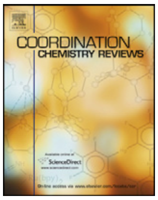
Coordination Chemistry Reviews 255 (2011) 2025–2038

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Syntheses and NLO properties of metal alkynyl dendrimers

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Contents

ARTICLE INFO

Article history:
Received 6 December 2010
Accepted 26 May 2011
Available online 7 July 2011

Keywords:
Organometallic
Dendrimer
Nonlinear Optics
Hyperpolarizabilities
Alkynyl complexes

ABSTRACT

Metal-containing (particularly organometallic) dendrimers are briefly introduced, the origin of nonlinear optical (NLO) effects in molecules is briefly summarized, and the syntheses of metal alkynyl dendrimers and progress in employing metal alkynyl dendrimers as NLO materials are reviewed.

1. Introduction

Dendrimers are mono-disperse hyper-branched molecules comprised of dendrons (tree-shaped units) attached to a central core; their well-defined and controllable structures have made them of great interest for a vast array of applications including drug transportation, light harvesting and optics [1]. Dendrimers containing metal centers have been synthesized for applications in (among others) catalysis, luminescence, sensing, and magnetic resonance imaging (MRI).

Dendritic materials with enhanced nonlinear optical (NLO) properties have also attracted significant recent attention, because of the interest in modifying the propagation characteristics of intense light beams, of crucial importance to the emerging photonics industries. While the focus of most studies in the NLO properties of dendrimers has been with purely organic dendrimers [2], metal-containing dendrimers for nonlinear optics is a field of increasing interest. Following brief overviews of dendrimers and nonlinear optics, this review summarizes the syntheses and nonlinear optical studies of metal alkynyl dendrimers.

Abbreviations: BBO, β-barium borate; KTP, potassium titanyl phosphate; MRI, magnetic resonance imaging; NLO, nonlinear optical; OPL, optical power limiting; TPA, two-photon absorption.

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doi:10.1016/j.ccr.2011.05.017

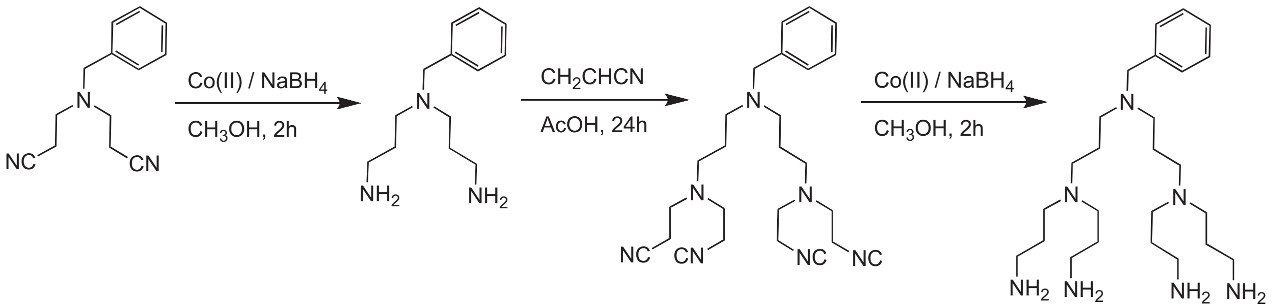


Fig. 1. The synthesis of one of Vögtle's dendrons [3].

2. Dendrimers

2.1. Syntheses and structure

The first controlled synthesis of a dendron was carried out by Vögtle and co-workers [3] (Fig. 1). This dendron was formed by the stepwise repetition of two types of reactions: the reaction of a primary amine with acrylonitrile and the cobalt(II)-catalyzed reduction of the nitrile group. This method of "cascade" reactions, where a few types of reactions are repeated to build up large structures, has since been used to synthesize a vast array of dendritic molecules.

Vögtle's dendron was synthesized using a "divergent" method starting at the core and building out stepwise. Alternatively, one can start from the outside and build up "wedges", couple wedges together to make larger wedges and finally couple the larger wedge to the core. Fréchet first described this "convergent" method in the synthesis of a series of 3,5-dihydroxybenzyl alcohol-based dendrimers [4], reporting dendrimers with molecular sizes up to the sixth generation; the synthesis of the third-generation dendrimer is shown in Fig. 2 as an example. In this synthesis, an alkyl bromide is reacted with 3,5-dihydroxybenzyl alcohol in the presence of potassium carbonate and 18-crown-6 to form a wedge. The alcohol is then converted to a bromide with tetrabromomethane in the presence of triphenylphosphine. This process can then be repeated until the desired generation level is reached, at which point the bromide wedge is reacted with a 1,1,1-tris(4-hydroxyphenyl)ethane core. This iterative synthesis provides a facile synthetic route to high-generation dendrimers, and this general convergent method has been widely used in the synthesis of a large variety of dendrimers.

There are advantages and disadvantages to both the divergent and convergent methods; the method that is more appropriate depends on the structure and size of the dendrimer to be synthesized. An advantage of the divergent method is that, because only small groups are being coupled each time, there is less chance of steric problems. The excess reactant may also be relatively easy to remove due to the large difference in size between it and the dendrimer. By building out from the center, it also gives one greater flexibility with the peripheral group (reactive groups can be placed

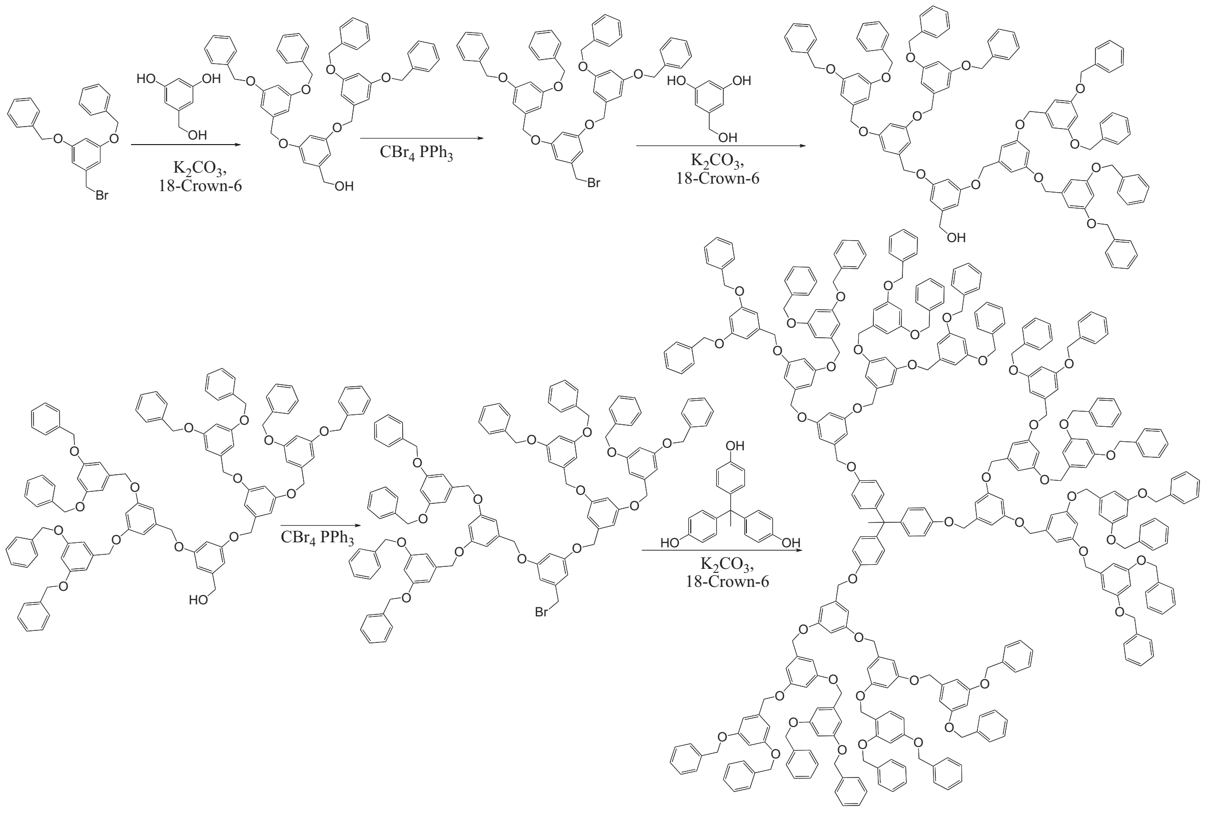


Fig. 2. Fréchet's convergent synthesis of a 3rd generation dendrimer [4].

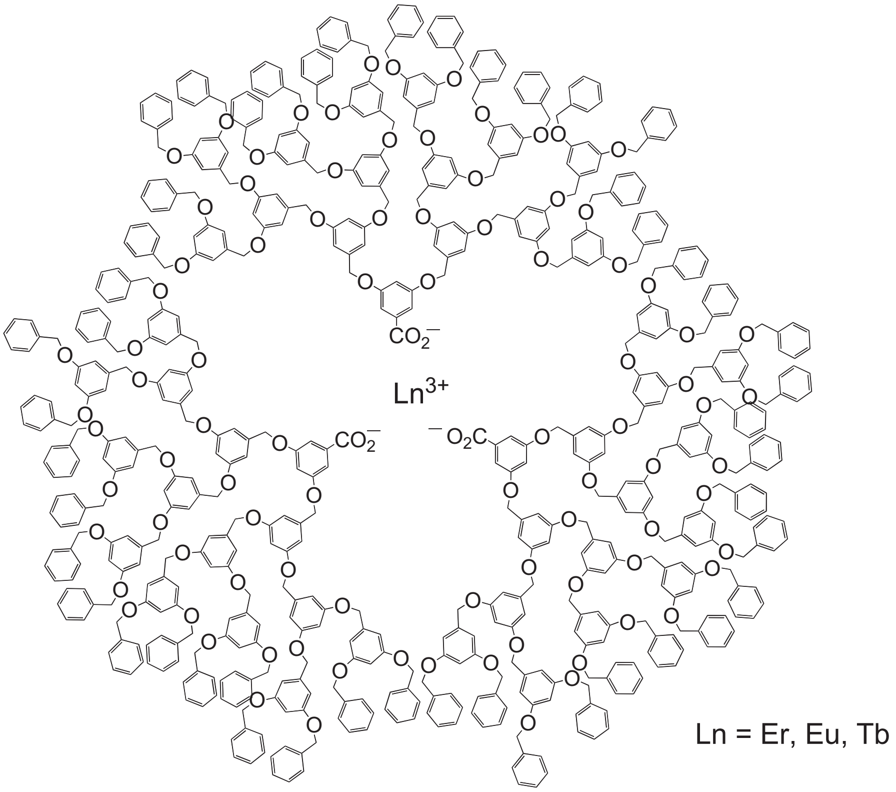


Fig. 3. Fréchet's luminescent lanthanide dendrimer [5].

on the outside). The major disadvantage to this method is that it may be difficult to detect and to remove structurally impure dendrimers in which the added unit has not reacted at every site. Structural impurities are likely to be a greater problem for higher generation dendrimers because the percentage of structurally imperfect dendrimers will grow with the increasing number of reactions. The convergent method, on the other hand, has fewer sites that are being reacted at each step; there is therefore less chance of structurally imperfect dendrimers, and it may be easier to detect and remove them. This method also allows greater flexibility with the composition of the core, because the core does not need to be stable under all reaction conditions. However, attaching large wedges to a core can result in steric problems for certain structures, and the growing wedge may be more difficult to purify at each step because the units being coupled may be of comparable size and composition. This method also limits the peripheral functionality, but this may sometimes be overcome by protecting the outside groups and then deprotecting at the periphery after the dendrimer has been formed.

The structural design of a dendrimer depends on its intended application. As the potential uses for dendrimers have expanded, so has the variety of structures. One way to increase the functionality of a dendrimer is to incorporate metal centers into the structure. Metal centers can be incorporated into the dendrimer in various positions: the core, the peripheral groups, or throughout the structure as branching points or spacers. Metal alkynyl dendrimers have been synthesized by both convergent and divergent routes, and examples with the metal centers at the periphery or throughout the dendritic structure have been reported.

2.2. Applications of metal-containing dendrimers

One of the major difficulties in catalysis is separating the products from the catalyst, of importance both in terms of efficiency, so that the catalyst can be recycled, and safety, as many catalysts can be harmful. The application of dendrimers in catalysis is a very large and rapidly expanding field of research. Attaching the catalytic centers to a large dendritic structure results in increased ease of catalyst recovery, resulting in a cleaner, more efficient process. The most common location for metal centers in dendrimers for catalytic applications is the periphery. The metals on the periphery are readily accessible for the desired molecular interaction; this structure also allows a high catalyst loading. There are several commercially available dendrimers that can be used to readily attach a catalytic center, allowing the testing of several centers without arduous synthesis. Core-metallated dendrimers for catalysis can permit steric control of the interaction. With such core-metallated dendrimers, the metal center is usually not the branching point of the core but is attached to a branching point so that the metal is somewhat accessible. Dendrimer catalysts with metal centers throughout the structure are quite rare because dendrimers often take on a globular shape, limiting access to the inner sites.

Luminescent materials have become of particular interest in recent years for applications in displays and as sensors. The majority of luminescent dendrimers have a metallated luminescent core surrounded by organic dendrons. Dendrimers are particularly useful for luminescence due to their large surface area and antenna-like structure that can be used to harvest light, funneling the photon energy to a luminescent core. The branches surrounding the dendrimer also create an isolated environment for the metal center, reducing self-quenching. Fig. 3 shows a lanthanide-cored fourth-generation dendrimer that has been explored in luminescence applications [5].

The large, well-defined surface area of a dendrimer makes them ideal for sensing ions and gases. The majority of dendrimers for sensors have the metal centers on the periphery so that they can readily respond to the interaction with the ion or gas. However, there are also some phosphorescent dendrimers for molecular oxy-

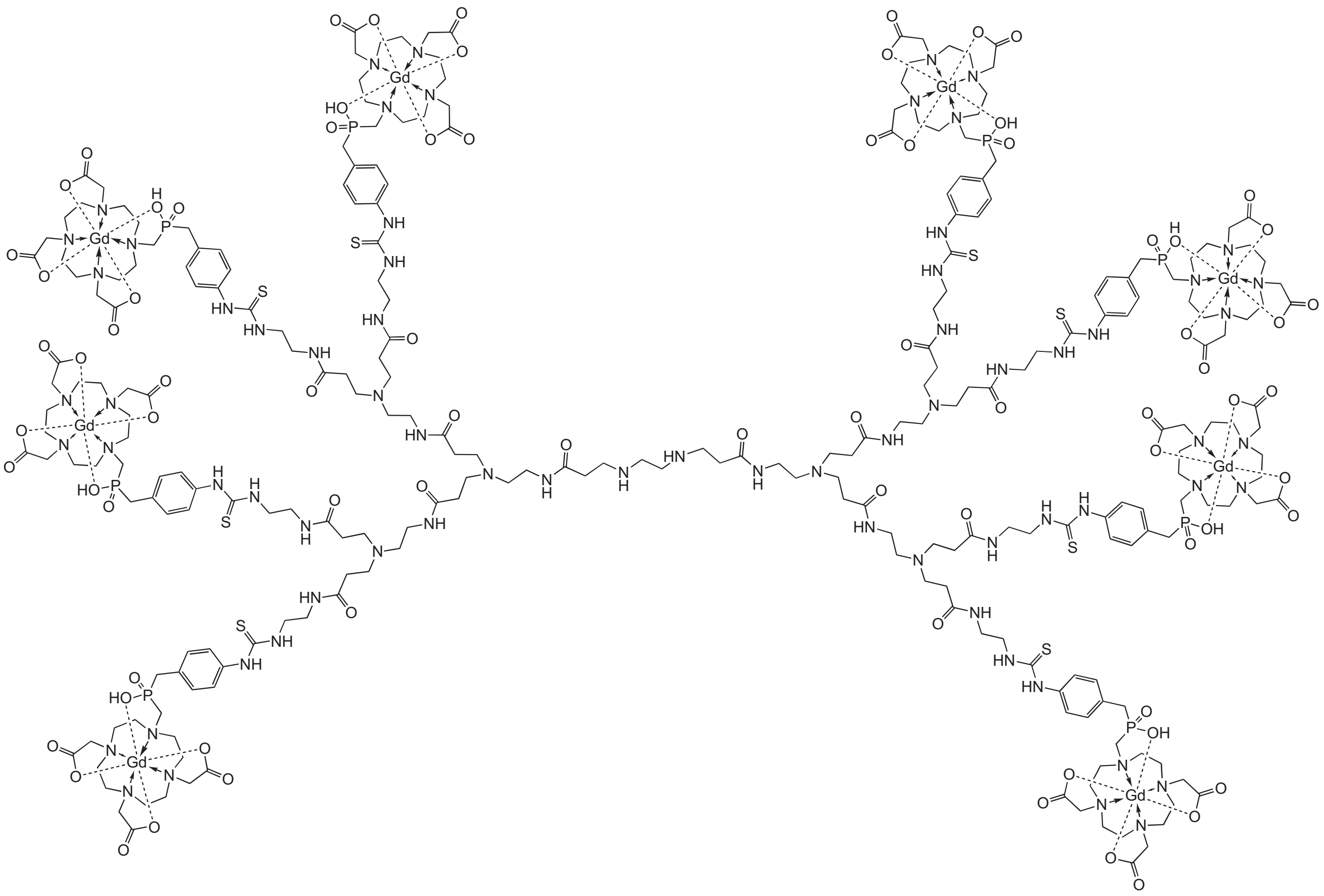


Fig. 4. A Gd(III) peripherally metallated dendrimer employed as a MRI contrast agent [7].

gen detection in which the metal centers are in the core of the dendrimer.

A variety of dendrimers have been synthesized for use as MRI contrast agents. The majority of these use Gd(III) metal centers but there have been other lanthanide(III) dendrimers reported [6]. The location of the metal center has been explored both at the periphery of the dendrimer and at the core. One of the peripherally metallated examples is shown in Fig. 4 [7].

Metal alkynyl dendrimers have also attracted interest as NLO materials. The results of these studies are discussed below, following an introduction to the NLO field and a summary of the syntheses of metal alkynyl dendrimers.

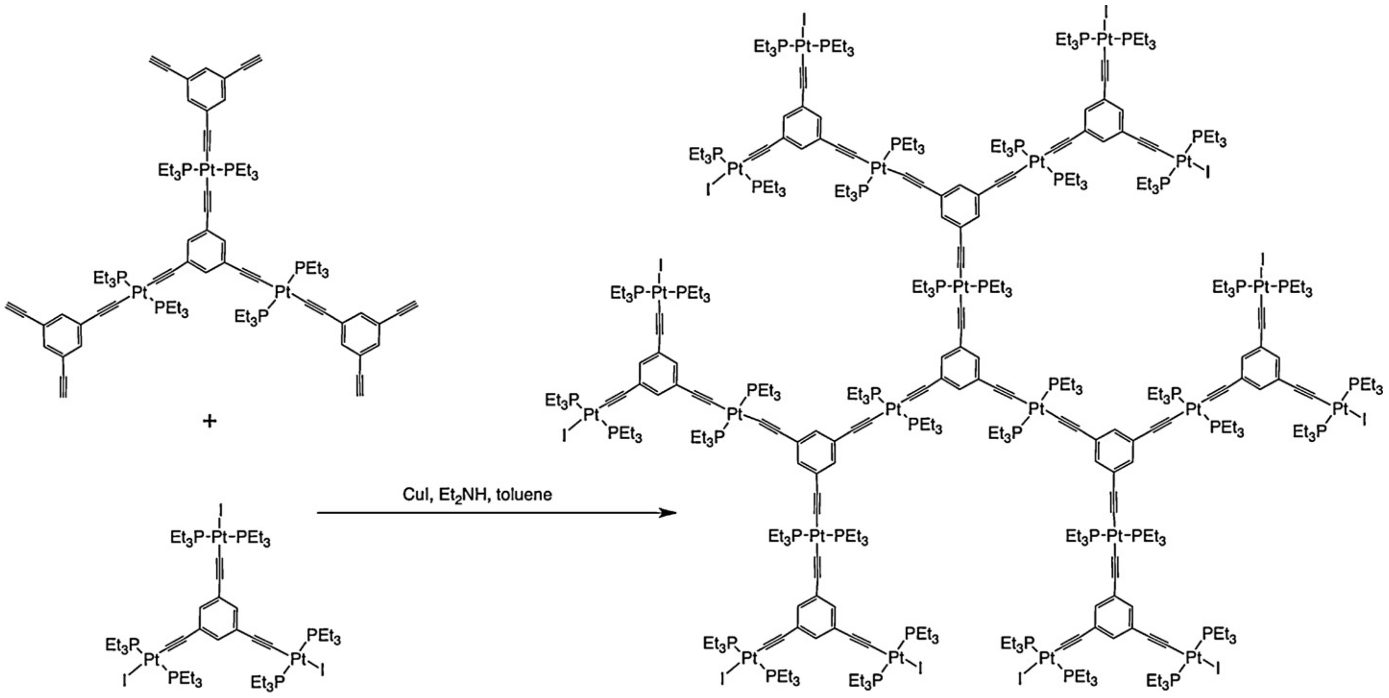
3. Nonlinear optics

3.1. Materials considerations

The advent of lasers in the 1960s led to the discovery that the optical properties of materials become dependent on the magnitude of the electromagnetic fields present in the light beams that interact with them, once the light intensities and thus the fields are sufficiently intense. This is especially striking in the case of the short pulse lasers that are available nowadays; mode-locked picosecond and femtosecond lasers are increasingly accessible and are finding use in numerous applications. The nonlinear optical (NLO) behavior of materials, usually interpreted as the power dependence of the material polarization with respect to the amplitude of the electric field, leads to effects such as the generation of new electromagnetic field components able to modify the amplitude, phase, frequency, path, and polarization of the light beams propagating in the nonlinear material. This leads to the possibility of applications in laser technology, data storage, telecommunications, optical signal and image processing, biological imaging, and nanofabrication. Many of these applications require materials and structures with optimized optical and especially NLO properties.

Since the discovery of NLO effects, several classes of materials have been developed for particular applications. Frequency conversion, which is crucial for frequency doubling of lasers and for parametric amplification used for the generation of new frequencies of coherent light, is currently dominated by inorganic salts such as borates (e.g. β-barium borate, known as BBO) and phosphates (e.g. potassium titanyl phosphate, known as KTP). $LiNbO_3$ is a ferroelectric crystal that is particularly suitable for applications involving frequency mixing and electro-optic modulation. On the other hand, glasses such as silica, chalcogenides and fluorides are often used for NLO applications involving nonlinear refraction (the dependence of the refractive index of a material on the light intensity). Silicon may also become an important NLO material because of the advent of so-called silicon photonics, where silicon planar waveguide structures are utilized for optical signal transmission and processing. The advantages of inorganic materials include their robustness and good mechanical properties such as hardness and high thermal conductivity. Some materials (e.g. borates) possess large transparency ranges, which permit applications in, for example, optical parametric generation and amplification over virtually the whole visible, UV and IR ranges, while crystals of chalcogenides with a reduced bandgap (e.g. $AgGaS_2$) are especially suited for infrared applications.

There are, however, important restrictions in the parameter ranges available from inorganic materials, as well as trade-offs due



Scheme 1. Synthesis of a peripherally iodinated second-generation arylalkynylplatinum dendrimer [10].

to the limited structural diversity in materials built from typical covalent and ionic units. Increased magnitudes of the nonlinear susceptibilities are usually accompanied by reduced transparency ranges and high values of the dielectric constant. The latter factor is particularly important for ferroelectric crystals with high values of the electro-optic coefficient, such as $LiNbO_3$, because it imposes limitations on the speed of devices employing the electro-optic (Pockels) effect. Many modern optical device concepts (e.g. those involving so-called photonic crystals) require the fabrication of micro- or nanoscale NLO structures. Material processing limitations inherent in inorganics restrict the applicability of those materials for such purposes.

It was realized as early as the 1970s that organic molecules can provide NLO responses with better "figures of merit" than are available with inorganics, and can possess much greater design flexibility than do inorganic compounds, which may allow for the fine-tuning of the NLO properties. Indeed, organics hold much promise for applications such as electro-optic modulation (although electro-optic polymer devices have not found widespread use yet). The most important NLO property of organics that is being applied at present is their nonlinear absorption (primarily two-photon absorption, TPA) [8]. The presence of nonlinear absorption is, however, one of the main obstacles to the utilization of the strong nonlinear refraction exhibited by some organics, since the optical losses due to linear and nonlinear absorption (as well as those due to scattering at material imperfections) make it impossible to achieve large nonlinear phase shifts in NLO devices, which are necessary for effects such as all-optical switching. A disadvantage of organic NLO chromophore-based materials is their susceptibility to photochemical and thermal damage at the high light intensities needed to operate NLO devices.

3.2. Theory

The NLO effects in organics or organometallics are usually considered in the so-called dipole approximation, where the interaction of an electric field $\mathbf{E}_{loc}$ with a molecule is expressed in terms of the dependence of the dipole moment of the molecule $\boldsymbol{\mu}$ on the amplitude of the field. This is usually represented as a power series:

$$\boldsymbol{\mu} = \boldsymbol{\mu}_0 + \boldsymbol{\alpha}\mathbf{E}_{loc} + \boldsymbol{\beta}\mathbf{E}_{loc}\mathbf{E}_{loc} + \boldsymbol{\gamma}\mathbf{E}_{loc}\mathbf{E}_{loc}\mathbf{E}_{loc} + \cdots \quad (1)$$

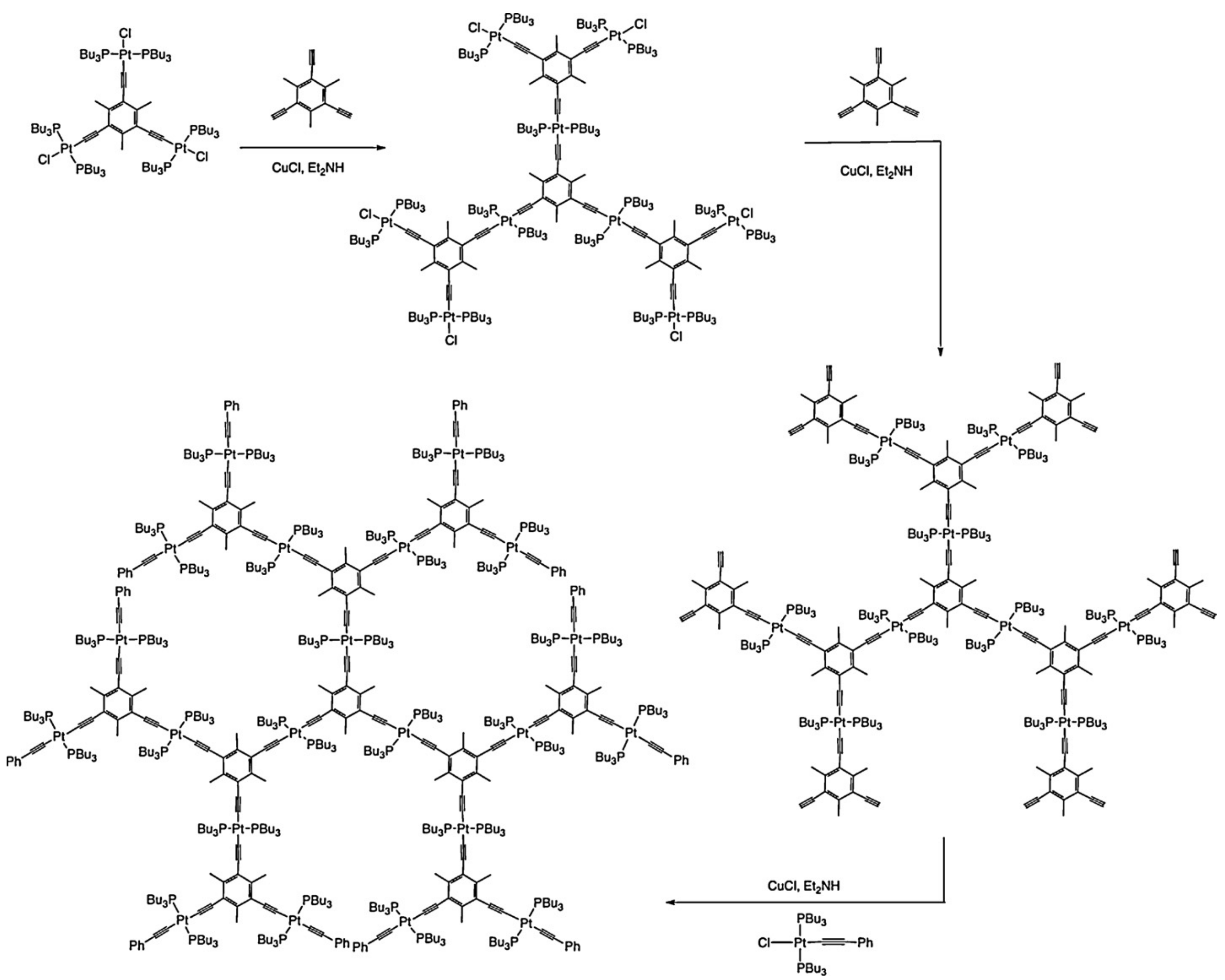
where $\boldsymbol{\mu}_0$ is the static dipole moment, the term with the linear polarizability $\boldsymbol{\alpha}$ is responsible for linear optical effects, and the terms containing the quadratic hyperpolarizability $\boldsymbol{\beta}$ and the cubic hyperpolarizability $\boldsymbol{\gamma}$ are responsible for the so-called second-order and third-order nonlinear optical effects, respectively. It should be noted that the polarizabilities $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$ and $\boldsymbol{\gamma}$ are tensors because they relate a vector $\boldsymbol{\mu}$ to products of components of the vector $\mathbf{E}_{loc}$ (the notation $\mathbf{E}_{loc}\mathbf{E}_{loc}$ and $\mathbf{E}_{loc}\mathbf{E}_{loc}\mathbf{E}_{loc}$ stands for tensors composed of such products, a 9 element tensor called a dyad product and a 27 element tensor, a triad product, respectively). Symmetry considerations and chemical intuition are helpful in unravelling the complexity of $\boldsymbol{\alpha}$, $\boldsymbol{\beta}$, and $\boldsymbol{\gamma}$ tensors [9]. For example, a centrosymmetric molecule can be shown to have all elements of the $\boldsymbol{\beta}$ tensor equal to zero. On the other hand, a linear conjugated molecule with charge transfer between a donor group and an acceptor group at the ends of a conjugated chain can be expected to have its $\boldsymbol{\beta}$ tensor dominated by the $\boldsymbol{\beta}_{zzz}$ component, z being the direction along the conjugated chain.

The electric field of a light wave can have an oscillating character, i.e. it can be expressed as

$$E(t) = E_0 \cos(\omega t) = \frac{E_0}{2}[\exp(i\omega t) + \exp(-i\omega t)] \quad (2)$$

Examination of Eq. (1) leads to the immediate conclusion that the presence of the quadratic term (the β term) results in, among others, frequency doubling, i.e. appearance of the $\exp(2i\omega t)$ term, while the γ term leads to frequency tripling. More complicated frequency conversion NLO processes appear if one considers the simultaneous presence of several electromagnetic field components.

To fully appreciate the importance of the NLO polarizabilities, one needs to note that Eq. (1) is not strictly valid for time-varying fields, because of the possibility of the damping of the oscillation of the molecular dipole due to the presence of resonances at certain frequencies. The phase lag of the dipole oscillation can be accom-



Scheme 2. Synthesis of a peripherally phenylethynylated second-generation arylalkynylplatinum dendrimer [11c].

modated by rewriting Eq. (1) in terms of Fourier components of the field and the dipole oscillation. This is straightforward in the case of the linear term in Eq. (1), which should be transformed into:

$$\Delta\mu^{(1)}(\omega) = \alpha(\omega)E(\omega) \tag{3}$$

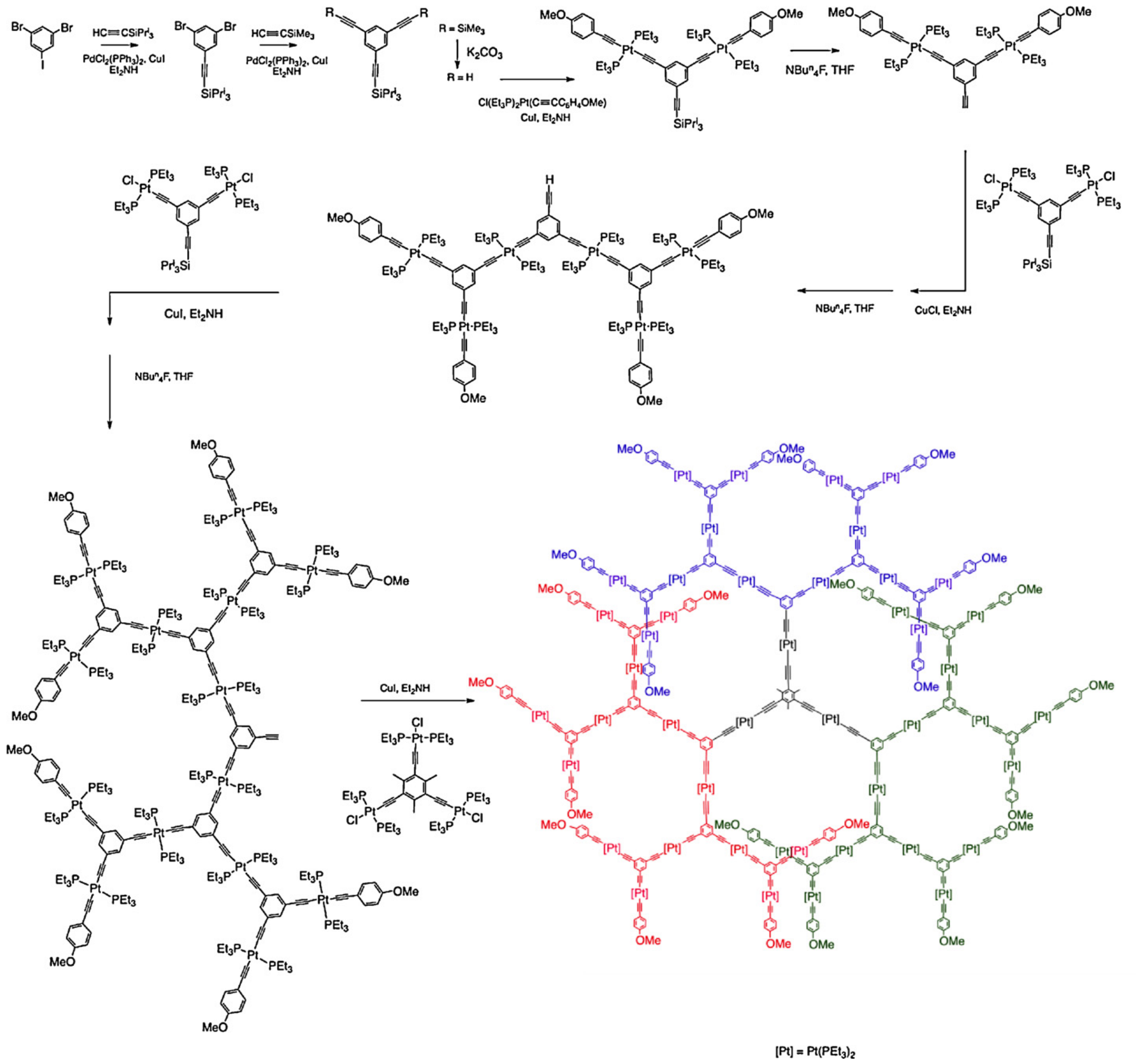
where $\Delta\mu^{(1)}(\omega)$ is the linear component of the oscillation of the dipole at frequency ω, and $E(\omega)$ is the Fourier amplitude of the field at that frequency. These Fourier amplitudes need to be related to each other through a frequency-dependent linear polarizability, $\alpha(\omega)$. The damping is accounted for by treating $\alpha(\omega)$ as a complex quantity whose real part describes the in-phase molecular response, and thus is responsible for refractive properties, and whose imaginary part causes the phase shift between the electromagnetic field and the dipole oscillation, thereby leading to the absorption of radiation.

The nonlinear terms in Eq. (1) require a more complicated notation. They may be written as:

$$\Delta\mu^{(2)}(\omega_3) = \beta(-\omega_3;\omega_1,\omega_2)E(\omega_1)E(\omega_2) \tag{4}$$

$$\Delta\mu^{(3)}(\omega_4) = \gamma(-\omega_4;\omega_1,\omega_2,\omega_3)E(\omega_1)E(\omega_2)E(\omega_3) \tag{5}$$

for the quadratic and cubic terms, respectively. It should be noted that the second-order NLO effects can be broadly treated as frequency mixing events where the dipole oscillation is at $\omega_3 = \omega_1 + \omega_2$. In a similar way, for the third-order NLO effects the dipole oscillation occurs at $\omega_4 = \omega_1 + \omega_2 + \omega_3$. In these combinations of frequencies, some of the field components may enter the summation with negative signs; Eq. (4) is therefore suitable for both of the technologically important processes of sum frequency and difference frequency generation. The electro-optic (Pockels) effect, an important NLO phenomenon used for modulation of light beams, involves a low-frequency field component (dc or radio frequency, and thus much lower than the frequency of the visible light). The hyperpolarizability relevant to this frequency mixing case is written as $\beta(-\omega;\omega,0)$ while that for the second-harmonic generation process is $\beta(-2\omega;\omega,\omega)$. In the case of third-order NLO effects, there may be many combinations of frequencies and the relevant processes are often called four-wave mixing processes. Technologically, the most important case is that of a degenerate cubic hyperpolarizability $\gamma(-\omega;\omega,-\omega,\omega)$, which corresponds to the interaction of four fields (three input fields and the output field generated by the dipole oscillation), all at the same frequency. It can be shown that the real part of this hyperpolarizability is related to the so-called nonlinear refraction, i.e. to the dependence of the refractive index of a material on the light intensity, which is usually expressed as $n = n_0 + n_2I$, where n_0 is the low intensity refractive index, n_2 is the so-called nonlinear refractive index, and I is the light intensity. At the same time, the imaginary part of the degenerate



Scheme 3. Synthesis of a third-generation arylalkynylplatinum dendrimer [11b].

cubic hyperpolarizability is responsible for nonlinear absorption. This may cover both the case of degenerate two-photon absorption (TPA, the instantaneous absorption of two photons of the same frequency ω) and the dependence of the linear absorption coefficient on light intensity. The two-photon absorption is often quantified using the so-called two-photon absorption cross-section σ_2, which is thus related to the imaginary part of the degenerate γ.

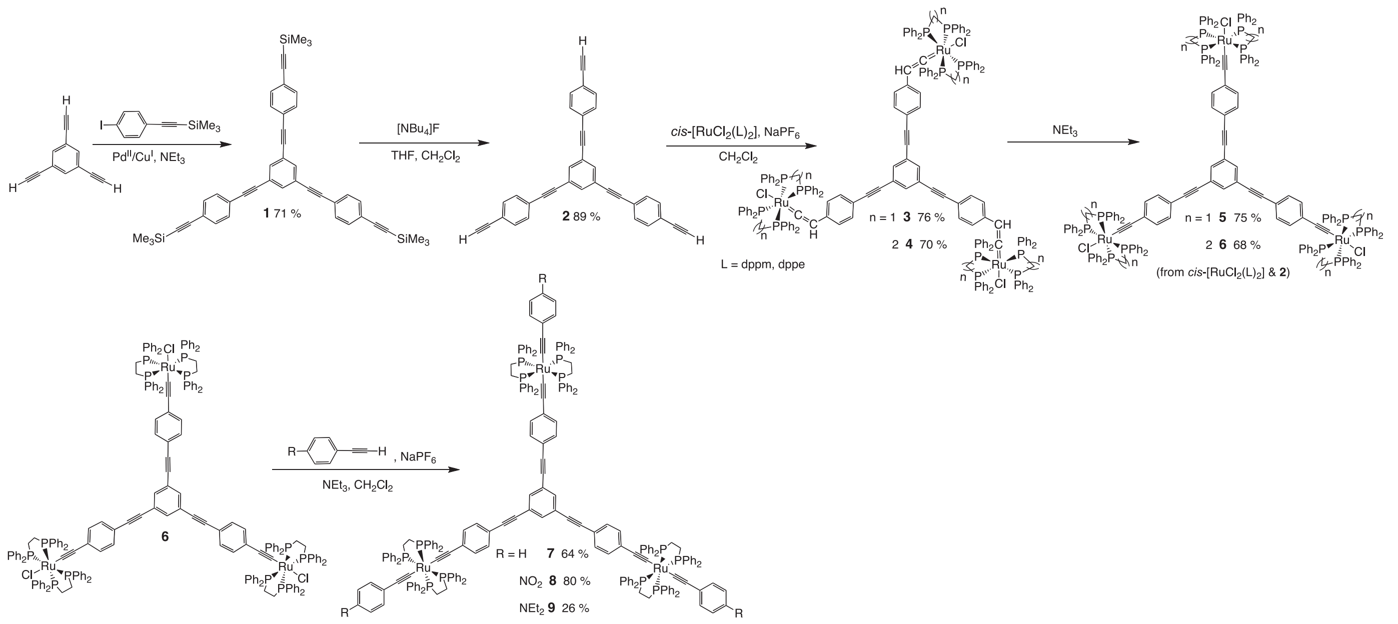
4. Syntheses and NLO properties of metal alkynyl dendrimers

4.1. Syntheses of metal alkynyl dendrimers

Metal-containing dendrimers have been explored for diverse applications, as summarized above, with a broad array of compositions. NLO effects generally necessitate a large polarizable π-electron system, and so for such applications π-delocalizable dendrimers have been of interest. While a variety of metal-containing π-delocalizable architectures are conceivable, metal alkynyl linkages can be synthesized in high yield by established methodologies and afford robust complexes, so dendrimers constructed via metal alkynyl bonds have been a natural choice for study. The syntheses of extant metal alkynyl dendrimers are summarized in this section.

Many platinum alkynyl dendrimers with 1,3,5-triethynylbenzene branching points and 1,3,5-triethynyl-2,4,6-trimethylbenzene cores have been prepared. Leininger et al. attempted the divergent synthesis of a second-generation dendrimer. While this was unsuccessful, a second-generation dendrimer could be prepared by reaction of a first-generation dendrimer with a zero-generation core (Scheme 1) [10].

Both the divergent and convergent methods have been used by Takahashi and co-workers in the synthesis of platinum alkynyl dendrimers up to the sixth-generation [11]. The divergent approach



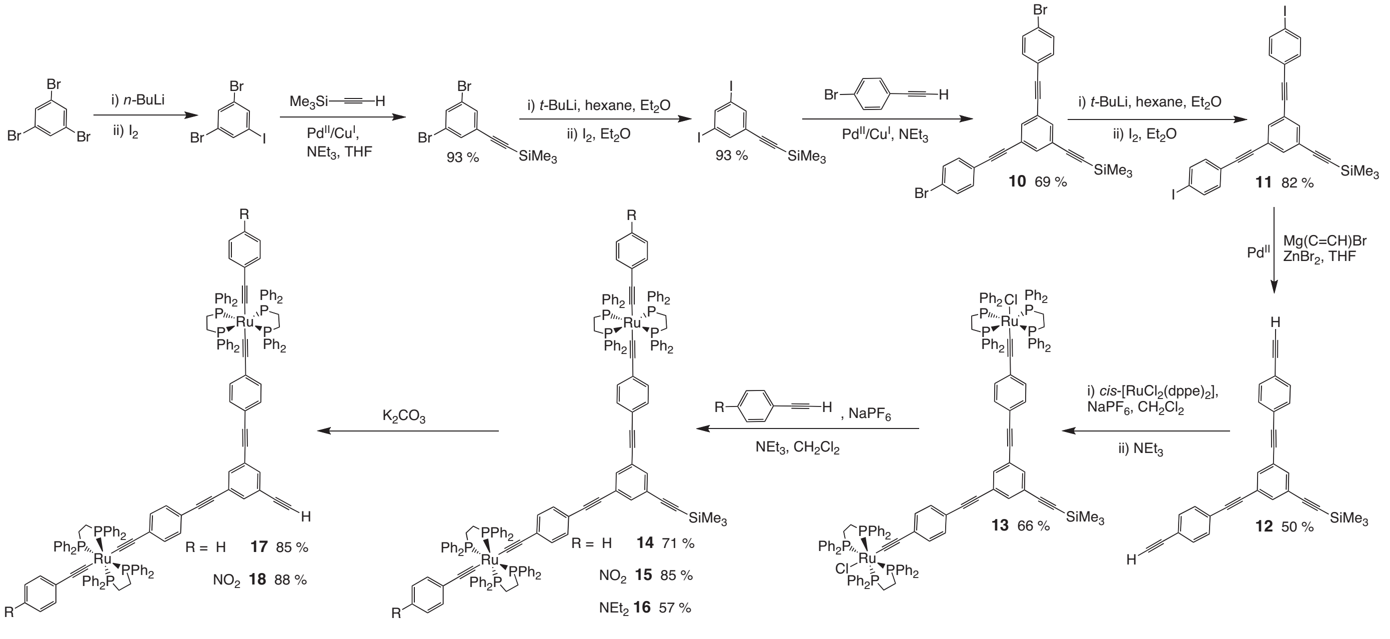
Scheme 4. Syntheses of **1**–**9**.

afforded examples up to third-generation in size (Scheme 2), at which point inseparable impurities were present [11c]. Successful divergent syntheses of increasing size (to sixth-generation) were achieved by using large excesses of the reactants to couple to the periphery of the growing dendrimer [11e]. Convergent procedures were used to afford examples up to third-generation in size (Scheme 3), inseparable impurities again causing problems with attempts to achieve larger species [11d].

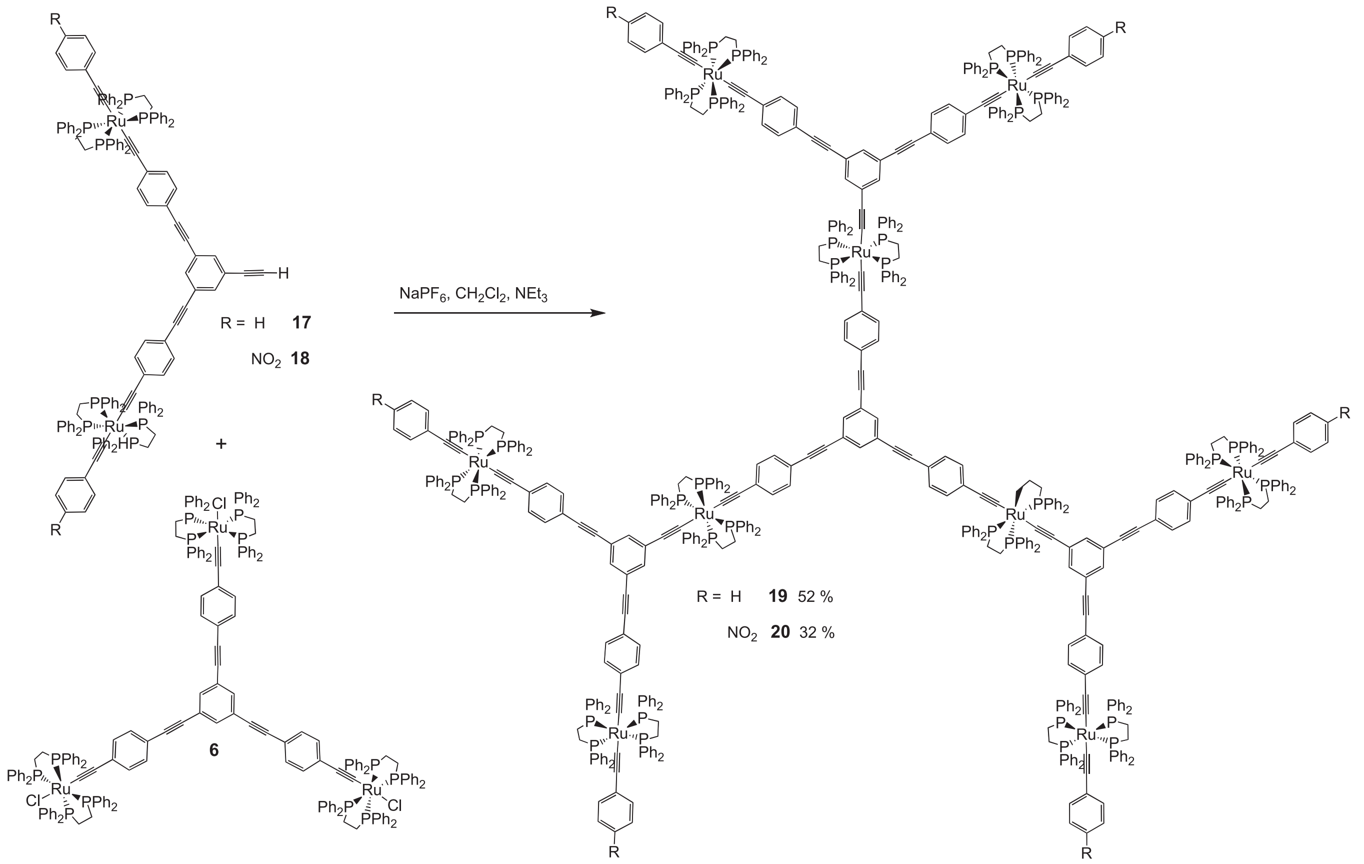
First-, second- and third-generation zinc porphyrin-cored dendrimers with four triethynylbenzene-derived platinum-containing dendrons (as above) attached to the core have been prepared; fluorescence studies indicated efficient energy transfer from the platinum alkynyl dendrons to the zinc porphyrin core [11g]. Mixed-metal dendrimers with palladium in the core attached by pyridylethynyl units to platinum alkynyl dendrons have also been reported; the pyridyl-coordinated dendrons can be displaced on treating the mixed-metal dendrimers with chloride [11f]. The examples described thus far involve platinum-containing units being employed to construct dendrimers, but it is possible to insert platinum into a pre-formed dendrimer; the tin centers in certain tin alkynyl dendrimers can be replaced with platinum while maintaining the dendritic structure [12].

Almost all of the ruthenium alkynyl dendrimers have been prepared by Humphrey and co-workers. Their initial syntheses of zero- and first-generation examples used organic methodologies to afford the necessary dendrons (Schemes 4–7) [13]; these syntheses are particularly lengthy in nature, and undesirable as a route to compounds for physical properties studies.

They subsequently showed that treating 1,3,5-triethynylbenzene with an excess of the chlororuthenium



Scheme 5. Syntheses of **10**–**18**.



Scheme 6. Syntheses of **19** and **20**.

precursor immediately affords the dimetallated dendron **26**, which is suitable for dendrimer synthesis, steric factors at the triethynylarene precluding trimetallation. The excess metal reagent can be readily removed, so this “steric control” methodology was exploited to rapidly afford a number of ruthenium and mixed ruthenium–platinum alkynyl dendrimers (Schemes 8–10) [14]. First- and second-generation ruthenium alkynyl dendrimers with a tris-(4-ethynylphenyl)amine core and branching units were reported by Takahashi and co-workers [15], the core of which was used by the Humphrey group to synthesize the N-cored, phenyl-branched dendrimer **45** (Scheme 10) [14e].

4.2. Single wavelength studies

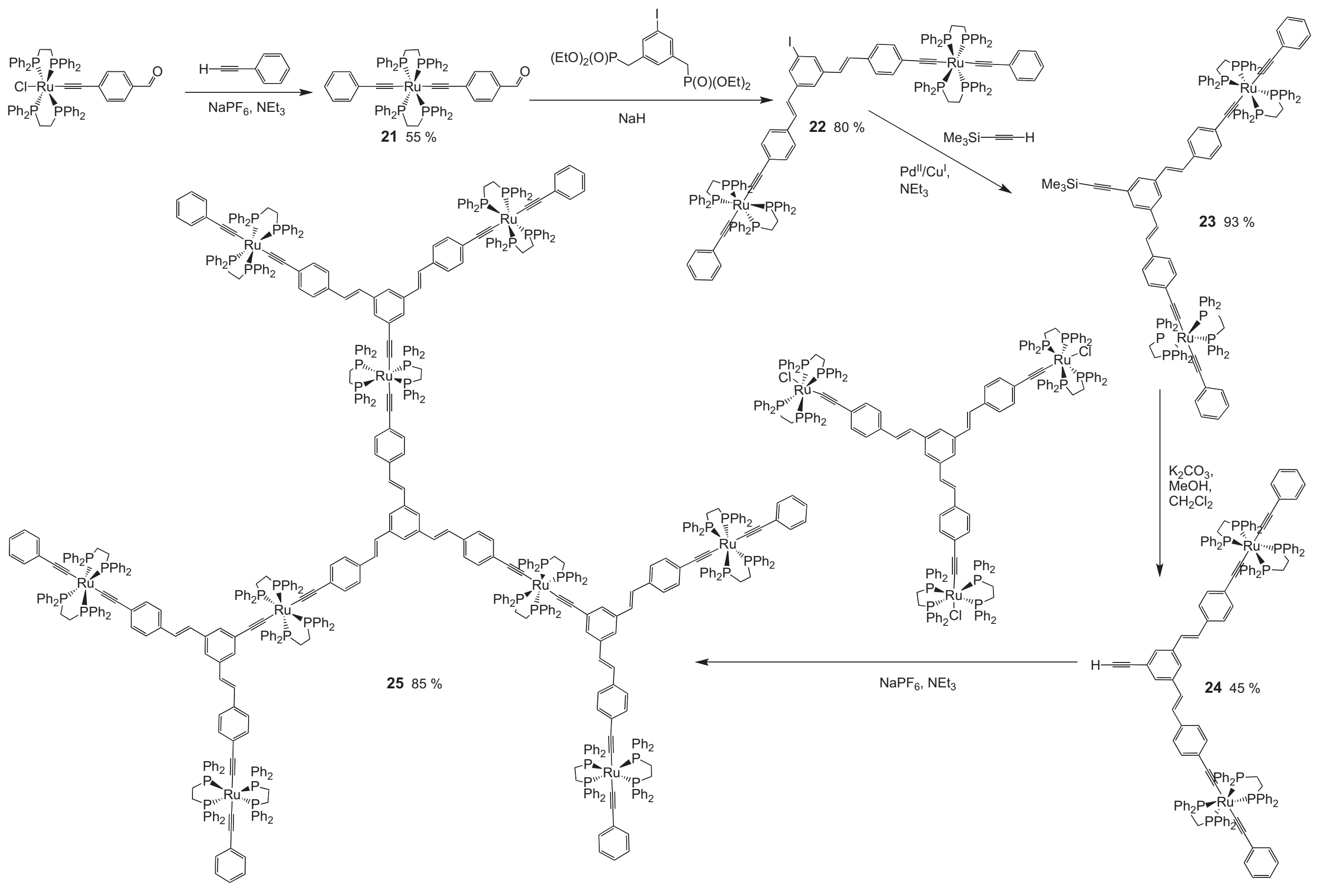
Quadratic nonlinearities of some of the ruthenium alkynyl dendrimers have been assessed by hyper-Rayleigh scattering at $1.064\,\mu m$, the results from which are collected in Table 1. The data are presented as the square root of the orientationally averaged square of the nonlinearity, permitting a comparison between linear analogues and the trigonal (“octupolar”) dendritic complexes. The complexes bearing no nitro-substituents have absorption bands relatively far from the second-harmonic wavelength of 532 nm, permitting assessment of the impact of structural variation on quadratic NLO merit. Within the error margins of the experiment (±10–15%), proceeding from linear analogue *trans*-[Ru(C≡C-4-C_6H_4C≡CPh)(C≡CPh)(dppe)$_2$] to the zero-generation dendrimer **6** results in a tripling of NLO response, consistent with the increase in number of ligated metal centers, but extending the π-system by replacing the *trans*-disposed chloro in **6** by a phenylalkynyl ligand to afford **7** results in no further increase [13a,16].

The dendrimer **19** results from the coupling of **6** and **17**. While its β value is larger than that of either of the component complexes, it is not substantially so, bearing in mind that it contains nine metal centers, compared to three or two for the components. Improvements in nonlinearity in dipolar systems are usually accompanied by a loss in optical transparency. This “multipolar” system is significant in that there is no loss in transparency on progressing from **7** to **19**. The absolute values of β_{HRS} for **7** and **19** are very large for multipolar compounds optically transparent at the second-harmonic, for which resonance enhancement is much less important. They are also very large for multipolar compounds lacking a formal acceptor moiety at the core [16].

The measured β values of the nitro-containing complexes are an order of magnitude greater that those of their non-nitro analogues. The β values of the nitro-containing complexes are, however, strongly resonance enhanced due to the proximity of the absorption band associated with the MLCT transition (assigned to the metal to nitrophenylalkynyl ligand charge-transfer) to the

Table 1
Quadratic NLO data measured in THF solvent by hyper-Rayleigh scattering at 1.064 mm.

Complex	λ_{max} (nm)	$\sqrt{\langle\beta\rangle}$ (10^{-30} esu)	Ref.
trans-[Ru(C≡CPh)Cl(dppe)$_2$]	319	6	[13a,16]
trans-[Ru(C≡C-4-C_6H_4C≡CPh)(C≡CPh)(dppe)$_2$]	383	34	[13a,16]
(**6**)	414	94	[13a,16]
(**7**)	411	93	[13a,16]
(**8**)	459	1220	[16]
(**13**)	412	101	[16]
(**14**)	408	105	[16]
(**15**)	461	900	[16]
(**17**)	407	104	[16]
(**18**)	463	1120	[16]
(**19**)	402	160	[16]



Scheme 7. Syntheses of **21**–**25**.

second-harmonic wavelength of 532 nm. Complexes **15** and **18** each contain two metal centers, and possess similar β values. Only a small increase in β is observed on progressing to the three metal-center complex **8**, a similar trend to that observed for the non-nitro analogues. A 50% gain in β is found on progressing from **8** to the nine metal-center dendrimer **20**. The β value of 1880×10^{-30} esu for the latter is large for an octupolar molecule, but as mentioned above, this is due in part to resonance enhancement.

The tensorial nature of β may be used to obtain information about the symmetry of the molecule being measured. Depolarization measurements involve measuring the intensity of the scattered second-harmonic light parallel, $I_{zz}^{2\omega}$, and perpendicular, $I_{zx}^{2\omega}$, to the plane of the incident polarized laser beam. The ratio of these two quantities is dependent on the molecular symmetry. For purely dipolar molecules with C_{2v} symmetry:

$$\rho = \frac{I_{zz}^{2\omega}}{I_{zx}^{2\omega}} = 5$$

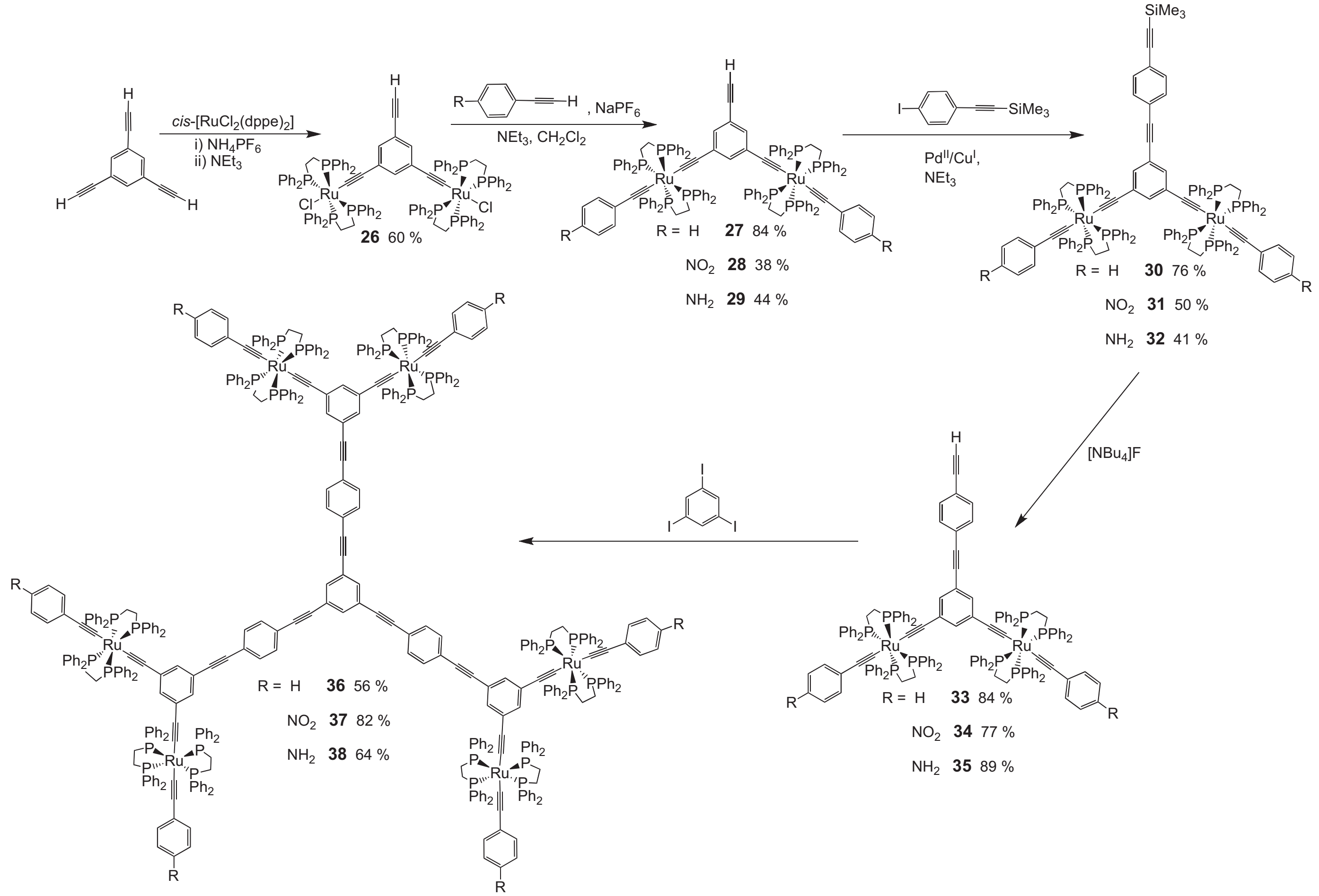
and for purely octupolar molecules with symmetry D_{3h}, T_d or D_{2d}:

$$\rho = \frac{I_{zz}^{2\omega}}{I_{zx}^{2\omega}} = 1.5$$

Depolarization measurements were undertaken for complexes **6** and **7**. The depolarization ratio of 1.4 ± 0.2 for complex **6** is within experimental error of the value expected for purely octupolar symmetry. Complex **7** has a depolarization ratio of 2.1 ± 0.1, a value larger than that expected for a molecule with octupolar symmetry. This increased value may result from a deviation from octupolar symmetry, most likely a lack of coplanarity of the peripheral phenylethynyl groups with the central π-system. A decrease in molecular symmetry would result in an increase in ρ because dipolar contributions to the first hyperpolarizability are introduced [16].

The third-order NLO properties of a number of ruthenium alkynyl complexes were assessed by the Z-scan technique using a Ti-sapphire laser producing ca. 100 fs pulses at 800 nm. Z-scan is advantageous in that it rapidly affords both the real (refractive) and imaginary (absorptive) components of the cubic nonlinearity, but its disadvantage is that it reveals nothing about the temporal nature of the NLO response. The results of these studies are summarized in Table 2.

Broadly speaking, cubic nonlinearities for alkynylruthenium complexes increase significantly on progression from monometallic linear ("one-dimensional") complex to zero-generation dendrimer (a "two-dimensional" complex), and nonametallic first-generation dendrimer, without significant loss of optical transparency. The dendritic ruthenium alkynyl complexes have very large cubic NLO coefficients. Inspection of γ values for *trans*-[Ru(C≡CC$_6$H$_4$-4-C≡CPh)(C≡CPh)(dppe)$_2$] and **7** reveals a significant increase in the imaginary component on progressing from the linear to the octupolar complex, but no increase in γ_{real}. Both real and imaginary components of the third-order hyperpolarizability for the dendrimer **19** are much larger than those of its components **17** and **6** or the related complex **7**. In particular, progressing from **7** to **19** results in increases in both γ_{real} and γ_{imag} proportionately greater than either the increase in the number of phenylethynyl groups or the extinction coefficient. Furthermore, comparison of the "ene-linked" complexes [1,3,5-(*trans*-[(dppe)$_2$ClRu{C≡C-4-C$_6$H$_4$-(*E*)–CH=CH}])$_3$C$_6$H$_3$] and [1,3,5-(*trans*-[(dppe)$_2$(PhC≡C)Ru{C≡C-4-C$_6$H$_4$-(*E*)–CH=CH}])$_3$C$_6$H$_3$] with the



Scheme 8. Syntheses of **26**–**38**.

analogous "yne-linked" complexes above demonstrates enhancement of third-order NLO properties by replacement of acetylene linkages with (*E*)-ene linkages.

Two-photon absorption (TPA) is a third-order NLO property that is of interest for applications in multiphoton microscopy, optical limiting, and optical data storage, and for which structure-activity trends are identical with those for γ_{imag}. For these complexes, TPA increases substantially on progression to larger π-delocalizable compounds, TPA cross-sections for the dendritic examples being of the same order of magnitude as the best organic compounds. Two-photon absorption cross-sections have been calculated, selected examples of which are listed in Table 2. The σ_2 values increase upon increase in dendrimer size and π-system, with the value for **19** among the largest for organometallic compounds.

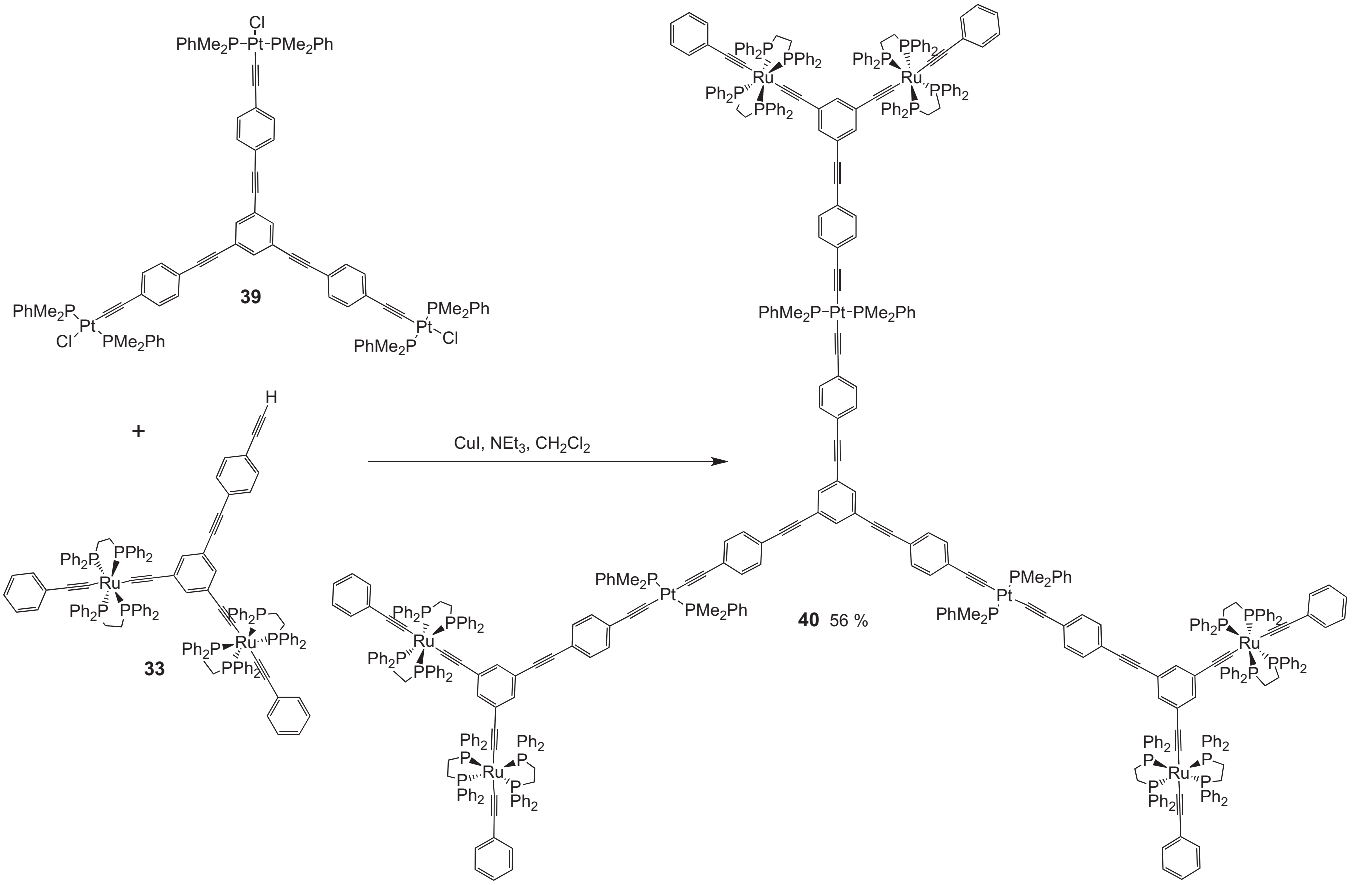
Platinum alkynyl complexes have attracted significant interest as optical limiters, so it is surprising that platinum alkynyl dendrimers have been little studied for optical power limiting (OPL). The optical limiting performance of the zero-generation dendrimer [1,3,5-(*trans*-[$(PMe_2Ph)_2ClPt(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}C)$])$_3C_6H_3$] was assessed at 523 nm using 5 mJ 40 ns pulses [14c]. It exhibits an effective absorption cross-section much larger than that of its linear "fragment" *trans*-[$Pt(C{\equiv}C\text{-}4\text{-}C_6H_4C{\equiv}CPh)Cl(PMe_2Ph)_2$] ($7 \times 10^{-19}$ cm^2 vs. 4×10^{-20} cm^2), but undergoes photodecomposition over time. Polyester dendrimers containing platinum alkynyl cores have been studied, with the OPL properties improving as the dendrimer generation (and thereby isolation from other platinum centers and the environment) increases [20]. The OPL behavior is dominated by excited-state absorption, with the dendritic units enhancing the excited-state lifetimes.

4.3. Wavelength-dependence studies

The data above highlight the potential of metal alkynyl dendrimers, but suffer from the problem that has stymied comparison of NLO merit of most complexes in the literature: the data are reported at one wavelength only. Just as the linear optical spectra show maxima at varying wavelengths, so do the nonlinear optical spectra, and so effective comparisons of NLO merit necessitate broad wavelength range spectral dependence studies to identify the maximal values. We have therefore commenced such studies of the wavelength-dependence of both nonlinear refraction and nonlinear absorption of metal alkynyl complexes. The data are collected point-by-point, the complete spectrum requiring over a week of data collection for one complex, but several dendrimers have now been examined, sufficient to provide preliminary trends in performance [13e,14b,14d,21].

By way of illustration, the NLO spectral dependence of **20** is shown in Fig. 5. The real component of the cubic nonlinearity is negative over a broad spectral range, while the imaginary component shows distinct maxima centered at ca 750 nm and 1100 nm, the former corresponding to two-photon absorption and the latter to three-photon absorption (3PA) and an exceptionally large 3PA cross-section [21].

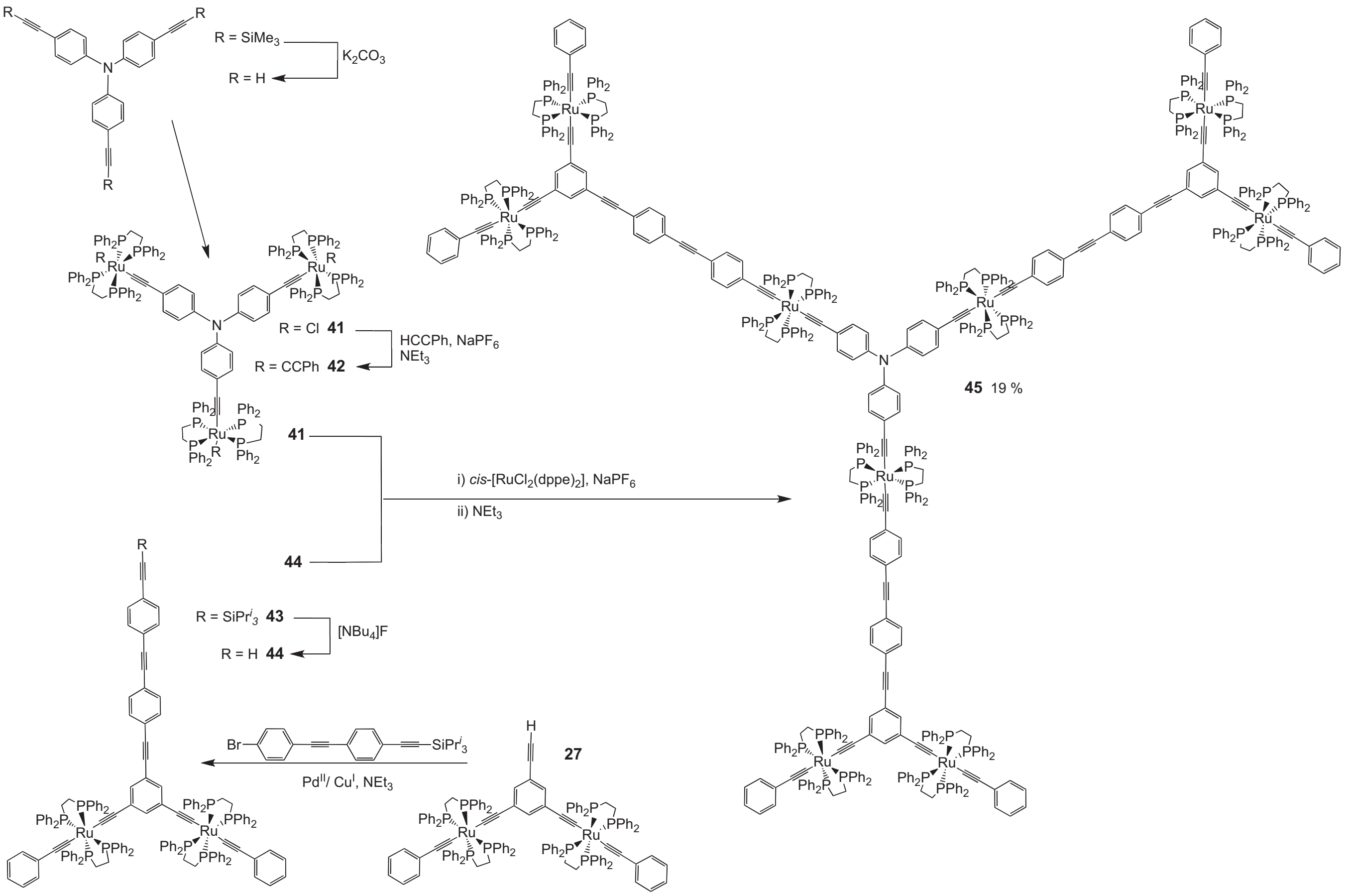
The maximal values of γ_{imag} for [1,3,5-(*trans*-[$(dppe)_2ClRu\{(E)\text{-}4\text{-}C{\equiv}CC_6H_4CH{=}CH\}$])$_3C_6H_3$] ($3000 \times 10^{-36}$ esu), [1,3,5-(*trans*-[$(dppe)_2(PhC{\equiv}C)Ru\{(E)\text{-}4\text{-}C{\equiv}CC_6H_4CH{=}CH\}$])$_3C_6H_3$] ($3000 \times 10^{-36}$ esu), **25** ($12{,}000 \times 10^{-36}$ esu) and **19** ($18{,}000 \times 10^{-36}$ esu) reveal a significant increase upon generation increase (proceeding from zeroth to first generation)



Scheme 9. Syntheses of **39** and **40**.

Table 2
Cubic NLO data measured by Z-scan at 800 nm.

	λ_{max} (nm)	Solvent	γ_{real} (10^{-36} esu)	γ_{imag} (10^{-36} esu)	$\|\gamma\|$ (10^{-36} esu)	σ_2 (10^{-50} cm^4 s)	Ref.
trans-[Ru(C≡CPh)Cl(dppm)$_2$]	308	THF	<120	0	<120	–	[17]
trans-[Ru(C≡CPh)Cl(dppm)$_2$]	318	CH$_2$Cl$_2$	<300	<200	≈0	–	[18]
trans-[Ru(C≡C-4-C$_6$H$_4$C≡CPh)Cl(dppm)$_2$]	381	THF	65 ± 40	520 ± 200	520 ± 200	–	[17]
trans-[Ru(C≡CPh)Cl(dppe)$_2$]	319	THF	−170 ± 40	71 ± 20	180 ± 45	–	[13a]
trans-[Ru{C≡C-4-C$_6$H$_4$-(*E*)–CH=CHPh}Cl(dppe)$_2$]	404	THF	300 ± 400	300 ± 100	420 ± 350	70 ± 30	[19]
trans-[Ru(C≡C-4-C$_6$H$_4$C≡CPh)Cl(dppe)$_2$]	387	CH$_2$Cl$_2$	−100 ± 100	450 ± 200	460 ± 200	–	[18]
trans-[Ru(C≡C-4-C$_6$H$_4$C≡CPh)(C≡CPh)(dppe)$_2$]	383	CH$_2$Cl$_2$	−670 ± 300	1300 ± 300	1500 ± 500	–	[13a,18]
[1,3,5-(*trans*-[(dppe)$_2$ClRu{(*E*)-4-C≡CC$_6$H$_4$CH=CH}])$_3$C$_6$H$_3$]	426	THF	−4600 ± 2000	4200 ± 800	6200 ± 2000	1000 ± 200	[13d,19]
[1,3,5-(*trans*-[(dppe)$_2$(PhC≡C)Ru{(*E*)-4-C≡CC$_6$H$_4$CH=CH}])$_3$C$_6$H$_3$]	421	THF	−11,200 ± 3000	8600 ± 2000	14,000 ± 4000	2100 ± 500	[13d,19]
(**7**)	411	THF	−600 ± 200	2900 ± 500	3000 ± 600	690 ± 120	[13a,13d,19]
(**6**)	414	CH$_2$Cl$_2$	−330 ± 100	2200 ± 500	2200 ± 600	–	[18b,19]
		THF	−330 ± 100	2200 ± 500	2200 ± 600	530 ± 120	[13a]
(**13**)	411	THF	−510 ± 500	4700 ± 1500	4700 ± 2000	1100 ± 360	[13b]
(**14**)	407	THF	−700 ± 100	2270 ± 300	2400 ± 300	550 ± 70	[13b]
(**17**)	408	THF	−830 ± 100	2200 ± 300	2400 ± 300	530 ± 70	[13b]
(**19**)	402	THF	−5050 ± 500	20,100 ± 2000	20,700 ± 2000	4800 ± 500	[13b]
(**26**)	334	THF	−900 ± 500	0 ± 100	900 ± 500		[14d]
(**27**)	335	THF	500 ± 400	200 ± 100	540 ± 100		[14d]
(**28**)	475	THF	−1300 ± 1000	150 ± 40	1300 ± 1000		[14d]
(**29**)	333	THF	1000 ± 400	0 ± 100	1000 ± 400		[14d]
(**30**)	335	THF	700 ± 1200	0 ± 0	700 ± 1200		[14d]
(**31**)	475	THF	−1100 ± 220	310 ± 60	1100 ± 230		[14d]
(**32**)	334	THF	−2200 ± 800	400 ± 200	2200 ± 800		[14d]
(**33**)	330	THF	1700 ± 500	0 ± 0	1700 ± 500		[14d]
(**34**)	474	THF	−5000 ± 1300	1320 ± 270	5200 ± 1300		[14d]
(**35**)	328	THF	−1400 ± 500	1300 ± 300	1900 ± 300		[14d]
(**36**)	339	THF	−1600 ± 2400	0 ± 0	1600 ± 2400		[14d]
(**37**)	475	THF	−23,000 ± 10,000	−6200 ± 2800	24,000 ± 10,000		[14d]
(**38**)	340	THF	−2900 ± 2300	4700 ± 1200	5500 ± 2600		[14d]



Scheme 10. Syntheses of **41**–**45**.

and replacing ene- with yne-linkage (proceeding from **25** to **19**) [13e]. Studies of N-cored dendrimers revealed a dramatic increase in maximal TPA value in proceeding from [1,3,5-(*trans*-[(dppe)$_2$(PhC≡C)Ru(4-C≡CC$_6$H$_4$)])$_3$N] (1250 GM at 605 nm) to **45** (10,600 GM at 582 nm) [14e]. Subsequent comparisons to related N-cored organic dendrimers revealed that the metal alkynyl dendrimers were more efficient when scaling the TPA efficiency by the effective number of electrons [14e], the square of the effective number of electrons [22], the molecular weight [23], molecular volume [23], or the cost of production of 1 mol of substance [23].

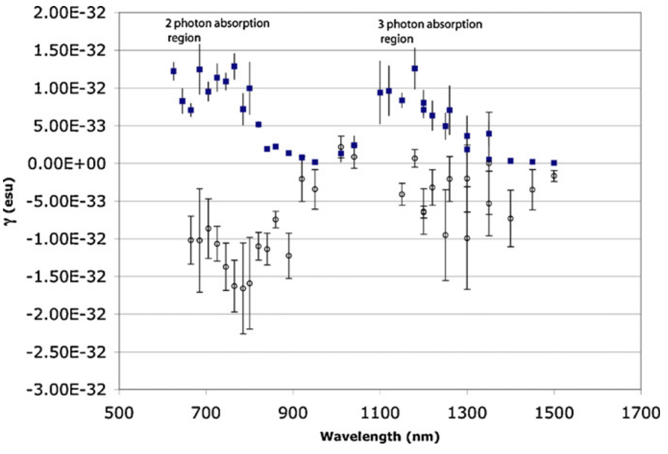


Fig. 5. NLO spectral dependence of **20**. Blue squares are γ_{imag}, open circles are γ_{real}. The γ values in the 3PA region are "effective" values because of the influence of fifth-order NLO processes [21].

5. Concluding remarks

Metal alkynyl dendrimers have been shown to have nonlinearities comparable to the best organic materials, but possess increased design flexibility permitting further tailoring of response. Most NLO data thus far has been obtained at a single wavelength, obfuscating structure–property relationship development. Spectral dependence studies are now starting to afford data suitable for the development of such structure–property relationships, and the recent development of techniques such as white light continuum Z-scan, which permits rapid acquisition of an NLO "spectrum", should further accelerate research in this field.

Acknowledgements

We thank the Commonwealth of Australia for an Australian Postgraduate Award (K.A.G.), the Australian Research Council for an ARC Australian Professorial Fellowship (M.G.H.) and an ARC Australian Research Fellowship (M.P.C.), and the Foundation for Polish Science for the award of a Welcome Programme Laureateship (M.S.).

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