary parts of γ, resulting in the following parameters: (i) the values of the damping constants Γ_1 and Γ_2 were 2660 and 2211 cm^{-1}, respectively; (ii) the resonance frequencies taken for the calculations were ν_a = 20462 cm^{-1} and ν_b = 31250 cm^{-1}, corresponding to wavelengths of 489 and 320 nm (slightly shifted from the absorption spectra maxima); and (iii) the values of the constants *A*, *B*, and *C* were 5.17×10^{-21}, 4.05×10^{-21}, and 6.78×10^{-21} in cm^2 stat V^{-2}, respectively. The first two terms in the square brackets are two-photon resonant at the two respective frequencies, ν_a and ν_b, while the third term is one-photon resonant at ν_a. The negative sign in front of the third term accounts for the absorption saturation.

Figure 2 shows experimental results obtained in this study, as well as an interpretation of the dispersion of the refractive and absorptive parts of the nonlinearity using the simplified dispersion formulas. The nonlinear absorption results reveal a

Table 2. Linear and Cubic Nonlinear Optical Data

		800 nm			660 nm		
complex	λ_{max}, ϵ^a	Re γ^b	Im γ^b	$\lvert\gamma\rvert^b$	Re γ^b	Im γ^b	$\lvert\gamma\rvert^b$
1	334, 3.8	−900 ± 500	0 ± 100	900 ± 500	−300 ± 150	180 ± 50	350 ± 180
2a	335, 8.0	500 ± 400	200 ± 100	540 ± 100	−200 ± 500	0 ± 30	200 ± 500
2b	475, 4.8	−1300 ± 1000	150 ± 40	1300 ± 1000			
2c	333, 2.3	1000 ± 400	0 ± 100	1000 ± 400			
3a	335, 9.5	700 ± 1200	0 ± 0	700 ± 1200	−910 ± 700	330 ± 60	970 ± 680
3b	475, 4.7	−1100 ± 220	310 ± 60	1100 ± 230			
3c	334, 5.6	−2200 ± 800	400 ± 200	2200 ± 800			
4a	330, 9.9	1700 ± 500	0 ± 0	1700 ± 500	−250 ± 400	250 ± 50	350 ± 320
4b	474, 4.1	−5000 ± 1300	1320 ± 270	5200 ± 1300			
4c	328, 9.3	−1400 ± 500	1300 ± 300	1900 ± 300			
5a	339, 34.2	−1600 ± 2400	0 ± 0	1600 ± 2400	−3100 ± 600	2000 ± 400	3700 ± 700
5b	475, 10.9	−23000 ± 10000	−6200 ± 2800	24000 ± 10000			
5c	340, 34.2	−2900 ± 2300	4700 ± 1200	5500 ± 2600			

[a] λ_{max} in nm, ϵ in 10^4 M^{-1} cm^{-1}, THF solvent. [b] In 10^{-36} esu, THF solvent.

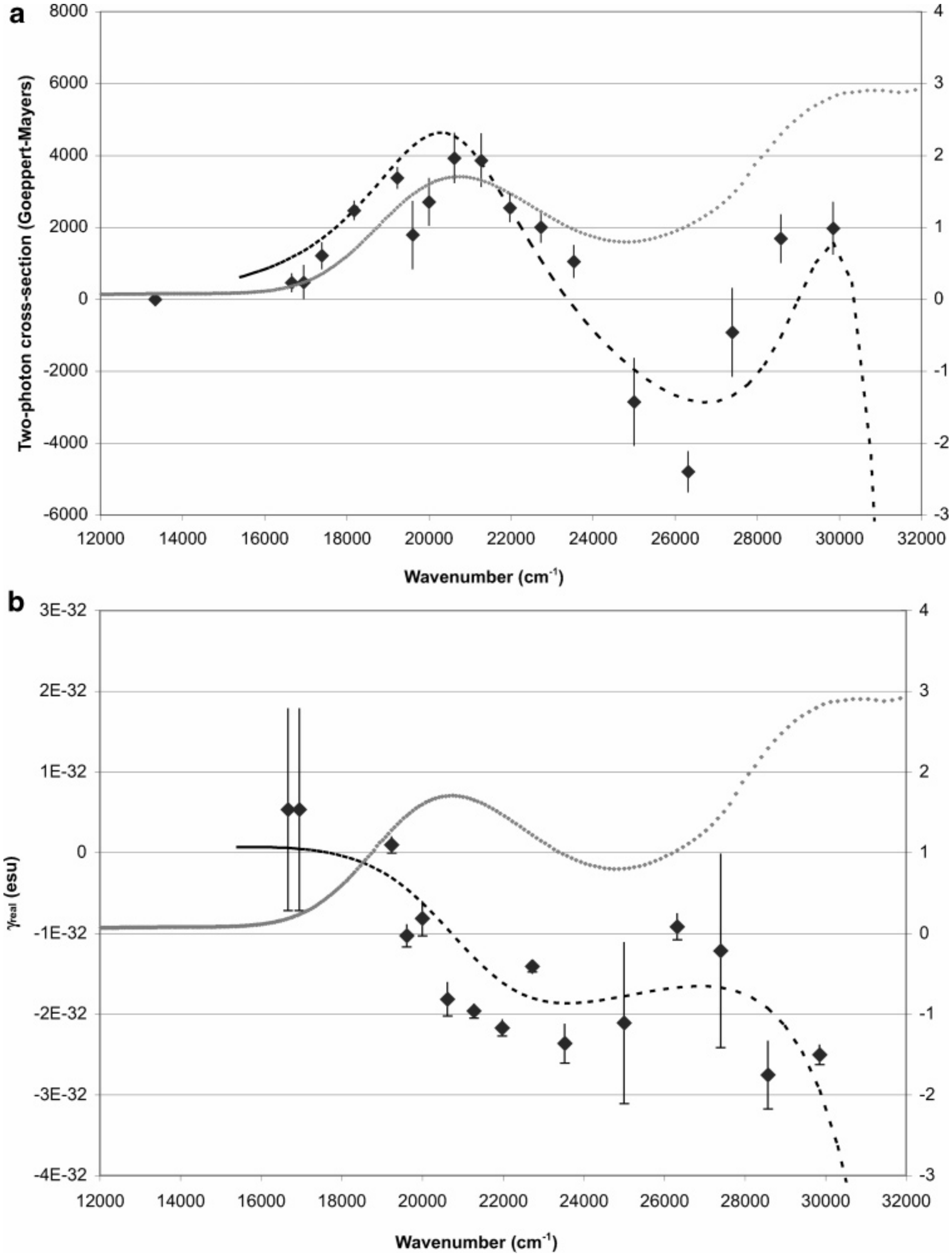

Figure 2. (a) Two-photon absorption profile of **5b** as compared to the one-photon absorption spectrum. Profiles are plotted as a function of ν for the one-photon profile and as a function of 2ν for the two-photon profile. Dotted line is the one-photon absorption spectrum. Dashed line is the simulation by the equation given in the text. (b) Dispersion of the real part of the hyperpolarizability as compared with the one-photon absorption spectrum. Real part of the hyperpolarizability is plotted against 2ν. Dotted line is the one-photon absorption spectrum.

range (ca 700−850 nm) in which the sign of σ_2 (and γ_{imag}) is negative, corresponding to absorption saturation. Outside this range, the sign of σ_2 is positive, indicating the dominance of two-photon absorption.

The two-photon absorption profile of **5b** exhibits two major features. Both absorption transitions are two-photon active, and competition between two-photon absorption and absorption bleaching appears to be the main reason for the distortion of the two-photon profile, leading to the absence of an enhancement of two-photon absorption by a second excited state as described by Kamada et al.[57] These features are quite different from those seen by us in a dendrimer with metals at each generation, for which the long wavelength transition was found to be essentially two-photon inactive.[1]

Conclusion

This work has demonstrated the use of steric control of the extent of reaction as a new and rapid methodology for dendron synthesis, a procedure that should be applicable to other metal-containing systems. The sterically controlled synthetic methodology employed for the facile preparation of alkynylruthenium dendrons **1**, **2a**−**c**, **3a**−**c**, and **4a**−**c**, and thereby the alkynylruthenium dendrimers **5a**−**c**, should be applicable to the synthesis of other organometallic dendrimers, judicious modification of the ligand sphere providing a ready means to modify the steric environment and thereby control the extent of reaction. Overall, this methodology affords rapid access to nanometer-sized π-delocalized organometallic complexes. Such species can have interesting electronic and optical properties. In the present work, **5b** anomalously (cf. all other complexes prepared for this study) shows absorption saturation behavior at 800 nm, which prompted us to carry out a wavelength dependence study of both its refractive and its absorptive nonlinearity. Spectral dependences of two-photon absorption cross-sections (related to the imaginary part of the third-order polarizability) have been studied,[58−60] but there is very little data on the dispersion of both real and imaginary parts of the third-order polarizability γ,[61,62] without which the structure−property relationships are difficult to develop; at the time of this study, there were no extant studies of the dispersion of γ_{real} and γ_{imag} of organometallic (or indeed inorganic) complexes.[63] The present work is consistent with the dispersion of cubic nonlinearity in this organometallic dendrimer resulting from an interplay of two-photon absorption and absorption saturation and suggests that simple dispersion relations can reproduce the behavior of both real and imaginary components of the hyperpolarizability, but the radically different behavior of **5b** and the related dendrimer with metal atoms at each generation[1] suggests that our understanding is still incomplete. Studies to address this deficiency are currently underway.

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(63) We have very recently reported the second example of wavelength dependence of γ_{real} and γ_{imag} for an organometallic dendrimer: see ref 1.