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Syntheses and Nonlinear Optical (NLO) Properties of Ru(II) and Pt(II) - Acetylide Dendrimers

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Abstract: Organometallic dendrimers and its applications have been introduced. Bis((4-(phenylethynyl)phenyl)ethynyl)bis-(tributylphosphine)platinum(II) with dendritic acetonide end groups have been synthesised by divergent method. 1,3,5-benzyl(4-ethynyl(phenylethynyl))-*trans*-[Ru(dppe)$_2$]ethynyl-3,5-phenyl{4-ethynyl(phenylethynyl)-*trans*-[Ru(4-(phenylethynyl))(dppe)$_2$]}$_2$)$_3$ with nine dialkynylruthenium centers have been synthesised by convergent method. Optical power limiting measurements performed at 532 nm show that the OPL properties improve with increasing size of the dendritic substituent. *Z*-scan measurements carried out at different pulse-repetition frequencies show that the two-photon absorption cross section is 10 GM. Significant increase in NLO properties seen on generation increase is maintained when the coefficients are scaled by the number of metal atoms, the dendrimer molecular weights, or hyperpolarizability (π-delocalizable electrons) in the dendritic structures. Nonlinear optical (NLO) properties are required for various applications, including processing of optical signals, optical data storage, nanophotonics, and biophotonics.

Keywords: Organometallic; Dendrimer; Nonlinear Optics; Acetylide.

تحضير ودراسة الخصائص الضوئية الغير خطية لمركبات أسيتليد الروثينيوم والبلاتينيوم الشجرية

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الملخص: المركبات الشجرية العضوفلزية وخاصةً تلك التي تحتوي على الفلزات الإنتقالية مثل الروثينيوم والبلاتينيوم تُستخدم على نطاق واسع في كثير من التطبيقات الكيميائية والفيزيائية والحيوية. تم في هذا البحث مناقشة تحضير مركب أسيتليد البلاتينيوم الشجري والمنتهي بمجموعات الأسيتونيد الطرفية حيث يشكل البلاتينيوم مركزاً لهذا المركب. بالإضافة إلى ذلك، تم مناقشة تحضير مركب أسيتليد الروثينيوم الشجري حيث يتمركز الروثينيوم في تسع نقاط تفرع لهذا المركب. بواسطة تطبيق العديد من القياسات الضوء فيزيائية، تم مناقشة تأثير قطبية المركبات الشجرية على خواصها الضوئية الغير خطية والتي تم تعزيزها بإدخال العناصر الإنتقالية والإيثاينايل. كان من الواضح أن زيادة الوزن الجزيئي للمركب الشجري وكذلك زيادة عدد ذرات الفلز له تأثيراً إيجابياً على امتصاص هذه المركبات للضوء بفوتونين وبالتالي تحسين خواصها الضوئية الغير خطية حيث إن هذه الخصائص لا يمكن الاستغناء عنها في العديد من التطبيقات الفيزيائية الضوئية والفيزيائية الحيوية.

الكلمات المفتاحية: عضوفلزية; مركب شجري;ضوئية غير خطية;أسيتليد.

1- Introduction

The dendritic polymer includes both dendrimers and hyper branched polymer. Dendrimers are a new class of polymeric materials, first discovered in the early 1980's by Donald Tomalia and co-workers, these hyperbranched molecules were called dendrimers.[1] At the same time, Newkome's group independently reported synthesis of similar macromolecules.[2] They called them arborols from the Latin word 'arbor' also meaning a tree. The term cascade molecule is also used, but 'dendrimer' is the best established one. Dendrimers are tree like in structure and appearance. A large number of branches during polymer synthesis lead to formation of macromolecule with many end groups. Out of highly branched polymers, dendrimers are perfectly branched uniform structure and hyper branched polymers are randomly branched. 'Dendrimer' is not a compound; it is only an architectural motif.

Generally accepted definition of dendrimer is a monodisperse macromolecule with perfectly branched regular structure and having at least one branched junction at each repeat unit that built around a small molecule or a linear polymer core. Dendrimers are a new class of polymeric belongings. Their chemistry is one of the most attractive and rapidly growing areas of modern chemistry.

Dendrimers are well-defined three-dimensional macrostructures. The pseudospherical shape of a dendrimer arises from its structure, which consists of an internal region (the core) which is connected to repeating units (grow through a variety of chemical reactions), constituting a radial branching pattern. These macromolecules tend to linearly increase in diameter and adopt a more globular shape with increasing dendrimer generation **(Figure 1)**.[3] Therefore, dendrimers have become an ideal delivery vehicle candidate for exploit study of the effects of polymer size, charge and composition on biologically relevant properties including lipid bilayer interactions, cytotoxicity, internalization, blood plasma retention time, biodistribution and filtration.[4] There is a debate about the exact structure of dendrimers, in particular whether they are fully extended with maximum density at the surface or whether the end-groups fold back into a densely packed interior. Dendrimers of lower generations (0, 1, and 2) have highly asymmetric shape and possess more open structures as compared to higher generation dendrimers. As the chains growing from the core molecule become longer and more branched (in 4 and higher generations) dendrimers, adopting a globular structure. Dendrimers become densely packed as they extend out to the periphery, which forms a closed membrane-like structure. When a critical branched state is reached, dendrimers cannot grow because of a lack of space. This is called the 'starburst effect'.[5, 6]

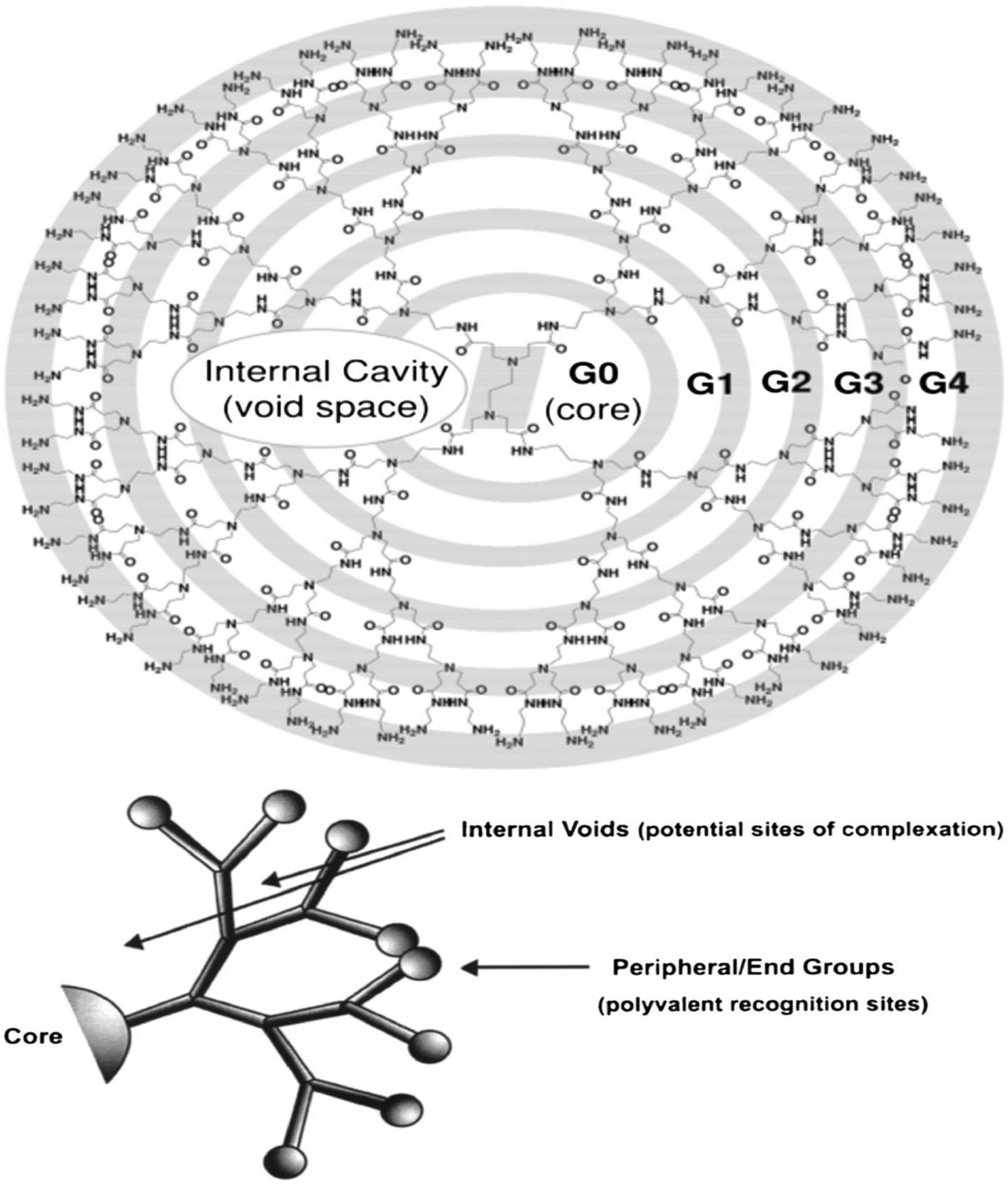


Figure (1) The dendrimer structure and its composition.

2- Organometallic Dendrimers

2.1. Structure and Chemistry

Although the majority of the dendrimers produced to date are organic and natural molecules, there has recently been great effort towards incorporation of main group elements and transition metals at the core, throughout the structure, or at the periphery of a dendrimer as a worthy strategy for materials of economical value. Puddephatt and co-workers in 1994 reported a dendrimer constructed in which an organometallic species, incorporating a Pt(IV) center, was used as an integral structural feature.[7] This was the first example of a dendrimer where an organometallic fragment was incorporated into every generation. This merging will incorporate the properties of dendrimers, such as site isolation,[8] precise steric environments, recyclability[9] and possible cooperative results with the benefits generally attributed to organometallic or transition metal species, such as light harvesting, electrochemical, catalytic,[10] optical and magnetic properties. Besides their appealing architecture and globular shape, the most striking properties of dendrimers are their controllable size and good solubility in a huge range of solvents, which make them suitable for anchoring organometallic species that can be applied in homogeneous catalysis. So far, metals such as Fe, Cu, Zn, Ni, Au, Co, Pd/Pt, Os/Ru, Rh, and Ge have been incorporated as branching units or periphery of dendrimers.

The design of organometallic dendrimers involves taking into consideration the position and repetition of the metal site in the dendrimer framework, such as on the periphery (A), at the core (B), at branching points (C) or dendrimer-encapsulated metal nanoparticles (DEMNs) (D). **Figure 2** shows schematic representations of different types of metallodendrimers.[11] . Interestingly, the versatile coordination of transition metals and their variety of stable oxidation states offer a unique chance for tailoring metallodendrimer to attain desirable properties.

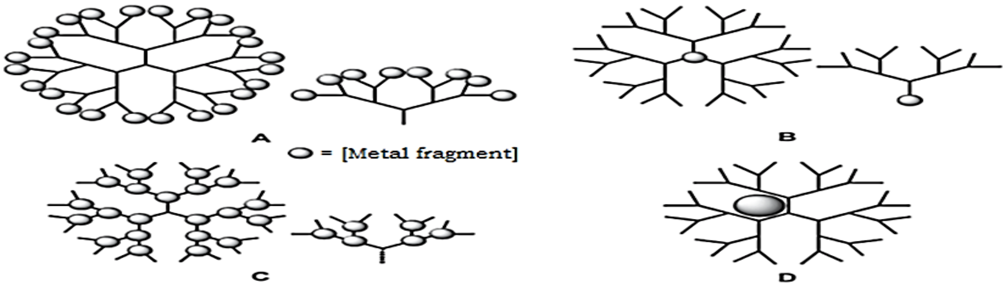
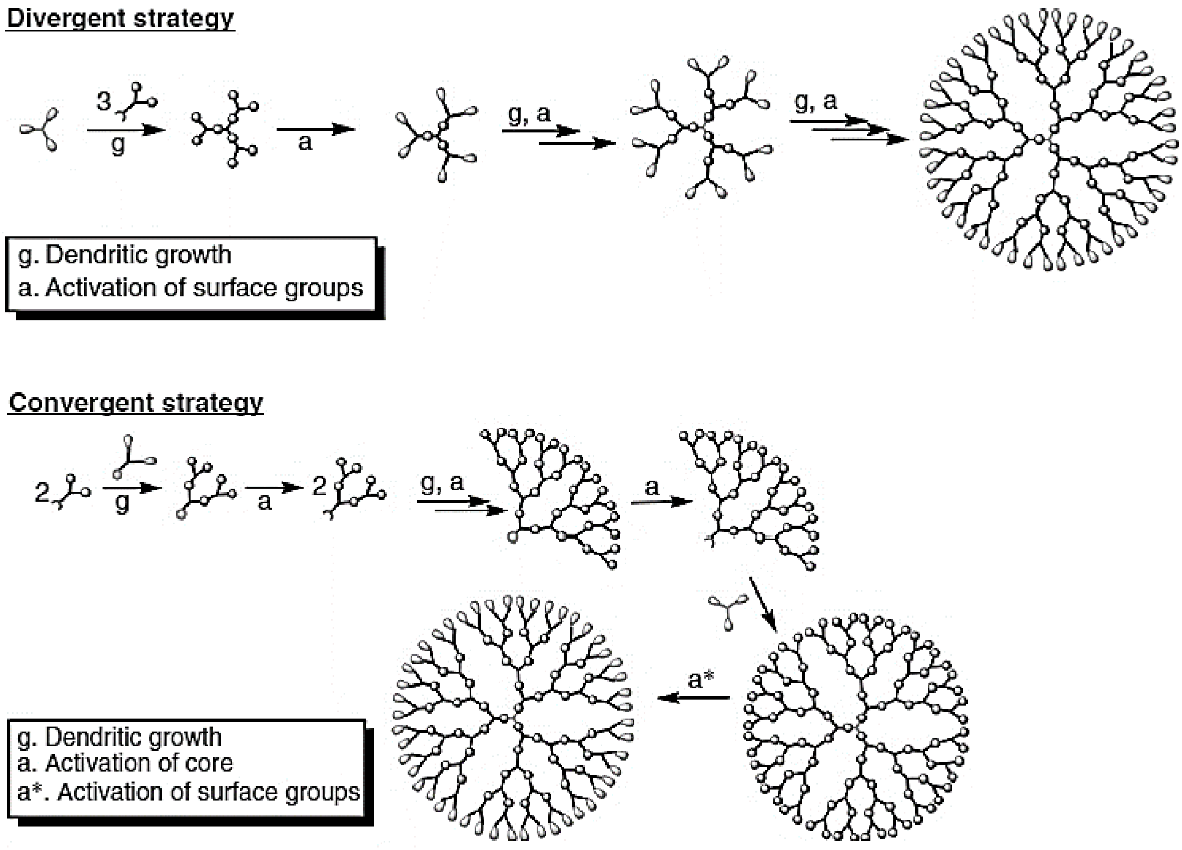


Figure (2) Schematic representations of metallodendritic architectures according to the metal (catalyst) location.

2.2. Strategies of Synthesis

Dendrimers are just in between molecular chemistry and polymer chemistry. They relate to the molecular chemistry by virtue of their step-by-step controlled synthesis, and they relate to the polymer world because of their repetitive structure made of monomers. Dendrimers are generally prepared using either a divergent strategy; synthesis starts from the core of the dendrimer to which the arms are attached by adding building blocks in an exhaustive and step-wise manner, or a convergent strategy; synthesis starts from the exterior, beginning with the molecular structure that ultimately becomes the outermost arm of the final dendrimer **Scheme 1**.[12]



Scheme (1) A schematic summary of the different routes used to construct globular dendrimers.

In the early 1980s, Tomalia and coworkers achieved the synthesis of Polyamidoamine PAMAM dendrimer as a first divergent synthesis of these monodisperse hyperbranched macromolecules (Figure 3),[3] and coined the term dendrimer concurrently with the development of Newkome's "arborol" systems.

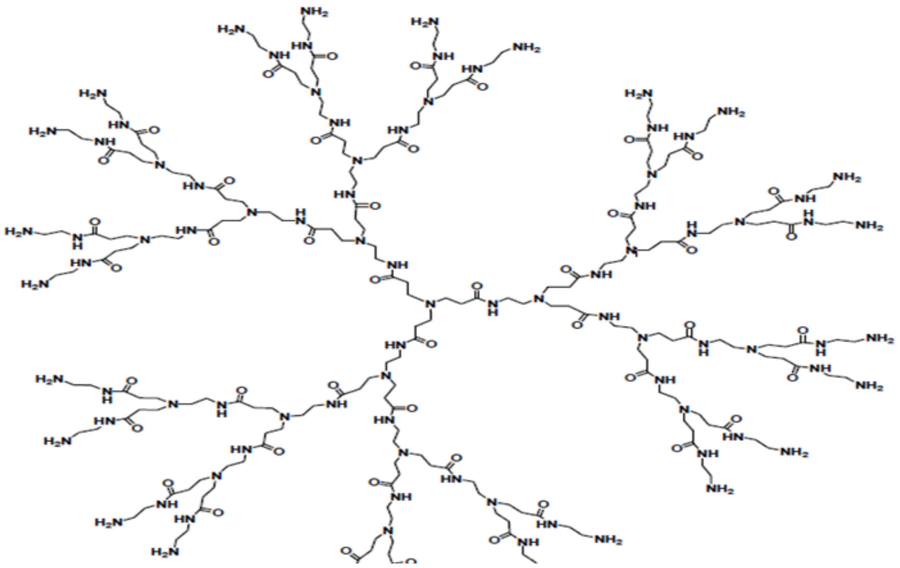


Figure (3) Tomalia's amine-terminated PAMAM dendrimer.

Convergent approach was achieved by Hawker and Fréchet in synthesis of poly-benzylether containing dendrimers. Photo-responsive dendrimers such as poly(arylether) dendrons which called Frechet-type dendrons are prepared by means of this method.[13] Moreover, forming benzyl ethers from phenols and benzylic halides in quantitative yields as the first Fréchet-type convergent synthesis.

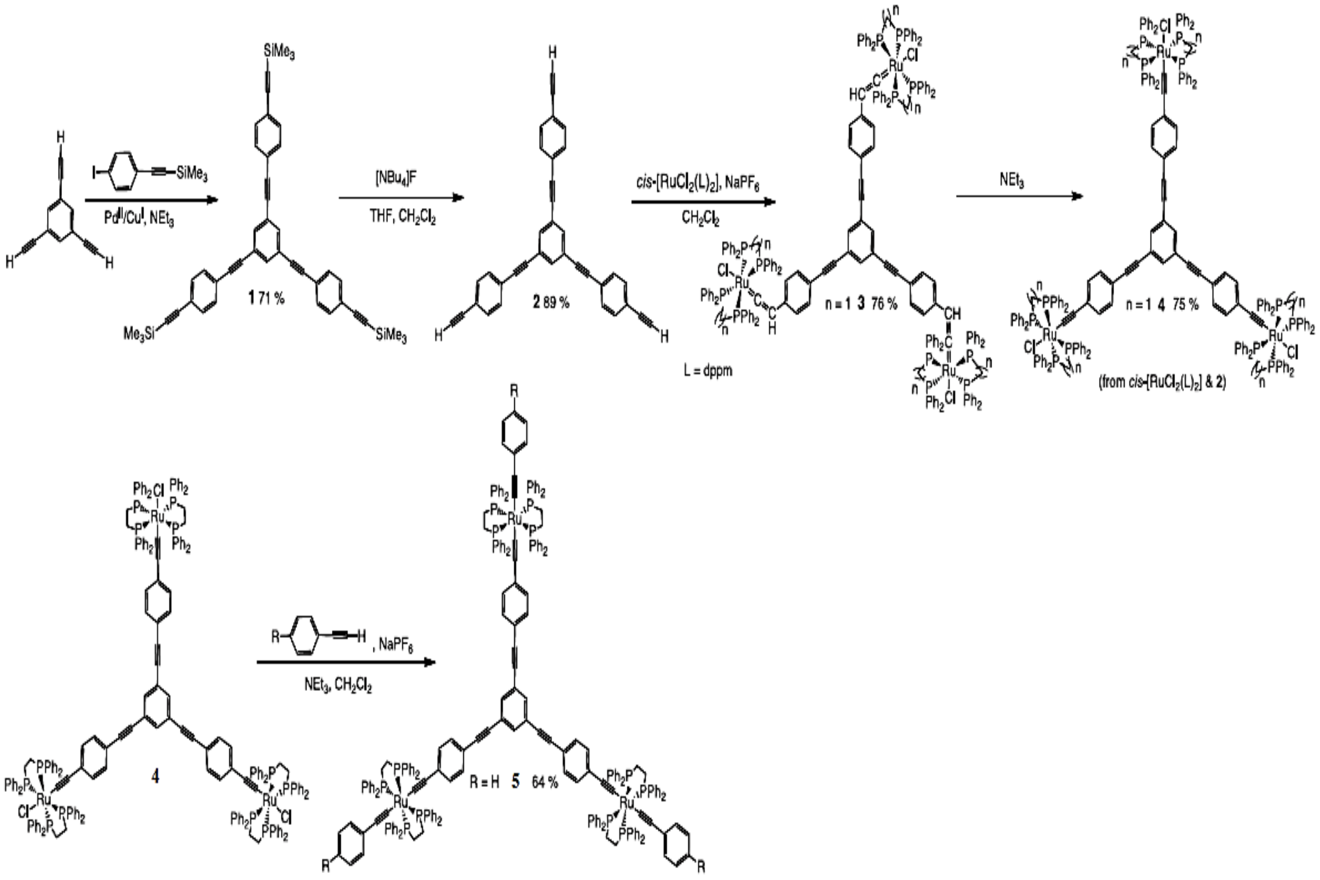
Platinum(II) and ruthenium(II) phosphines are known to form bis(alkynyl) complexes with *trans* geometry. Therefore, they have been used extensively as bridging units in producing dendrimers with multiple generations. Recently, the metal alkynyl dendrimers can be construct with phenylene(ethynylene) bridges by either; divergent or convergent methods. In divergent approach, there is a need to use excess reagent in every step to ensure perfect growth of dendrimers. This process was employed by Onitsuka *et al* to synthesize platinum alkynyl dendrimers.[14] The convergent method has recently proven to be a better choice, as it is relatively easier to follow the progress of reaction by spectroscopic techniques. In contrast, a first-generation dendrimer containing six ruthenium atoms achieved by Hurst *et al* who used Sonogashira coupling between free acetylene groups on the wedges and a tri-iodo core.[15]

2.3. Syntheses of Ru(II)-Acetylide Dendrimer

By Humphrey and co-workers, almost all of the Ru-acetylide dendrimers have been prepared by convergent strategie.[16,17]

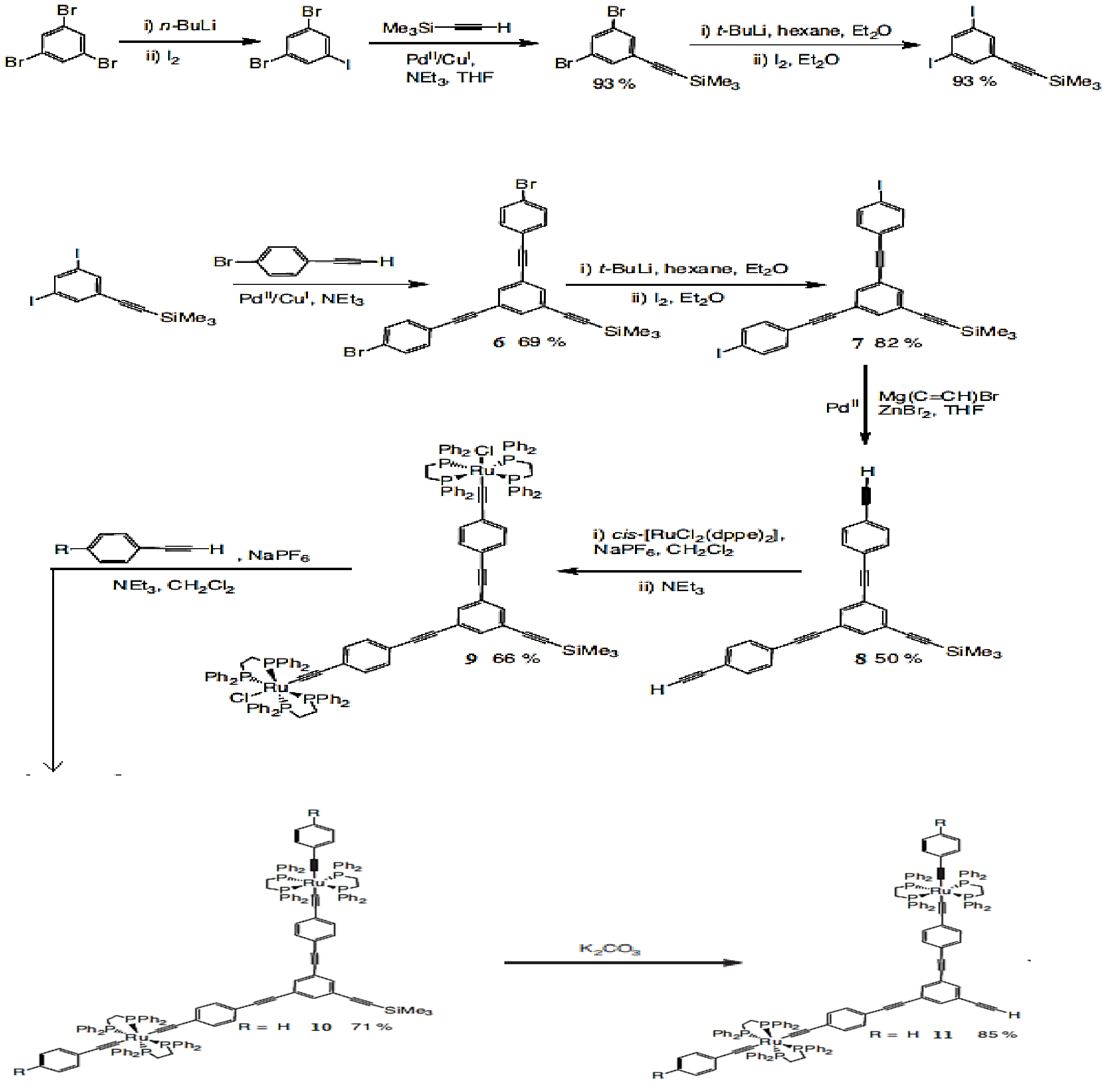
Zero- and first-generation was prepared by a Sonogashira-type coupling reaction[18] and other organic methodologies (Schemes 2–5). These syntheses are particularly lengthy in nature, and undesirable as a route to compounds for physical properties studies.

1,3,5-triethynylbenzene was treated with 3 equiv of 1-iodo-4-trimethylsilylethynylbenzene in the presence of a $[PdCl_2(PPh_3)_2]$/CuI catalyst in triethylamine (Sonogashira coupling) afforded the tris(4-trimethylsilylethynylphenyl) derivative **1**. Subsequently, desilylation of the silyl-containing compound **1** with fluoride giving the tris(4-ethynylphenyl) **2**. The reactive ethynyl groups in **2** were sufficiently removed from one another to permit smooth metalation with bulky bis(diphosphine)ruthenium units at each ethynyl group. Reaction of **2** with cis-$[RuCl_2(dppe)_2]$ in dichloromethane in the presence of PF_6 gave the trivinylidene complex **3** (**Scheme 2**). Deprotonation of the trivinylidene complexes **3** with NEt_3 gave the trialkynyl complex **4**. Reaction of **4** with phenylacetylene proceeded via the intermediacy of trivinylidene complexes (which were not isolated here or in any subsequent steps) to give trisdi(alkynyl) complexes **5** (**Scheme 2**).



Scheme (2) Syntheses of complexes 1-5.

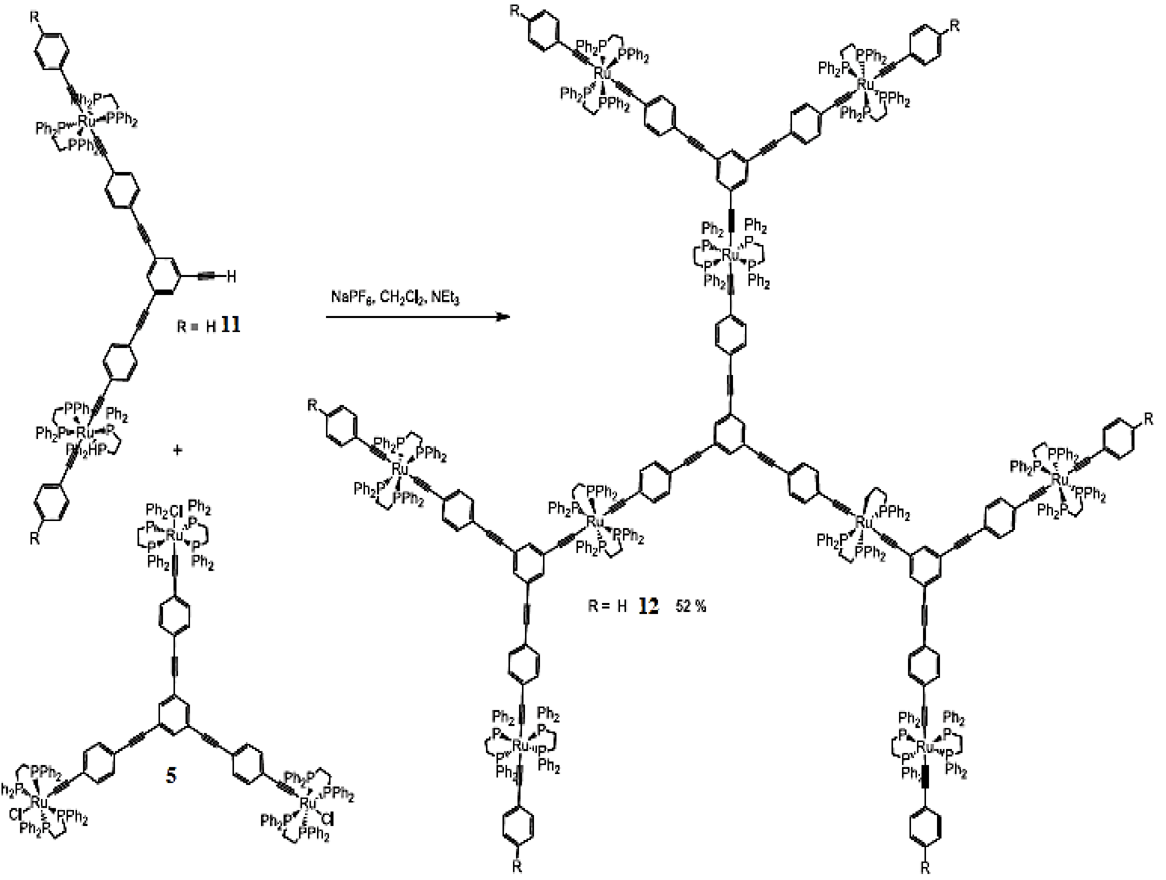
Sonogashira coupling of 1,3-diiodo-5-trimethylsilylethynylbenzene with 1-bromo-4-ethynylbenzene in the presence of palladium(II)/copper(I) catalysts afforded 1,3-(4-$BrC_6H_4C{\equiv}C)_2$-5-(Me_3-$SiC{\equiv}C)C_6H_3$ **6**. The diiodo analogue **7** was afforded by transhalogenation of compound **6** in the presence of *tert*-butyllithium. To incorporating a terminal alkyne onto the aryl iodide **7** directly, it was treated subsequently with situ generation of Zn(C≡CH)Br from the Grignard reagent Mg(C≡CH)Br, zinc(II) bromide and palladium(II)/copper(I) catalysts affording the organic dendron 1,3-(4-$HC{\equiv}CC_6H_4C{\equiv}C)_2$-5-($Me_3SiC{\equiv}C)C_6H_3$ **8**. Reacting of the dendron **8** with *cis*-[$RuCl_2(dppe)_2$] in the presence of $NaPF_6$ afforded a divinylidene complex, which was not isolated, but instead deprotonated by triethylamine in situ to give the dialkynyl complex **9**. Then the peripheral groups of the nascent dendrimer were incorporated by reacting the dialkynyl complex **9** with the alkyne 4-$HC{\equiv}CC_6H_4H$ in the presence of $NaPF_6$ and base before treating with basic (K_2CO_3) conditions geving the bis-di(alkynyl) complex **11**. Replacement of chloro ligands also removing the possibility of the wedge coupling with itself in the final step of dendrimer construction (**Scheme 3**).



Scheme (3) Syntheses of complexes 6-11.

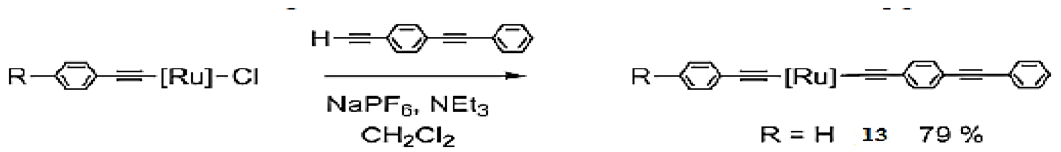
Scheme 3 Syntheses of the bis-di(alkynyl) complex 11.

Reaction of 5 with 3 equiv of the trialkynyl complex **4** in the presence of $NaPF_6$ and triethylamine gave the first generation dendrimer complex **12** (**Scheme 4**).



Scheme (4) Syntheses of complex 12.

For comparison, linear analogue of the dendrimers was prepared by reaction of *trans*-[Ru-(4-$C{\equiv}CC_6H_5$)Cl(dppe)$_2$] with 4-$HC{\equiv}CC_6H_4C{\equiv}CPh$ in dichloromethane in the presence of $NaPF_6$ and triethylamine afforded complex **13 (Scheme 5)**.

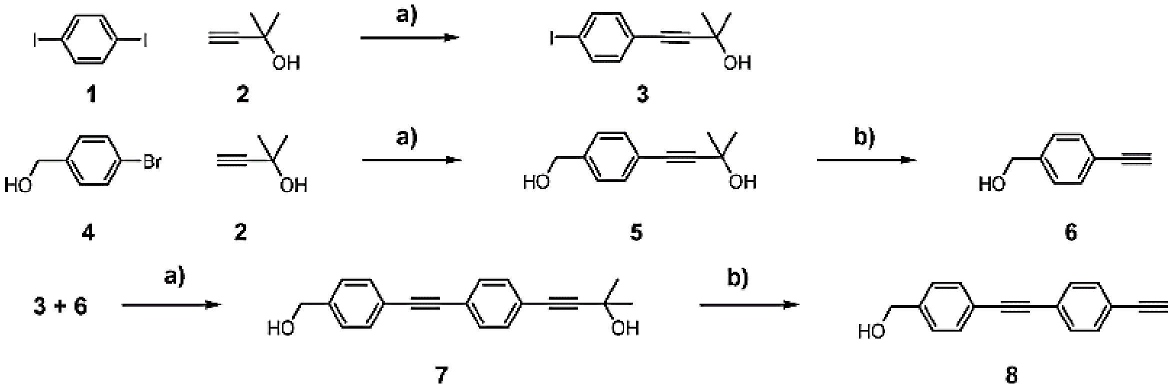


Scheme (5) Syntheses of linear complex 13.

2.4. Syntheses of Pt(II)-Acetylide Dendrimer

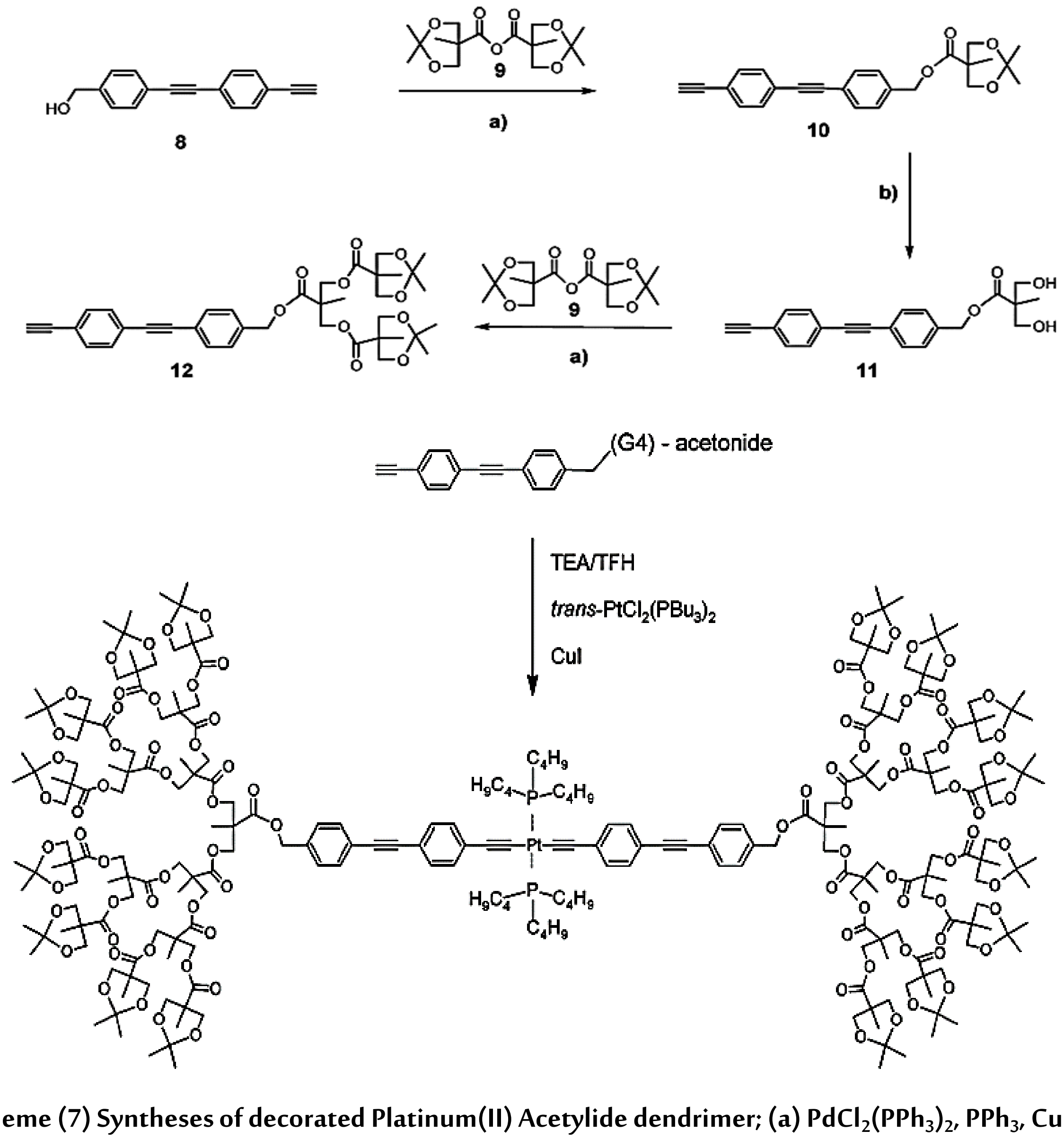
Both the divergent and convergent methods have been used by Takahashi and co-workers in the synthesis of many Pt-acetylide dendrimers with 1,3,5-triethynyl-2,4,6-trimethylbenzene cores.[19]

Successful divergent syntheses of the dendron decorated Pt-acetylides were achieved by first preparing the arylalkynyl "arms" through Sonogashira coupling reactions,[20] followed by stepwise synthesis of the dendrons from the arylalkynyls Finally, the arylalkynes dendron were coupled to the platinum core (**Scheme 6**). The dendrons (generation one to four) were grown by means of divergent synthesis utilizing the versatile chemistry of the acetonide protected bis-MPA anhydride. The 1,4-diiodobenzene **1** was first monosubstituted with aprotected alkyne **2** to yield **3** (**Scheme 6**). This reaction was performed using a palladium(II)/copper(I) catalysts Sonogashira coupling reaction in pyridine and triethylamine. Then, by using similar reaction conditions, the 4-bromobenzyl alcohol **4** was coupled with the protected alkyne **2**. The resulting protected alkynylbenzyl alcohol **5** was activated for further Sonogashira couplings by treating with basic (KOH) conditions. The alkyne benzyl alcohol **6** was coupled to the protected alkyne benzyl iodide **3** using the Sonogashira coupling. This coupling doubles the conjugation length of the arm by incorporating two aromatic rings and two alkynes. Subsequently, the terminal alkyne on **7** was coupled with platinum(II) core. After each reaction, the products were purified by medium-pressure liquid chromatography system on silica gel. Before the growth of the dendrons, the deprotection of the alkyne was conducted to avoid the hydroxyl of the protecting group to attach to the dendrons.



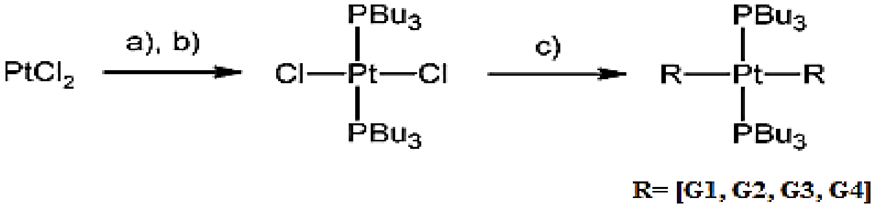
Scheme (6) Syntheses of complexes 1-8; (a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, pyridine, TEA, 120°C; (b) KOH, THF, Dean-Stark, 80°C.

The first generation dendron 10 was grown from the benzyl alcohol 8 utilizing the acetonide protected bis-MPA anhydride 9 (Scheme 7). The reaction was carried out in pyridine and dichloromethane using 4-(dimethylamino)pyridine (DMAP) as catalyst. The acetonide protecting groups were removed by an acid-catalyzed reaction in methanol using DOWEX-50-X2 resin. The resulting first generation dendron 11 was then coupled with the anhydride 9 again to yield the hydroxy-functional second-generation dendron 12. Higher generations were achieved by repetitive acidic deprotections and additions with the acetonide protected bis-MPA anhydride 9.



Scheme (7) Syntheses of decorated Platinum(II) Acetylide dendrimer; (a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, pyridine, TEA, 120°C; (b) KOH, THF, Dean-Stark, 80°C.

The core of Pt(II) acetylide dendrimers was synthesized by stirring $PtCl_2$ and PBu_3 in water to 80°C for 8 h, which gave a mixture of cis- and trans-$PtCl_2(PBu_3)_2$ (Scheme 8). The crude product was melted and converted to trans-$PtCl_2(PBu_3)_2$ and purified by flash chromatography over silica. The synthesis of the dendron decorated Pt acetylide compound was carried out by a Sonogashira coupling reaction of the suitable decorated arylalkynyl ligands to $PtCl_2(PBu_3)_2$ with CuI as catalyst, which was carried out in TEA and THF and by immediately heating the solution to 60°C for 5 min. The dendrons (generation one to four) were obtained in excellent yields, above 88% relative to Pt compound.



Scheme (8) Syntheses of the core of Platinum(II) acetylides; (a) PBu_3 (2 equiv), H_2O 80 °C; (b) heat 15 min; (c) TEA, THF, CuI, 60°C for 5 min.

In the other hand, bis((4-(phenylethynyl)phenyl)ethynyl)bis-Pt(tributylphosphine)platinum(II) (Pt-ethynyl) without dendrons was synthesized for comparison according to a similar procedure.

2.5. NLO Properties of Ru(II) and Pt(II)-Acetylide Dendrimers

NLO effects generally necessitate a large polarizable π-electron system, and so for such applications π-delocalizable dendrimers have been of interest. Examples of some π-delocalizable organometallic used for NLO applications are substituted thiophenes, porphyrins and metal-coordinated phenylacetylenes such as Ru(II) and Pt(II)-acetylides.[16] Nonlinear optical properties are required for various applications such as processing of optical signals, optical data storage, nanophotonics, and biophotonics.[21,22]

Broadly speaking, cubic nonlinearities for Ru(II)-acetylide 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 Ru(II)-acetylide complexes have very large cubic NLO coefficients.[23] The UV-vis spectra of zero-generation dendrimer 13 and first-generation dendrimer 12 of Ru(II)-acetylides show absorption bands above 30000 cm^{-1} assigned to transitions associated with the phosphine ligands. Illustrative spectra are shown in Figure 4. There is no loss of optical transparency in proceeding from the zero-generation Ru(II)-acetylide dendrimer 13 to the first generation Ru(II)-acetylide dendrimer 12 (Figure 4); in fact, a small gain in transparency is seen, which may indicate that the dendrimer 12 has a nonplanar geometry. On set of noncoplanarity is consistent with the general observation that, upon increasing the size of dendritic systems, the initially planar disposition will eventually become a globular array. Interestingly, the extinction coefficient for ν_{max} increases more than 3-fold in proceeding from 13 to 12.

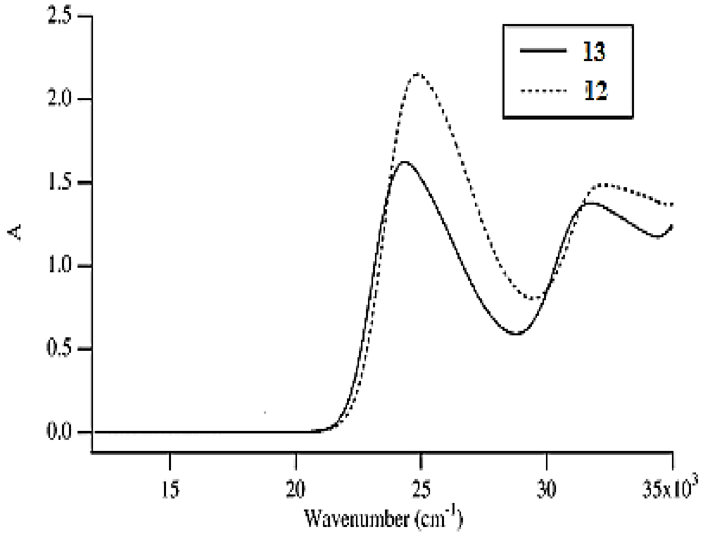


Figure (4)UV-vis spectra of zero-generation dendrimer 13 and first-generation dendrimer 12.

By way of illustration, the NLO spectral dependence of first-generation Ru(II)-acetylide dendrimer 12 is shown in Figure 5. The real component of the cubic nonlinearity is negative over a broad spectral range, while the imaginary component shows distinct maxima centered at 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.[24]

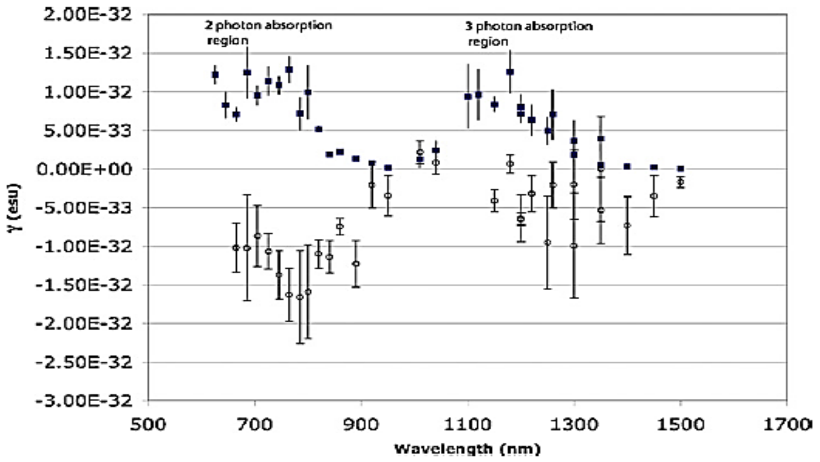


Figure (5) NLO spectral dependence of first-generation dendrimer 12. Blue squares are γ_{imag}, open circles are γ_{real}.

Pt(II)-acetylides have attracted significant interest as optical power limiters (OPL), so it is surprising that Pt(II)-acetylide dendrimers have been little studied for optical power limiting. It has been shown that both two-photon absorption (TPA) and excited state absorption (ESA) contribute to OPL for Pt(II)-acetylides. As is believed, the larger dendrons provide more efficient shielding of the dye moiety.

Accordingly, less quenching will occur and the lifetimes of the excited states should be increased and give rise to more efficient ESA. Moreover, the larger dendrons acted as "molecular bumpers" to decrease the triplet-triplet annihilation recombination rate, and hence longer decay times for the triplets of the larger dendron decorated compounds in oxygen-evacuated samples.[25] Moreover, the shielding may prevent aggregation of the dyes and thereby increase the NLO absorption of the chromophore.

Fluorescence spectra of platinum(II) acetylides (G1-G4) at 375 nm excitation in THF are shown in Figure 6. Two strong bands can be seen at 395 and 422 nm and two weaker bands at approximately 525 and 555 nm. All the emission spectra showed the same shape. For the entire emission It can be seen that the nondecorated platinum(II) acetylide showed a small blue shift of about 3.5 nm. This is probably an effect of the benzyl ester groups interacting with the π-conjugated system. This blue shift shows that there is a photophysical difference between the nondecorated and the decorated dendrons, which could be the reason why the decorated platinum(II) acetylides have improved OPL properties.

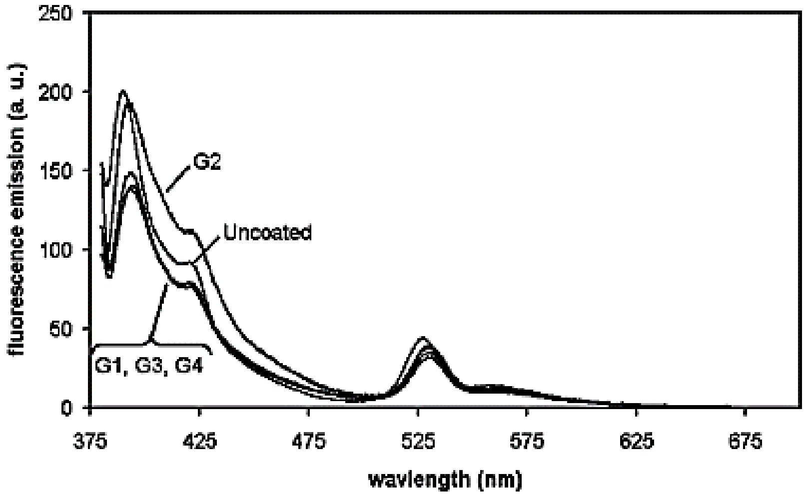


Figure (6) Steady-state fluorescence emission in THF at 10 μM.

The OPL properties were measured at wavelength 532 nm. Figure 7 shows the representative OPL curves for a series of samples, where the output energy is plotted as a function of the input energy when focusing through the sample. The sample without dendritic substitution (Pt-ethynyl) is the least efficient. In addition to an effect of increased dendrimer generatinon (G2-G4), by which chromophores are prevented to come into close contact followed by potential self-induced triplet-triplet annihilation quenching, the NLO effects of the material may be improved by the electron-withdrawing property of the ester groups.[26]

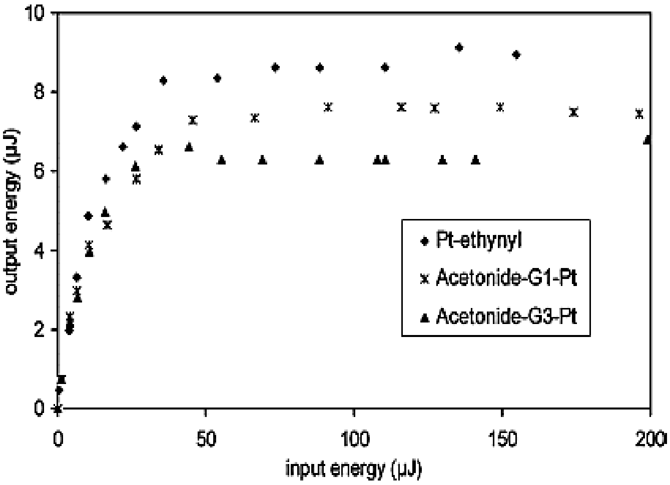


Figure (7) OPL for Pt-ethynyl, Acetonide-G1-Pt, and Acetonide-G3-Pt, in THF (30 µM) at 532 nm.

The long-lived triplets had an impact not only on the OPL measurements but also on *z*-scans using various pulse repetition rates. **Figure 8** shows in panel B a dramatic increase in the *z*-scan response going from the nondecorated Pt(II)-acetylide to Acetonide-G2-Pt and Acetonide-G4-Pt (the concentration of the nondecorated variant is more than 3 times higher). Apparently, since the triplet states of the nondecorated (Pt-ethynyl) are strongly quenched, the *z*-scan of this sample at a high pulse repetition frequency is weak. On the other hand, Pt- acetylide dendrimers (Acetonide-G2-Pt and Acetonide-G4-Pt) show deep absorptions in the *z*-scan traces due to more dominating ESA (especially for the Acetonide-G4-Pt) because of less quenching of the triplets.[17]

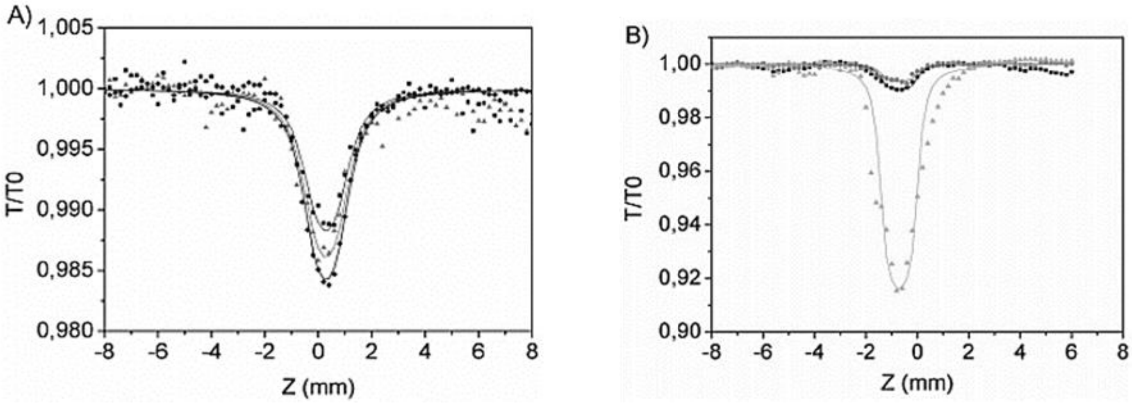


Figure (8) (A) *Z*-scans of 50 mM Acetonide-G1-Pt at 740 nm using various pulse repetition frequencies: 9 kHz (squares), 20 kHz (triangles), 100 kHz (diamonds). (B) *Z*-scan of selected Pt acetylides at 720 nm excitation wavelength and 4.75 MHz pulse repetition frequency: Pt1 (100 mM, diamonds), Acetonide-G2-Pt (30 mM, squares), and Acetonide-G4-Pt (30 mM, triangles).

3- Conclusion

Ru(II) and Pt(II)-acetylide 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 of these hyper molecules has been obtained at a single wavelength, obfuscating structure–property relationship development. Ru(II) and Pt(II)-acetylide dendrimers have among the largest two-photon absorption cross-sections. The ESA of the chromophore is greatly improved with this type of molecules.

4- Recommendations

A rapid increase of importance in the chemistry of Ru(II) and Pt(II)-acetylide dendrimers has been observed since the first dendrimers were prepared. These materials are designed to have a high transmission for low-intensity light and to significantly reduce the transmission of high-intensity light to energy levels. So the author suggest that many studies should be done in this field.

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