Dendron Decorated Platinum(II) Acetylides for Optical Power Limiting

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ABSTRACT: The effect of dendritic substituents on a nonlinear optical chromophore for optical power limiting (OPL) has been investigated. Synthesis and characterization of bis((4-(phenylethynyl)phenyl)ethynyl)bis(tributylphosphine)platinum(II) with dendritic end groups are described. Polyester dendrimers up to the fourth generation were grown divergently using the anhydride of 2,2-bis(methylol)propionic acid (bis-MPA). The introduction of the dendritic moieties onto the NLO chromophore enables further processing of the materials using polymeric and related techniques. OPL measurements performed at 532, 580, and 630 nm show that the OPL properties improve with increasing size of the dendritic substituent. It is also shown that the addition of the dendrons increase the OPL as compared to the nondecorated bis((4-(phenylethynyl)phenyl)ethynyl)bis(tributylphosphine)platinum(II). By use of femtosecond *z*-scan measurements carried out at different pulse-repetition frequencies, it is shown that the two-photon absorption cross section is ∼10 GM. Using pulse repetition frequencies (100 kHz−4.75 MHz) so that the time between the pulses is comparable with the triplet excited lifetime, the *z*-scans become dominated by excited-state absorption of excited triplet states.

Introduction

Because of the rapid development of new lasers with shorter pulses, higher peak intensities, and tunable wavelengths, there is a demand for materials to protect optical sensors against high-energy light. Lasers are used for example in atmospheric chemical sensing, range measurements, and active illumination imaging. To protect against laser light, optical power limiting (OPL) materials are being developed.[1,2] 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 where no damage on the protected object is observed. Materials considered for OPL are often nonlinear optical[3−7] (NLO) organic chromophores. Such chromophores[8−10] are generally highly conjugated, heterocyclic compounds and often coordinated to a metal. Examples of some chromophores used for OPL and other NLO applications are substituted thiophenes,[11−15] porphyrins,[16−20] and metal-coordinated phenylacetylenes such as Pt acetylides.[5,21−24] Synthetic, spectroscopic, and theoretical evaluations of the design of the chromophores and the mechanisms involved have been conducted.[15,25−28] The NLO mechanisms for OPL can be two-photon absorption (TPA) together with excited-state absorption (ESA).[1,7] Also, other mechanisms such as nonlinear refraction and optically induced scattering could lead to OPL behavior. One approach to increase the OPL would be to control the intersystem crossing to triplet states and their pertinent lifetimes. Such engineering is possible using nanotechnology in terms of encapsulation of the dye, protecting it from quenching through collision with quenchers or other dye molecules.[29,30] A consequence of a longer lifetime of the excited state could be an enhanced ESA.

In this study the results of decorating OPL chromophores with dendritic substituents have been investigated. The research area of dendritic macromolecules has grown rapidly over the past two decades.[10,31−34] Dendrimers have a number of unique properties arising from the highly branched, well-defined structure. Some of their properties are increased solubility compared to their linear analogues[35,36] and high number of modifiable end groups.[37] Another interesting feature is the possibility to encapsulate molecules into the inner parts of the dendritic structure.[38] The encapsulation has been studied for a number of different applications, such as shape selective catalysis[39,40] and protection against quenching.[29,30,41−43] In addition, the large number of end groups give rise to a high degree of freedom in tailoring the properties of the dendrimers, such as solubility, hydrophobicity, and cross-linkability.[44−47]

If an NLO chromophore is encapsulated in a dendritic structure, the chemical stability might be improved by protection from the surrounding environment. Additionally, collision-induced quenching of excited states may decrease due to the shielding effect of the dendrons, leading to greater ESA and better OPL. Further, since aggregates can scatter light and result in poor linear transmission as well as a decrease of NLO properties,[15,48] aggregation of chromophores might be prevented with dendritic wedges. Moreover, dendritic substituents can allow further material processing using conventional polymer technology. As the future aim of this work is to prepare protective devices for optical sensors against lasers, a broadband OPL material operating in the whole visible wavelength region is required. To accomplish a broadband OPL device, it might be necessary to prepare a cocktail of different NLO precursors where the dendron decorated platinum(II) acetylide presented herein could be one of the ingredients.

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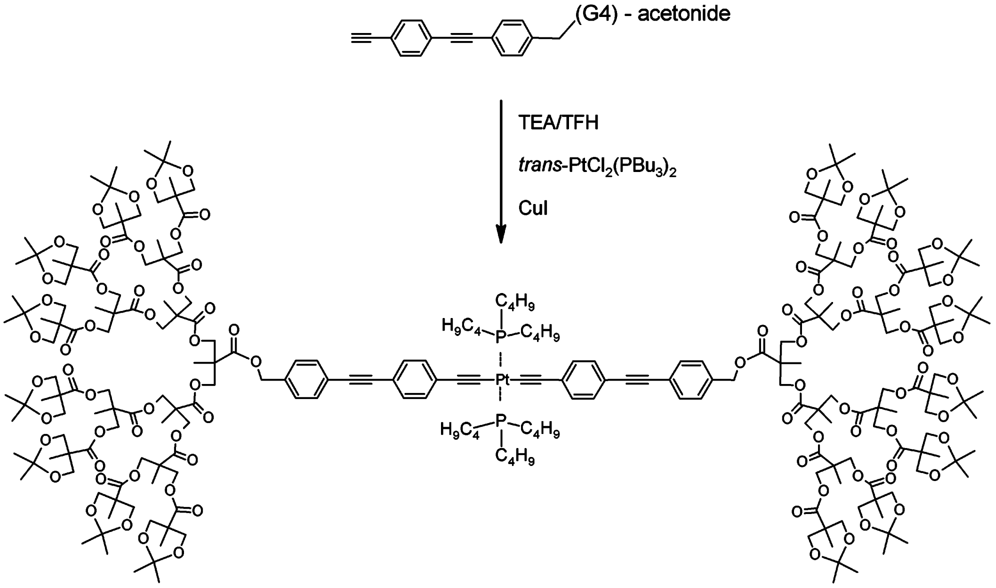
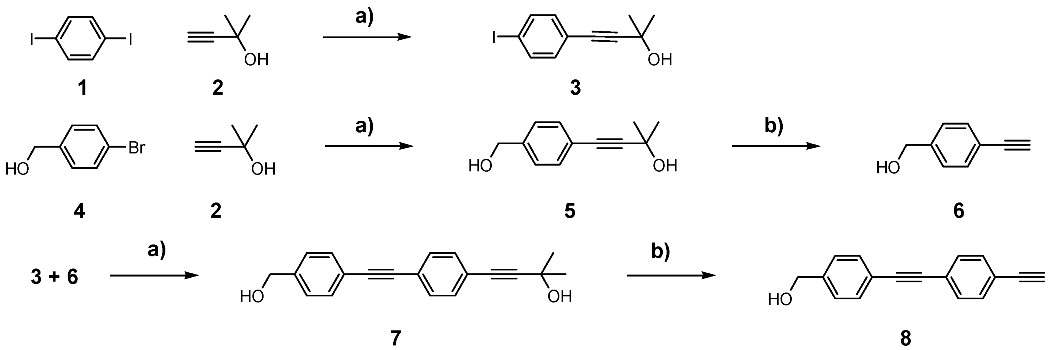
Scheme 1. Overview of Platinum(II) Dendron Synthesis



Scheme 2. Synthesis of the Arylalkynyl Ligand[a]



[a] (a) $PdCl_2(PPh_3)_2$, PPh_3, CuI, pyridine, TEA, 120 °C; (b) KOH, THF, Dean-Stark, 80 °C.

Earlier we reported on the influence of dendrimer substitution on the OPL and photophysical properties on thiophenes[49] and porphyrins.[50] Those results showed that for the porphyrins the larger dendrons affected the absorption and emission properties, while for the thiophenes the dendrons did not seem to affect the OPL to any larger extent. In the work presented here, we decorate Pt acetylide[5,21−24] compounds with dendrons of 2,2-bis(methylol)propionic acid (bis-MPA). Pt acetylides have proven to be NLO compounds that could have potential use as OPL materials.[51−56] The incorporation of the platinum nuclei into the structure promotes delocalization of π-electrons as well as intersystem crossing between the singlet and triplet states due to spin−orbit coupling. It has been shown that the Pt−ethynyl compound bis((4-(phenylethynyl)phenyl)ethynyl)bis(tributylphosphine)platinum(II) shows OPL by ESA from the triplet states over a wide part of the visible spectrum and also TPA at longer wavelengths.[51−56] Here we present results of the successful synthesis of dendrons attached to such OPL moieties and moreover investigate how the dendritic substituents affect the OPL properties of this organometallic chromophore. The dendrons (generation one to four) were grown by means of divergent synthesis utilizing the versatile chemistry of the acetonide protected bis-MPA anhydride.[57−62]

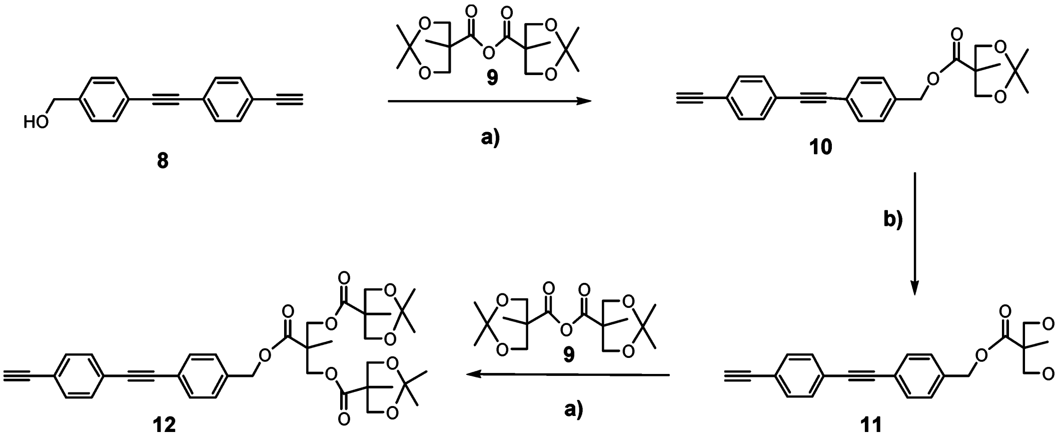
Results and Discussion

Synthesis. The dendron decorated Pt acetylides were synthesized by first preparing the arylalkynyl “arms” through Sonogashira coupling reactions,[63] followed by stepwise synthesis of the dendrons from the arylalkynyls in a divergent growth approach.[33] Finally, the dendron decorated arylalkynes were coupled to the platinum core (Scheme 1).

The 1,4-diiodobenzene **1** was first monosubstituted with a protected alkyne **2** to yield **3** (Scheme 2).[64,65] This reaction was performed using a palladium(II)- and copper(I)-catalyzed Sonogashira coupling reaction in pyridine and triethylamine (TEA). Then, 4-bromobenzyl alcohol **4** was coupled with the protected alkyne **2** using similar reaction conditions. The resulting protected alkynylbenzyl alcohol **5** was deprotected under basic (KOH) conditions,[66] activating the alkyne for further Sonogashira couplings. 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”, incorporating two aromatic rings and two alkynes. Subsequently, the protected terminal alkyne on **7** was deprotected to render coupling with platinum(II) possible. After each reaction step medium-pressure liquid chromatography (MPLC) on silica gel was performed to purify the products. The deprotection of the alkyne had to be conducted before the growth of the dendrons to avoid the hydroxyl of the protecting group to attach to the dendrons.

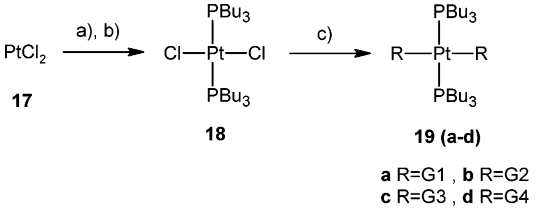
The first generation dendron **10** was grown from the benzyl alcohol **8** utilizing the anhydride of the acetonide protected bis-MPA **9** (Scheme 3).[57−60] The reaction was carried out in pyridine and dichloromethane using 4-(dimethylamino)pyridine (DMAP) as catalyst. The acetonide protecting groups were removed by an acid-catalyzed reaction in methanol using

Scheme 3. Synthesis of Dendrons[a]



[a] (a)pyridine, DMAP, RT; (b) MeOH, THF, DOWEX-resin.

Scheme 4. Synthesis of Dendritic Alkynyl Pt(II) Compounds 19a−d[a]



[a] (a) PBu$_3$ (2 equiv), H$_2$O 80 °C; (b) heat 15 min; (c) TEA, THF, CuI, 60 °C for 5 min.

DOWEX-50-X2 resin.[67] The resulting hydroxy-functional first-generation dendron **11** was then coupled with the anhydride **9** again to yield the second-generation dendron **12**. Higher generations were achieved by repetitive acidic deprotections and additions with the anhydride **9**.

trans-PtCl$_2$(PBu$_3$)$_2$ (**18**) was synthesized by stirring PtCl$_2$ (**17**) 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 4). The crude product was melted and converted to the trans isomer **18**[68] and purified by flash chromatography over silica. The synthesis of the dendron decorated Pt acetylide compounds **19a**−**d** was carried out by a Sonogashira-type coupling reaction of the suitable decorated arylalkynyl ligands (**10**, **12**, **14**, **16**) to PtCl$_2$(PBu$_3$)$_2$ with CuI as catalyst. The reaction was carried out in TEA and THF and by immediately heating the solution to 60 °C for 5 min. Compounds **19a**−**d** were obtained in excellent yields, above 88% relative to Pt compound.

For a comparison, bis((4-(phenylethynyl)phenyl)ethynyl)bis-(tributylphosphine)platinum(II) (Pt−ethynyl) without dendrons was synthesized according to a similar procedure.

Molecular weights were measured by SEC utilizing both universal calibration and conventional calibration using polystyrene standards (Table 1). There is a slight difference between the molecular weights and polydispersities obtained by the different methods. It has also been found earlier for dendron decorated thiophenes with similar structure that the SEC results deviate in this manner even though the thiophenes were found to be monodisperse by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF).[49]

MALDI-TOF analysis was also utilized to characterize the molecules synthesized in this study. However, extensive fragmentation of the samples was observed which made the interpretation very uncertain.

Optical Characterization. The absorption measurements were performed in tetrahydrofuran (THF) at a concentration of 10 μM. The spectra showed no differences for the different sizes of the dendrons attached. One of the obtained spectra is shown in Figure 1. The spectrum shows two absorption bands: one at 304 nm and a larger peak at 357 nm.

The OPL properties were measured at three different wavelengths: 532, 580, and 630 nm. The measurements were performed in THF at a concentration of 30 mM. The overall transmission (UV−vis spectroscopy) at these wavelengths and this concentration is >90% for all samples (including reflections of the glass−air interfaces). The high transmission at low intensities is appropriate for OPL since the concentration of the dye can be made higher, and most likely this will lead to better limiting properties. Representative OPL curves for a series of samples are shown in Figure 2, where the output energy is plotted as a function of the input energy when focusing through the sample.[70,71] The plots display a typical OPL curvature where the output energy levels off at higher input energies because of the NLO properties of the material. At input energies above 50−100 μJ the output energy is constant; i.e., the clamping level is reached. The behavior was similar for all the samples at the three wavelengths measured. The output intensities at the clamping level for all the samples are summarized in Table 2. A general trend is that the higher the generation of the dendron the lower is the clamping level. It is believed that the larger dendrons provide more efficient shielding of the dye moiety, and hence less quenching will occur. Accordingly, the lifetimes of the excited states should be increased and give rise to more efficient ESA. Further photophysical characterization supported this finding, and an important oxygen quenching effect was revealed as well as important concentration and size effects. Specifically, the larger dendron decorated variants spontaneously expelled oxygen from the solvent and prevented diminished oxygen quenching. Moreover, the larger dendrons acted as “molecular bumpers” to decrease the triplet−triplet annihilation recombination rate, leading to longer decay times for the triplets of the larger dendron decorated compounds in oxygen-evacuated samples.[72] Thus, the shielding may prevent aggregation of the dyes and thereby increase the NLO absorption of the chromophore. As mentioned in the Introduction, it has been shown that both TPA and ESA contribute to OPL for Pt(II)-acetylides.[5,21,22,51−56]

At all the wavelengths the sample without dendritic substitution (Pt−ethynyl) is the least efficient. In addition to an effect of increased ligand size, 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

Table 1. Molecular Weights of Dendron Decorated Platinum(II) Acetylides

compound	MW[a] (g/mol)	M_n[b] (g/mol)	PDI[b]	M_n[c] (g/mol)	PDI[c]
acetonide-G1-Pt	1375	1400	1.09	1400	1.01
acetonide-G2-Pt	1919	2000	1.07	2100	1.01
acetonide-G3-Pt	3008	3700	1.06	3100	1.02
acetonide-G4-Pt	5187	6800	1.04	4900	1.01

[a] Theoretical molecular weight. [b] SEC with universal calibration. [c] SEC with conventional calibration using polystyrene standards.

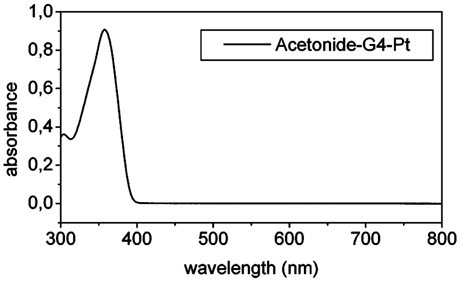


Figure 1. Absorption spectrum of Acetonide-G4-Pt, 10 μM in THF.

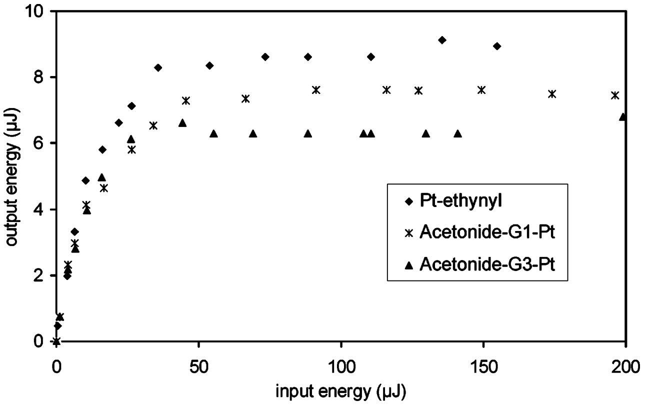


Figure 2. OPL for Pt-ethynyl, Acetonide-G1-Pt, and Acetonide-G3-Pt, in THF (30 mM) at 532 nm.

Table 2. Clamping Levels at Different Wavelengths

compound	clamping (532 nm) (μJ)	clamping (580 nm) (μJ)	clamping (630 nm) (μJ)
Pt−ethynyl	9.0	9.5	18.4
acetonide-G1-Pt	7.6	7.5	12.7
acetonide-G2-Pt	7.1	7.2	11.9
acetonide-G3-Pt	6.3	6.3	10.2
acetonide-G4-Pt	6.6	6.2	9.9

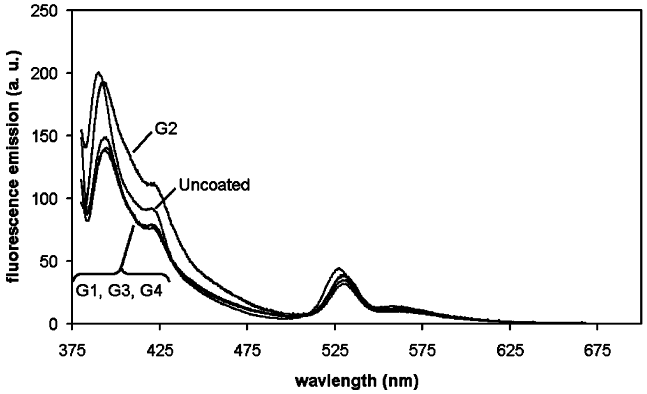


Figure 3. Steady-state fluorescence emission in THF at 10 μM (excitation 375 nm).

of the ester groups.[15,25,26] *Z*-scan measurements have been performed between 9 kHz and 76 MHz, where a response below 100 kHz pulse repetition rate is believed to originate in "instantaneous" TPA, whereas at higher frequencies the ESA and thermal effects should be the dominant factor to the NLO response. At the very low frequency, there was no prominent difference between the nondecorated Pt−ethynyl and the dendron decorated platinum(II) acetylides. However, above ~1 MHz there was an essential difference between the nondecorated and dendron decorated chromophores (to be further discussed below). At intermediate pulse frequencies (say 100 kHz to 5 MHz) the time between the pulses become comparable to the triplet excited state lifetime. This indicates that the dendritic substituents should have a shielding effect on the chromophore, leading to longer lifetimes of the excited states and accordingly a stronger ESA.

It is not straightforward to compare the OPL results with those reported by other research groups since the optical setups are different, and the data are acquired at various concentrations and wavelengths. Moreover, since ESA is present, the laser pulse time and pulse repetition frequency are decisive factors, which can differ between different laboratories. It may be noted that the aim of this study was not to optimize the OPL response of the material but instead to investigate the influence of the dendrons on the chromophore activity. However, the performance can be compared to the results reported by Shirk et al.,[69] who obtained 0.2 μJ output energy at a pulse of 20 μJ input energy for the Pb−tetrakis(cumylphenoxy)phthalocyanine in chloroform (0.43 mM) with a similar instrument setup. Although such an OPL result is better than for the dendron decorated Pt(II)-acetylides presented here, the transmission of the Pb−phthalocyanine sample was significantly lower (68%) as compared to our samples at the particular laser wavelength.

Luminescence studies were also performed, and fluorescence spectra for 10 μM samples in THF are shown in Figure 3. 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 have basically the same shape. It can be seen that the nondecorated platinum(II) acetylide (Pt−ethynyl) shows a small blue shift of about 3.5 nm for the entire emission. This is probably an effect of the benzyl ester groups interacting with the conjugated system. This blue shift shows that there is a photophysical difference between the nondecorated and the decorated chromophores, which could be the reason why the dendron decorated platinum(II) acetylides have improved OPL properties. It can also be seen that the nondecorated Pt−ethynyl and the Acetonide-G2-Pt show slightly higher emission levels. This we believe is mainly an effect of differences in concentration stemming from the preparation of the solutions. The emission bands around 400 nm originates from fluorescence of the S_1 state. The associated decay time was fast (multicomponent decay with times <~1 ns). The emission around 550 nm is phosphorescence from the triplet states. At low concentration the decay time of the triplet phosphorescence was ~150−200 ns due to quenching of triplet states by oxygen in the solvent. Thus, a considerably longer decay time (~150−300 μs) was measured in oxygen-evacuated samples or in samples with high generation (G2−G4) dendritic substituents at high concentrations. The results of more detailed time-resolved photophysical experiments will appear elsewhere.[72]

It was noted that the presence of the long-lived triplets, present in the Pt acetylides with high generatinon (G2−G4) dendritic

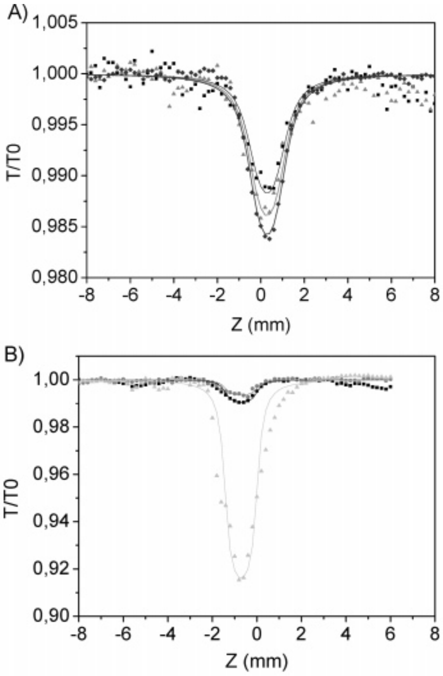


Figure 4. (A) *Z*-scans of 50 mM Acetonide-G1-Pt at 740 nm using various pulse repetition frequencies: 9 kHz (squares), 20 kHz (triangles), 100 kHz (diamonds). (B) *Z*-scan of selected Pt acetylides at 720 nm excitation wavelength and 4.75 MHz pulse repetition frequency: Pt1 (100 mM, diamonds), Acetonide-G2-Pt (30 mM, squares), and Acetonide-G4-Pt (30 mM, triangles).

substituents, considerably enhanced the triplet phosphorescence. The long-lived triplets had an impact not only on the OPL measurements but also on *z*-scans using various pulse repetition rates. Using the output of a femtosecond Ti:sapphire laser operating at 76 MHz in the wavelength range 720−740 nm and a pulse-picker operating at various pulse repetition frequencies between 9 kHz and 4.75 MHz, it was possible to determine the "instantaneous" two-photon absorption cross section and vary the efficient contribution from excited-state absorption in the *z*-scans. The results of two experiments are shown in Figure 4.

In panel A, the pulse repetition frequency was varied for a sample of Acetonide-G1-Pt from 9 to 100 kHz. At these low pulse repetition frequencies there is a relatively long time between the pulses, and the *z*-scan is dominated by contribution from instantaneous two-photon absorption. The solid lines are fits assuming pure instantaneous two-photon absorption corresponding to the cross sections 8.9, 10.6, and 12.0 GM for the 9, 20, and 100 kHz data, respectively. In panel B a considerably higher pulse repetition frequency was used (4.75 MHz), allowing successive pulses in the pulse train to excite triplet states that have not been depopulated. Thus, panel B shows a dramatic increase in the *z*-scan response going from the nondecorated Pt acetylide to Acetonide-G2-Pt and Acetonide-G4-Pt (the concentration of the nondecorated variant is more than 3 times higher). Apparently, the *z*-scan of the bare Pt−ethynyl at a high pulse repetition frequency is weak since the triplet states are strongly quenched. The dendron decorated Pt−ethynyls, on the other hand, 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. According to the *z*-scan, the two-photon absorption cross section is determined to be ∼10 GM (Gøppert−Mayer; 1 GM = 10^{-50} cm^4/(photon molecule)) at the low pulse repetition limit (such as in panel A). Fitting the data as in panel B according to a pure "instantaneous" two-photon absorption model gives erroneous results. Specifically, the solid lines following the *z*-scan traces in panel B are for the apparent TPA cross-section values 215, 16, and 7 GM for Acetonide-G4-Pt, Acetonide-G2-Pt, and nondecorated Pt acetylide, respectively. We note that the low pulse repetition frequency values we obtained are considerably lower than the values reported by Staromlynska et al. for the similar nondecorated compound[52] using picosecond excitation pulses. The results of a more detailed study on nonlinear absorption and excited-state luminescence of related compounds are underway.[73]

Conclusions

The nonlinear optical chromophore bis((4-(phenylethynyl)-phenyl)ethynyl)bis(tributylphosphine)platinum(II) was prepared and decorated with dendritic substituents up to the fourth generation. The chromophore itself has great potential as an OPL substance. By attaching dendritic substituents to the chromophore, the OPL properties can be enhanced. Furthermore, lower clamping levels can be reached by increasing the size of the dendritic wedges. According to *z*-scan measurements, the ESA of the chromophore is greatly improved with dendritic substituents. The improved OPL properties are suggested to originate from the shielding effect of the dendritic surrounding which offers the chromophore site isolation, in turn resulting in longer lifetimes of the excited triplet states. The instantaneous two-photon absorption cross section was obtained from low-power femtosecond *z*-scans at low pulse repetition frequency, determined to be ∼10 GM.

Experimental Section

Methods. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DRX 400 MHz. ^{1}H and ^{13}C chemical shifts are reported relative to TMS as internal reference, while ^{31}P chemical shifts are given relative to external 0.1 M $P(C_6H_5)_3$ in $CDCl_3$ with $\delta = -4.89$, which corresponds to $\delta = 0$ for 85% H_3PO_4. $CDCl_3$ was used as solvent for the NMR measurements. Size exclusion chromatography (SEC) was performed using a TDA model 301 equipped with one or two GMH_{HR}-M columns with TSK-gel (Tosoh Biosep), a VE 5200 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser, all of which were supplied by Viscotek Corp. THF (1.0 mL min^{-1}) was used as the mobile phase. The SEC apparatus was calibrated by universal calibration with linear polystyrenes (PS), 11 narrow standards (M_p 0.580−185 kg mol^{-1}), and one broad standard. Corrections for flow rate fluctuations were made by using the DRI signal of the injected THF as an internal standard. The right angle laser light scattering (RALLS) was calibrated with linear PS standards ($M_w = 90.1$ kg mol^{-1}, PDI = 1.04, concentration = 1.00 mg/mL; $M_w = 250$ kg mol^{-1}, PDI = 2.5, concentration = 1.00 mg/mL). The columns and all detectors were thermostated to 35 °C. Viscotek Trisec 2000 version 1.0.2 software was used to process data. Absorption measurements were performed at room temperature with a WPA S2000 Lightwave UV/vis diode-array spectrophotometer. MALDI analysis was performed using a Bruker Reflex III MALDI-MS instrument, equipped with a N_2 laser, 337 nm (Bruker Daltonik GmbH, Bremen, Germany). All mass spectra have been obtained in reflection mode. Calibration was performed in order to secure good mass accuracy. As for the samples, solutions of 2−5 mM in THF were prepared. The matrices utilized were either *trans*-3-indoleacrylic acid (t3iA) or 2,5-dihydroxybenzoic acid (DHB). Matrix solutions were prepared as 0.1 M solutions in THF. The samples were prepared both as sample-matrix solutions and as sample-matrix-NaTFA- or LiTFA solutions, employing 0.1 M of either NaTFA or LiTFA solution in THF. The preparation protocol included mixing of 0.5−1.0 μL of sample with 10 μL of matrix and/or 0.5−1.0 μL of the cationization agent. Then 0.2−0.4 μL of the mixture was spotted on the MALDI target and was left to crystallize at room temperature. Normally, 50 pulses were acquired for each sample. To achieve good mass accuracy and resolution, the analysis was performed at the laser threshold of each individual matrix/sample combination. The sample molecules were also analyzed with the above-stated instrumental parameters in laser desorption mode (without any matrix being present in the preparation). Continuous wave fluorescense spectra were recorded using a Hitachi F-4500 spectrometer equipped with a Xe-lamp. The optical limiting experiments were performed in a f/5 setup[70,71] with a frequency-doubled Nd:YAG laser operating at 10 Hz, delivering 5 ns pulses. 2 mm quartz cells were used for both linear and nonlinear transmission experiments.

Z-scans were recorded with a MIRA 900 with a Coherent 9200 Pulse-Picker. A Newport M-ILS200CC linear translation stage controlled by a Newport ESP300 universal motor controller was used to perform the *z*-scan movement. The transmitted intensity was measured using a calibrated Newport power meter model 2930-C and the 918-SL or 918-UV detectors. Samples were made using tetrahydrofuran as solvent. A wavelength of 720 or 740 nm was used. A 100 FL lens was used to focus a 10 mm top-hat beam to a minimum spot size (radius) of $w_0 = 7.2\ \mu$m, giving a Rayleigh length of 0.23 mm. The power from the laser was in the range 3.3−1.9 nJ/pulse, and experiments were made at different pulse-repetition frequency. The typical peak on-axis intensity (using a Gaussian temporal profile with fwhm pulse length of 180 fs) was 21 GW/cm^2 (3.3 nJ pulse energy).

4-(4-Methyl alcohol phenyl)-2-methyl-3-butyne-2-ol (5). 4-Bromobenzyl alcohol, **4** (8.00 g, 42,8 mmol), was dissolved in 50 mL of pyridine/triethylamine (TEA) (50/50). To the solution were added PPh_3 (550 mg, 2.10 mmol), CuI (200 mg, 1.05 mmol), and $PdCl_2(PPh_3)_2$ (300 mg, 0.43 mmol). 2-Methyl-3-butyne-2-ol, **2** (7.20 g, 85.60 mmol, 2 equiv), was then added dropwise at 120 °C, and the solution was stirred for 4−5 h. The reaction was followed by TLC in 40/60 (ethyl acetate/hexane). When complete, the solvents were evaporated, and the crude reaction mixture was redissolved in ethyl acetate (EtOAc). The solution was extracted with $NaHSO_4$ (10%), dried with $MgSO_4$, and then purified by medium-pressure liquid chromatography (MPLC) on silica using 20/80 EtOAc/hexane gradually increasing to 80/20 EtOAc/hexane. The product was obtained as a white solid in a 75% yield.^{1}H NMR (acetone-d_6): δ 1.53 (s, 6H, $-CH_3$), 4.30 (t, 1H, $J = 6.0$ Hz, $-CH_2-OH$), 4.44 (s, 1H, $-C-OH$), 4.63 (d, 2H, $J = 6.0$ Hz, $-CH_2-$), and 7.34 (s, 4H, Ar$-H$). ^{13}C NMR (acetone-d_6): δ 33.22 ($-CH_3$), 65.38 ($-C-(CH_3)_2$), 66.27 ($-CH_2-$), 82.83 ($-Ar-C\equiv C-$), 96.78 ($-Ar-C\equiv C-$), 123.73 (Ar$C-C\equiv C$), 128.47 (*m*-Ar*C*), 133.19 (*o*-Ar*C*), and 144.71 (*p*-Ar*C*).

4-Ethynylbenzyl Alcohol (6). 4-(4-Methyl alcohol phenyl)-2-methyl-3-butyne-2-ol, **5** (3.30 g, 17.4 mmol), was dissolved in THF (300 mL). Ground KOH (3.30 g, 59 mmol) was added, and the reaction was stirred at reflux using a Dean-Stark apparatus (80 °C).[66] The reaction was monitored by TLC using 40/60 EtOAc/hexane. When complete, the THF was evaporated, and the crude reaction mixture was redissolved in dichloromethane, extracted with water, and dried with $MgSO_4$. The crude product was purified using MPLC on silica using hexane gradually increasing to 20/80 EtOAc/hexane, yielding 50% of white solid. ^{1}H NMR ($CDCl_3$): δ 2.30 (t, 1H, $-CH_2-OH$), 3.06 (s, 1H, $-C\equiv C-H$), 4.61 (s, 2H, $-CH_2-$), 7.26 (d, 2H, $J = 8.0$ Hz, *m*-Ar*H*), and 7.44 (d, 2H, $J = 8.0$ Hz, *o*-Ar*H*). ^{13}C NMR ($CDCl_3$): δ 64.77 ($-CH_2-$), 77.35 ($-Ar-C\equiv C-$), 83.58 ($-Ar-C\equiv C-$), 121.30 (*p*-Ar*C*), 126.81 (*o*-Ar*C*), 132.36 (*m*-Ar*C*), and 141.64 (Ar$C-CH_2-$).

4-(4-Iodophenyl)-2-methyl-3-butyne-2-ol (3).[64,65] To a stirred solution of 25 mL of pyridine and 25 mL of triethylamine at 120 °C was added *p*-diiodobenzene, **1** (10 g, 30 mmol), $PdCl_2P(Ph_3)_2$ (50 mg, 70 μmol), PPh_3 (65 mg, 0.24 mmol), and CuI (50 mg, 0.26 mmol). 2-Methl-3-butyne-2-ol, **2** (2.5 g, 30 mmol), was added dropwise at which the color changed from deep orange to pale yellow. The reaction was refluxed for 3 h and followed by TLC. The solution was allowed to cool and was poured into 150 mL of cold 0.5 M HCl. The precipitate was collected by filtration, washed with water, and allowed to dry. The product was purified with MPLC eluting with hexane, gradually increasing to 10/90 EtOAc/hexane, followed by recrystallization from hexane. The product was obtained as a white fluffy solid in a 45% yield. ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 6H, $-CH_3$), 2.09 (s, 1H, $-OH$), 7.12 (d, 2H, $J = 8.0$ Hz, *o*-Ar*H*), and 7.63 (d, 2H, $J = 8.0$ Hz, *m*-Ar*H*). ^{13}C NMR ($CDCl_3$): δ 31.52 ($-CH_3-$), 65.76 ($-C-(CH_3)_2$), 81.38 ($-Ar-C\equiv C-$), 94.24 ($-Ar-C\equiv C-$), 95.30 (*p*-Ar*C*), 122.39 (Ar$C-C\equiv C-$), 133.39 (*o*-Ar*C*), and 137.54 (*m*-Ar*C*).

(4-(4-(4-Methyl alcohol phenylethynyl)phenylethynyl))-2-methyl-3-butyne-2-ol (7). 4-(4-Iodophenyl)-2-methyl-3-butyne-2-ol, **3** (4.39 g, 15.34 mmol), was dissolved in 100 mL of pyridine/TEA (50/50) together with $PdCl_2P(Ph_3)_2$ (200 mg, 0.28 mmol), PPh_3 (240 mg, 0.89 mmol), and CuI (80 mg, 0.42 mmol) at 120 °C. 4-Ethynylbenzyl alcohol, **6** (2.43 g, 19.01 mmol), was dissolved in 5 mL of pyridine/TEA (50/50) and added dropwise. The reaction was then refluxed for 2 h and checked by TLC in 30/70 EtOAc/hexane. After completion the solvents were evaporated, and the crude product was redissolved in ethyl acetate and extracted four times with $NaHSO_4$ (10%). The crude product was purified using MPLC on silica using 20/80 EtOAc/hexane, gradually increasing to 60/40 EtOAc/hexane. The product was obtained as a white solid in 70% yield. ^{1}H NMR (acetone-d_6): δ 1.50 (s, 6H, $-CH_3$), 4.28 (s, 1H, $-C-OH$), 4.44 (s, 1H, $-CH_2-OH$), 4.63 (s, 2H, $-CH_2$), 7.36 (d, 4H, $J = 8.4$ Hz, Ar*H*), and 7.46 (d, 4H, Ar*H*). ^{13}C NMR (acetone-d_6): δ 31.94 ($-CH_3$), 64.22 ($-C-(CH_3)_2$), 65.16 ($-CH_2-$), 81.22 ($-Ar-C\equiv C-Ar-C\equiv C-$), 89.13 ($-Ar-C\equiv C-Ar-C\equiv C-$), 91.87 ($-Ar-C\equiv C-Ar-C\equiv C-$), 98.18 ($-Ar-C\equiv C-Ar-C\equiv C-$), 122.05 (Ar*C*), 123.79 Ar*C*), 124.21 (Ar*C*), 127.47 (Ar*C*), 132.20 (Ar*C*), 132.30 (Ar*C*), 132.38(Ar*C*), and 144.40 ($-CH_2-$(*p*-Ar*C*)$-C\equiv C-$Ar).

4-(4-Methyl alcohol phenylethynyl)phenylethynyl (8). (4-(4-(4-Methyl alcohol phenylethynyl)phenylethynyl))-2-methyl-3-butyne-2-ol, **7** (3.32 g, 10.7 mmol), was dissolved in THF (300 mL). Ground KOH (3.3 g, 59 mmol) was added and followed by reaction at reflux using a Dean-Stark apparatus (80 °C).[66] The reaction was monitored by TLC (40/60 EtOAc/hexane). When the reaction was complete, the THF was evaporated and the crude reaction mixture was redissolved in dichloromethane, extracted with water, and dried with $MgSO_4$. The crude product was purified using MPLC eluting with hexane, gradually increasing to 20/80 EtOAc/hexane yielding 40% of white solid. ^{1}H NMR (DMSO-d_6): δ 1.74 (s, 1H, $-OH$), 3.18 (s, 1H, $-C\equiv C-H$), 4.72 (s, 2H, $-CH_2$), 7.35 (d, 4H, $J = 8.0$ Hz, Ar*H*), 7.47 (s, 8H, *ArH*), and 7.52 (d, 4H, $J = 8.0$ Hz, Ar*H*). ^{13}C NMR (DMSO-d_6): δ 65.08 ($-CH_2-$), 79.04 ($-Ar-C\equiv C-Ar-C\equiv C-$), 83.41 ($-Ar-C\equiv C-Ar-C\equiv C-$), 89.04 ($-Ar-C\equiv C-Ar-C\equiv C-$), 91.34 ($-Ar-C\equiv C-Ar-C\equiv C-$), 122.03 (Ar*C*), 122.30 Ar*C*), 123.87 (Ar*C*), 126.98 (Ar*C*), 131.60 ($-$Ar*C*), 131.96 (Ar*C*), 132.21 (Ar*C*), and 141.44 ($-CH_2-$(*p*-Ar*C*)$-C\equiv C-$Ar).

General Procedure of Anhydride Coupling Step Exemplified with 4-(4-(Acetonide-G1)benzylethynyl)phenylethynyl (10).[58,59] 4-(4-Methyl alcohol phenylethynyl)phenylethynyl, **8** (1.00 g, 4.31 mmol), and DMAP (118 mg, 0.97 mmol, 0.225 equiv) were dissolved in pyridine (15 mL). Acetonide-2,2-bis(methoxy)propanoic anhydride, **9** (2.13 g, 6.47 mmol, 1.5 equiv), was dissolved in 5 mL of dichloromethane and then added to the reaction mixture. The reaction was left overnight at RT and checked with NMR. The residual anhydride was quenched by reaction with ∼10 mL of water under rigorous stirring for a couple of hours. The reaction mixture was then taken up into ∼100 mL of dichloromethane and extracted 3 times with 50 mL of $NaHSO_4$ (10%), 3 times with 50 mL of $NaHCO_3$ (10%), and finally 1 time with (50 mL) brine. The organic layer was dried with $MgSO_4$, the solvent was evaporated, and the crude product was purified by MPLC using hexane gradually increasing to 10/90 EtOAc/hexane. The product was obtained as a white solid of 82% yield. ^{1}H NMR ($CDCl_3$): δ 1.19 (s, 3H, $-CH_3$), 1.39 (s, 3H, $-O-C-CH_3$), 1.44 (s, 3H, $-O-C-CH_3$), 3.18 (s, 1H, $-C\equiv C-H$), 3.67 (d, 2H, $J = 12.0$ Hz, $-CH_2-O-$), 4.23 (d, 2H, $J = 12.0$ Hz, $-CH_2-O-$), 5.21 (s, 2H, $-Ar-CH_2-$), 7.34 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.47 (s, 4H, *ArH*), and 7.51 (d, 2H, $J = 8.0$ Hz, Ar*H*). ^{13}C NMR ($CDCl_3$): δ 18.68 ($-CH_3$), 22.41 ($-O-C-CH_3$), 25.18 ($-O-C-CH_3$), 42.15 ($-C-$), 66.09 ($-Ar-CH_2-$), 66.21 ($-CH_2-O-$), 79.10 ($-Ar-C\equiv C-Ar-C\equiv C-$), 83.39 ($-Ar-C\equiv C-Ar-C\equiv C-$), 89.37 ($-Ar-C\equiv C-Ar-C\equiv C-$), 91.11 ($-Ar-C\equiv C-Ar-C\equiv C-$), 98.17 ($-O-C-CH_3$), 122.14 (Ar*C*), 122.91 Ar*C*), 123.77 (Ar*C*), 127.86 (Ar*C*), 131.63 (−Ar*C*), 131.94 (Ar*C*), 132.22 (Ar*C*), 136.57 (−CH$_2$−(*p*-Ar*C*)-C≡C−Ar), and 174.16 (*C*═O).

General Procedure for the Deprotection of Acetonides Exemplified with 4-(4-(Hydroxy-G1)benzylethynyl)phenylethynyl (11).[67] 4-(4-(Acetonide-G1)-benzylethynyl)phenylethynyl, **10** (1.44 g, 3.71 mmol), was dissolved in methanol/THF (50 mL/50 mL), and a spoon of DOWEX-50-X2-resin was added. The reaction was performed at 50 °C and followed by TLC in 60/40 EtOAc/hexane. When complete, the DOWEX resin was removed by filtration and the solvents were evaporated. The product was obtained as a white solid in 97% yield. ^{1}H NMR (MeOD): *δ* 1.40 (s, 3H, −C*H*$_3$), 3.62 (s, 1H, −C≡C−*H*), 3.66 (d, 4H, *J* = 10.7 Hz, −C*H*$_2$−OH), 3.74 (d, 2H, *J* = 10.4 Hz, −CH$_2$−O*H*), 5.17 (s, 2H, −Ar−C*H*$_2$−), 7.40 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.45 (s, 4H, *ArH*), and 7.51 (d, 2H, *J* = 8.0 Hz, Ar*H*). ^{13}C NMR (MeOD): *δ* 17.60 (−*C*H$_3$), 51.94 (−*C*−), 66.13 (−*C*H$_2$−OH), 66.99 (−Ar−*C*H$_2$−), 80.88 (−Ar−C≡C−Ar−C≡*C*−), 84.16 (−Ar−C≡C−Ar−*C*≡C−), 90.04 (−Ar−C≡*C*−Ar−C≡C−), 92.05 (−Ar−*C*≡C−Ar−C≡C−), 123.99 (Ar*C*), 124.06 Ar*C*), 125.09 (Ar*C*), 129.16 (Ar*C*), 132.78 (−Ar*C*), 132.92 (Ar*C*), 133.36 (Ar*C*), 138.72 (−CH$_2$−(*p*-Ar*C*)-C≡C−Ar), and 176.61 (*C*═O).

4-(4-(Acetonide-G2)benzylethynyl)phenylethynyl (12). MPLC was performed eluting with hexane increasing the polarity to 20/80 EtOAc/hexane, yielding (97%) a white solid. ^{1}H NMR (CDCl$_3$): *δ* 1.10 (s, 6H, −C*H*$_3$), 1.31 (s, 3H, −C*H*$_3$), 1.34 (s, 6H, −O−C−C*H*$_3$), 1.41 (s, 6H, −O−C−C*H*$_3$), 3.18 (s, 1H, −C≡C−*H*), 3.59 (d, 4H, *J* = 12.0 Hz, second generation −C*H*$_2$−O−), 4.10 (d, 4H, *J* = 12.0 Hz, second generation −C*H*$_2$−O−), 4.34 (s, 4H, first generation −C*H*$_2$−O−), 5.16 (s, 2H, −Ar−C*H*$_2$−), 7.33 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.47 (s, 4H, *ArH*), and 7.51 (d, 2H, *J* = 8.0 Hz, Ar*H*). ^{13}C NMR (CDCl$_3$): *δ* 17.83 (first generation −*C*H$_3$), 18.59 (second generation −*C*H$_3$), 22.22 (−O−C−*C*H$_3$), 25.25 (−O−C−*C*H$_3$), 42.17 (second generation −*C*−), 47.00 (first generation −*C*−), 65.45 (first generation −*C*H$_2$−O−), 66.05 (second generation −*C*H$_2$−O−), 66.60 (−Ar−*C*H$_2$−), 79.13 (−Ar−C≡C−Ar−C≡*C*−), 83.35 (−Ar−C≡C−Ar−*C*≡C−), 89.54 (−Ar−C≡*C*−Ar−C≡C−), 93.46 (−Ar−*C*≡C−Ar−C≡C−), 98.24 (−O−*C*−CH$_3$), 122.17 (Ar*C*), 123.26 Ar*C*), 123.68 (Ar*C*), 128.32 (Ar*C*), 131.62 (−Ar*C*), 131.99 (Ar*C*), 132.21 (Ar*C*), 135.93 (−CH$_2$−(*p*-Ar*C*)−C≡C−Ar), 172.49 (first generation *C*═O), and 173.66 (second generation *C*═O).

4-(4-(Hydroxy-G2)benzylethynyl)phenylethynyl (13). 82% yield of a white solid. ^{1}H NMR (MeOD): *δ* 1.11 (s, 6H, −C*H*$_3$), 1.31 (s, 3H, −C*H*$_3$), 3.63 (s, 1H, −C≡C−*H*), 3.64 (m, 8H, −C*H*$_2$−OH), 4.31 (s, 4H, −C*H*$_2$−O−), 5.20 (s, 2H, −Ar−C*H*$_2$−), 7.41 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.46 (s, 4H, *ArH*), and 7.52 (d, 2H, *J* = 8.0 Hz, Ar*H*). ^{13}C NMR (MeOD): *δ* 17.28 (first generation −*C*H$_3$), 18.22 (second generation −*C*H$_3$), 47.93 (first generation −*C*−), 51.77 (second generation −*C*−), 65.81 (second generation −*C*H$_2$−OH), 66.42 (first generation −*C*H$_2$−O−), 67.49 (−Ar−*C*H$_2$−), 80.72 (−Ar−C≡C−Ar−C≡*C*−), 83.93 (−Ar−C≡C−Ar−*C*≡C−), 90.03 (−Ar−C≡*C*−Ar−C≡C−), 91.74 (−Ar−*C*≡C−Ar−C≡C−), 123.80 (Ar*C*), 124.20 Ar*C*), 124.79 (Ar*C*), 129.47 (Ar*C*), 132.58 (−Ar*C*), 132.83 (Ar*C*), 133.13 (Ar*C*), 137.87 (−CH$_2$−(*p*-Ar*C*)−C≡C-Ar), 174.23 (first generation *C*═O), and 175.92 (second generation *C*═O).

4-(4-(Acetonide-G3)benzylethynyl)phenylethynyl (14). MPLC was performed eluting with hexane increasing the polarity to 30/70 EtOAc/hexane, yielding (79%) a white solid. ^{1}H NMR (CDCl$_3$): *δ* 1.13 (s, 12H, −C*H*$_3$), 1.21 (s, 6H, −C*H*$_3$), 1.27 (s, 3H, −C*H*$_3$), 1.33 (s, 12H, −O−C−C*H*$_3$), 1.40 (s, 12H, −O−C−C*H*$_3$), 3.18 (s, 1H, −C≡C−*H*), 3.59 (d, 4H, *J* = 12.0 Hz, third generation −C*H*$_2$−O−), 4.11 (d, 4H, *J* = 12.0 Hz, third generation −C*H*$_2$−O−), 4.27 (m, 12H, first and second generation −C*H*$_2$−O−), 5.16 (s, 2H, −Ar−C*H*$_2$−), 7.34 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.46 (s, 4H, *ArH*), and 7.51 (d, 2H, *J* = 8.0 Hz, Ar*H*). ^{13}C NMR (CDCl$_3$): *δ* 17.71 (first and second generation −*C*H$_3$), 18.62 (third generation −*C*H$_3$), 22.19 (−O−C−*C*H$_3$), 25.27 (−O−C−*C*H$_3$), 42.15 (third generation −*C*−), 46.85 (first generation −*C*−), 46.96 (second generation −*C*−), 65.01 (first generation −*C*H$_2$−O−), 66.04 (second generation −*C*H$_2$−O−), 66.08 (third generation −*C*H$_2$−O−), 66.16 (−Ar−*C*H$_2$−), 79.14 (−Ar−C≡C−Ar−C≡*C*−), 83.33 (−Ar−C≡C−Ar−*C*≡C−), 89.62 (−Ar−C≡*C*−Ar−C≡C−), 95.27 (−Ar−*C*≡C−Ar−C≡C−), 98.21 (−O−*C*−CH$_3$), 122.17 (Ar*C*), 123.37 Ar*C*), 123.65 (Ar*C*), 128.55 (Ar*C*), 131.62 (−Ar*C*), 132.02 (Ar*C*), 132.18 (Ar*C*), 135.80 (−CH$_2$−(*p*-Ar*C*)−C≡C−Ar), 171.95 (second generation *C*═O), 172.00 (first generation *C*═O), and 173.59 (third generation *C*═O).

4-(4-(Hydroxy-G3)benzylethynyl)phenylethynyl (15). 94% yield of a white solid. ^{1}H NMR (DMSO-*d*$_6$): *δ* 1.01 (s, 12H, −C*H*$_3$), 1.12 (s, 6H, −C*H*$_3$), 1.22 (s, 3H, −C*H*$_3$), 3.35−3.50 (broad m, 16H, −C*H*$_2$−OH), 4.12 (m, 12H, first and second generation −C*H*$_2$−O−), 4.36 (s, 1H, −C≡C−*H*), 4.64 (t, 8H, *J* = 5.2 Hz, −CH$_2$−O*H*), 5.18 (s, 2H, −Ar−C*H*$_2$−), 7.42 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.53 (s, 4H, *ArH*), and 7.58 (d, 2H, *J* = 8.0 Hz, Ar*H*). ^{13}C NMR (DMSO-*d*$_6$): *δ* 16.56 (third generation −*C*H$_3$), 16.62 (second generation −*C*H$_3$), 16.76 (first generation −*C*H$_3$), 46.19 (first generation −*C*−), 46.23 (second generation −*C*−), 50.19 (third generation −*C*−), 63.59 (−*C*H$_2$−OH), 64.82 (−*C*H$_2$−O−), 65.09 (−*C*H$_2$−O−), 66.98 (−Ar−*C*H$_2$−), 78.98 (−Ar−C≡C−Ar−C≡*C*−), 83.35 (−Ar−C≡C−Ar−*C*≡C−), 88.92 (−Ar−C≡*C*−Ar−C≡C−), 91.84 (−Ar−*C*≡C−Ar−C≡C−), 123.54 (Ar*C*), 124.84 Ar*C*), 124.88 (Ar*C*), 128.04 (Ar*C*), 131.52 (−Ar*C*), 131.55 (Ar*C*), 131.94 (Ar*C*), 136.77 (−CH$_2$−(*p*-Ar*C*)-C≡C−Ar), 170.95 (second generation *C*═O), 171.74 (first generation *C*═O), and 174.62 (third generation *C*═O).

4-(4-(Acetonide-G4)benzylethynyl)phenylethynyl (16). MPLC was performed eluting with hexane increasing the polarity to 40/60 EtOAc/hexane, yielding (79%) a white solid. ^{1}H NMR (CDCl$_3$): *δ* 1.13 (s, 24H, −C*H*$_3$), 1.20 (s, 6H, −C*H*$_3$), 1.26 (s, 12H, −C*H*$_3$), 1.30 (s, 3H, −C*H*$_3$), 1.34 (s, 24H, −O−C−C*H*$_3$), 1.40 (s, 24H, −O−C−C*H*$_3$), 3.17 (s, 1H, −C≡C−*H*), 3.60 (d, 4H, *J* = 12.0 Hz, fourth generation −C*H*$_2$−O−), 4.12 (d, 4H, *J* = 12.0 Hz, fourth generation −C*H*$_2$−O−), 4.15−4.35 (broad m, 12H, first, second, and third generation −C*H*$_2$−O−), 5.16 (s, 2H, −Ar−C*H*$_2$−), 7.35 (d, 2H, *J* = 8.0 Hz, Ar*H*), 7.47 (s, 4H, *ArH*), and 7.52 (d, 2H, *J* = 8.0 Hz, Ar*H*). ^{13}C NMR (CDCl$_3$): *δ* 17.81 (first, second, and third generation −*C*H$_3$), 18.64 (third generation −*C*H$_3$), 22.25 (−O−C−*C*H$_3$), 25.28 (−O−C−*C*H$_3$), 42.16 (fourth generation −*C*−), 46.96 (first, second, and third generation −*C*−), 66.04 (−*C*H$_2$−O−), 64.95 (−*C*H$_2$−O−) 66.04 (−*C*H$_2$−O−), 66.10 (−*C*H$_2$−O−), 66.15 (−Ar−*C*H$_2$−), 78.72 (−Ar−C≡C−Ar−C≡*C*−), 81.24 (−Ar−C≡C−Ar−*C*≡C−), 90.96 (−Ar−C≡*C*−Ar−C≡C−), 92.51 (−Ar−*C*≡C−Ar−C≡C−), 98.22 (−O−*C*−CH$_3$), 122.75 (Ar*C*), 123.54 Ar*C*), 123.65 (Ar*C*), 128.44 (Ar*C*), 131.64 (−Ar*C*), 132.05 (Ar*C*), 132.23 (Ar*C*), 138.80 (−CH$_2$−(*p*-Ar*C*)−C≡C−Ar), 171.76 (*C*═O), 172.79 (*C*═O), 171.93(*C*═O) and 173.59 (fourth generation *C*═O).

***trans*-PtCl$_2$(P(*n*-Bu)$_3$)$_2$ (18).** PtCl$_2$ (1.00 g, 0.376 mmol) was mixed with 20 mL of water. Air was evacuated and argon atmosphere was introduced. Tributylphosphine (1.52 g, 0.752 mmol) was added, and the reaction was stirred at 80 °C for 8 h. The water phase was removed, and the crude oily product was dissolved in CHCl$_3$, dried over MgSO$_4$, filtered, and concentrated. The product contains both *cis*- and *trans*-PtCl$_2$(P(*n*-Bu)$_3$)$_2$. Heating the Pt salt for 15 min converts the cis-salt to trans-configuration. The final product was purified by MPLC eluting with heptane and gradually increasing the polarity to 10/90 EtOAc/heptane. The product was obtained as yellow crystals in 60% yield. ^{1}H NMR (CDCl$_3$): *δ* 0.92 (t, 18H, −C*H*$_3$), 1.45 (m, 12H, C*H*$_2$−CH$_3$), 1.54 (m, 12H, Pt−CH$_2$−C*H*$_2$), 1.84 (m, 12H, Pt−C*H*$_2$).

General Procedure for Coupling of Dendrons to Pt Exemplified by *trans*-Bis[2,2,5-trimethyl-[1,3]dioxane-5-carboxylic acid 4-(4-ethynylphenylethynyl)benzyl ester]bis(triphenylphosphine)-platinum(II), Acetonide-G1-Pt (19a). *trans*-PtCl$_2$(P(*n*-Bu)$_3$)$_2$, **18** (270 mg, 0.403 mmol), CuI (15 mg, 0.08 mmol), and 4-(4-(acetonide-G1)benzylethynyl)phenylethynyl, **10** (313 mg, 0.805 mmol), were dissolved in TEA (6 mL) and THF (6 mL). The reaction flask was placed in a preheated oil bath (60 °C) for 5 min. The mixture was allowed to reach room temperature, diluted with CHCl$_3$, and washed three times with 1 M HCl(aq). The organic extract was dried with $MgSO_4$, filtered, and concentrated. Flash chromatography on silica eluting with 2/1 heptane/EtOAc gave a light-yellow solid in 99% yield. IR: υ 2954, 2869, 2094, 1725, 1594, 1513, 1452, 1371, 1216, 1149, 1078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, $J = 7.23$ Hz, 18 H, CH_2-CH_3), 1.19 (s, 6 H, $-CH_3$), 1.39 (s, 6 H, $-O-C-CH_3$), 1.50−1.41 (m, 18 H, $-O-C-CH_3$, $-CH_2-CH_3$), 1.67−1.56 (m, 12 H, $-CH_2-CH_2-CH_2-$), 2.18−2.08 (m, 12 H, $-P-CH_2-$), 3.67 (d, $J = 11.85$ Hz, 4 H, $-CH_2-O-$), 4.23 (d, $J = 11.85$ Hz, 4 H, $-CH_2-O-$), 5.20 (s, 4 H, $-Ar-CH_2-$), 7.22 (d, $J = 8.23$ Hz, 4 H, Ar*H*), 7.30−7.40 (m, 8 H, Ar*H*), and 7.50 (d, $J = 8.23$ Hz, 4 H, Ar*H*).^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8 ($-CH_2-CH_3$), 18.5 ($-CH_3$), 22.4 ($-O-C-CH_3$), 24.0 (apparent triplet, $J = 16.9$ Hz, $-CH_2-CH_3$), 24.4 (apparent triplet $J = 6.5$ Hz, $-CH_2-CH_2-CH_2-$), 24.8 ($-O-C-CH_3$), 26.4 ($-P-CH_2-$), 42.0 ($-C-$), 66.0 ($-Ar-CH_2-$, $-CH_2-O-$), 89.4 ($-Ar-C\equiv C-Ar-C\equiv C-$), 90.5 ($-Ar-C\equiv C-Ar-C\equiv C-$), 98.1 ($-O-C-CH_3$), 109.3 ($-C\equiv C-Pt-$), 111.9 (apparent triplet, $J = 15$ Hz, $-C\equiv C-Pt-$), 119.0 (Ar*C*), 123.4 (Ar*C*), 127.7 (Ar*C*), 129.2 (Ar*C*), 130.6 (Ar*C*), 131.2 (Ar*C*), 131.6 (Ar*C*), 135.8 ($-CH_2-(p$-Ar$C)$-$C\equiv C-Ar$), and 174.0 ($C{=}O$). ^{31}P NMR (146 MHz, $CDCl_3$): δ 3.76 ($J_{P-Pt} = 2345$ Hz).

Acetonide-G2-Pt (19b). Flash chromatography on alumina 60/40 heptane/EtOAc gave a light-yellow solid in 93% yield. IR υ 2956, 2931, 2869, 2093, 1731, 1594, 1515, 1454, 1371, 1214, 1120, 1078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, $J = 7.32$ Hz, 18 H, $-CH_2-CH_3$), 1.09 (s, 12H, $-CH_3$), 1.31 (s, 6 H, $-CH_3$), 1.34 (s, 12 H, $-O-C-CH_3$), 1.40 (s, 12 H, $-O-C-CH_3$), 1.49−1.41 (m, 12 H, $-CH_2-CH_3$), 1.54−1.67 (m, 12 H, $-CH_2-CH_2-CH_2-$), 2.22−2.06 (m, 12H, $-P-CH_2-$), 3.58 (d, $J = 12.0$ Hz, 8 H, second generation $-CH_2-O-$), 4.10 (d, $J = 12.0$ Hz, 8 H, second generation $-CH_2-O-$), 4.34 (dd, $J_1 = 12$ Hz, $J_2 = 12$ Hz, 8 H, first generation $-CH_2-O-$), 5.45 (s, 4H, $-Ar-CH_2-$), 7.22 (d, $J = 8.23$ Hz, 4 H, Ar*H*), 7.30−7.40 (m, 8 H, Ar*H*), and 7.48 (d, $J = 8.23$ Hz, 4 H, Ar*H*).^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7 ($-CH_2-CH_3$), 17.6 (first generation $-CH_3$), 18.4 (second generation $-CH_3$), 22.1 ($-O-C-CH_3$), 23.9 (apparent triplet, $J = 16.9$ Hz, $-CH_2-CH_3$), 24.3 (apparent triplet $J = 6.5$ Hz, $-CH_2-CH_2-CH_2-$), 25.0 ($-O-C-CH_3$), 26.3 ($-P-CH_2-$), 42.0 (second generation $-C-$), 46.8 (first generation $-C-$), 65.3 (first generation $-CH_2-O-$), 65.8 (second generation $-CH_2-O-$), 65.9 (second generation $-CH_2-O-$), 66.5 ($-Ar-CH_2-$), 89.2 ($-Ar-C\equiv C-Ar-C\equiv C-$), 90.6 ($-Ar-C\equiv C-Ar-C\equiv C-$), 98.0 ($-O-C-CH_3$), 109.3 ($-C\equiv C-Pt-$), 111.9 (apparent triplet, $J = 15$ Hz, $-C\equiv C-Pt-$), 118.9 (Ar*C*), 123.8 (Ar*C*), 128.1 (Ar*C*), 129.2 (Ar*C*), 130.6 (Ar*C*), 131.2 (Ar*C*), 131.6 (Ar*C*), 135.2 ($-CH_2-(p$-Ar$C)$-$C\equiv C-Ar$), 172.3 (first generation $C{=}O$), and 173.4 (second generation $C{=}O$). ^{31}P NMR (146 MHz, $CDCl_3$): δ 3.76 ($J_{P-Pt} = 2345$ Hz).

Acetonide-G3-Pt (19c). Flash chromatography on silica 38/62 heptane/EtOAc gave the product as a sticky oil. This was diluted with CH_2Cl_2 and concentrated in a vacuum which gave the product as yellow foam in 88% yield. IR υ 2958, 2871, 2096, 1731, 1454, 1371, 1214, 1118, 1078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 0.92 (t, $J = 7.29$ Hz, 18 H, $-CH_2-CH_3$), 1.14 (s, 24 H, $-CH_3$), 1.21 (s, 12H, $-CH_3$), 1.28 (s, 6 H, $-CH_3$), 1.35 (s, 24 H, $-O-C-CH_3$), 1.49−1.38 (m, 36 H, $-O-C-CH_3$, $-CH_2-CH_3$), 1.65−1.56 (m, 12 H, $-CH_2-CH_2-CH_2-$), 2.17−2.08 (m, 12 H, $-P-CH_2-$), 3.61 (d, $J = 12.00$ Hz, 16H, third generation $-CH_2-O-$), 4.14 (d, $J = 12.00$ Hz, 16H, third generation $-CH_2-O-$), 4.32−4.22 (m, 24 H, first and second generation $-CH_2-O-$), 5.16 (s, 4H, $-Ar-CH_2-$), 7.22 (d, $J = 8.01$ Hz, 4H, Ar*H*), 7.30−7.40 (m, 8 H, Ar*H*), and 7.49 (d, $J = 8.01$ Hz, 4H, Ar*H*). ^{13}C NMR (90 MHz, $CDCl_3$): δ 13.6 ($-CH_2-CH_3$), 17.4 (first and second generation $-CH_3$), 18.3 (third generation $-CH_3$), 21.9 ($-O-C-CH_3$), 24.0 (apparent triplet, $J = 16.9$ Hz, $-CH_2-CH_3$), 24.2 (apparent triplet $J = 6.5$ Hz, $-CH_2-CH_2-CH_2-$), 24.9 ($-O-C-CH_3$), 26.2 ($-P-CH_2-$), 41.8 (third generation $-C-$), 46.5 (first generation $-C-$), 46.6 (second generation $-C-$), 64.7 (first and second generation $-CH_2-O-$), 65.75 (third generation $-CH_2-O-$), 65.71 (third generation $-CH_2-O-$), 66.5 ($-Ar-CH_2-$), 89.1 ($-Ar-C\equiv C-Ar-C\equiv C-$), 90.6 ($-Ar-C\equiv C-Ar-C\equiv C-$), 97.9 ($-O-C-CH_3$), 109.2 ($-Ar-C\equiv C-Ar-C\equiv C-$), 111.8 (apparent triplet $J = 15$ Hz, $-Ar-C\equiv C-Ar-C\equiv C-$), 118.8 (Ar*C*), 123.7 (Ar*C*), 128.3 (Ar*C*), 129.0 (Ar*C*), 129.1 (Ar*C*), 130.4 (Ar*C*), 131.1 (Ar*C*), 135.0 ($-CH_2-(p$-Ar$C)$-$C\equiv C-Ar$), 171.6 (second generation $C{=}O$), 171.7 (first generation $C{=}O$), and 173.2 (third generation $C{=}O$).^{31}P NMR (146 MHz, $CDCl_3$): δ 3.76 ($J_{P-Pt} = 2345$ Hz).

Acetonide-G4-Pt (19d). Flash chromatography on silica 1/2 heptane/EtOAc gave the product as a sticky oil. The residue was diluted with CH_2Cl_2 and concentrated in a vacuum which gave the product as yellow foam in 90% yield: IR υ 2966, 2873, 2096, 1731, 1454, 1371, 1216, 1116, 1078 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92 (t, $J = 7.25$ Hz, 18 H, $-CH_2-CH_3$), 1.14 (s, 48 H, $-CH_3$), 1.21 (s, 12H, $-CH_3$), 1.27 (s, 24 H), 1.30 (s, 6 H, $-CH_3$), 1.34 (s, 48 H, $-O-C-CH_3$), 1.49−1.37 (m, 60 H, $-O-C-CH_3$, $-CH_2-CH_3$), 1.65−1.57 (m, 12 H, $-CH_2-CH_2-CH_2-$), 2.16−2.07 (m, 12 H, $-P-CH_2-$), 3.60 (d, $J = 12.0$ Hz, 32 H, fourth generation $-CH_2-O-$), 4.13 (d, $J = 12.0$ Hz, 32 H, fourth generation $-CH_2-O-$), 4.36−4.19 (m, 56 H, first, second, and third generation $-CH_2-O-$), 5.15 (s, 4 H, $-Ar-CH_2-$), 7.21 (d, $J = 8.25$ Hz, 4 H, Ar*H*), 7.38−7.31 (m, 8 H, Ar*H*), 7.49 (d, $J = 8.25$ Hz, 4 H, Ar*H*). ^{13}C NMR (90 MHz, $CDCl_3$): δ 13.6 ($-CH_2-CH_3$), 17.2 (second generation $-CH_3$) 17.3 (first generation $-CH_3$), 17.5 (third generation $-CH_3$), 18.3 (fourth generation $-CH_3$), 21.9 ($-O-C-CH_3$), 23.8 (apparent triplet, $J = 16.9$ Hz, $-CH_2-CH_3$), 24.2 (apparent triplet $J = 6.5$ Hz, $-CH_2-CH_2-CH_2-$), 24.9 ($-O-C-CH_3$), 26.2 ($-P-CH_2-$), 41.8 (fourth generation $-C-$), 46.5 (second, generation $-C-$), 46.6 (first generation $-C-$), 46.6 (third generation $-C-$), 64.6 ($-CH_2-O-$), 65.4 ($-CH_2-O-$), 65.7 ($-CH_2-O-$), 65.7 ($-CH_2-O-$), 66.1 ($-CH_2-O-$), 66.6 ($Ar-CH_2-$), 89.1 ($-Ar-C\equiv C-Ar-C\equiv C-$), 90.6 ($-Ar-C\equiv C-Ar-C\equiv C-$), 97.8 ($-O-C-CH_3$), 109.1 ($-Ar-C\equiv C-Ar-C\equiv C-$), 111.9 (apparent triplet $J = 15$ Hz, $-Ar-C\equiv C-Ar-C\equiv C-$), 118.8 (Ar*C*), 123.6 (Ar*C*), 128.0 (Ar*C*), 130.4 (Ar*C*), 130.4 (Ar*C*), 131.1 (Ar*C*), 131.5 (Ar*C*), 135.0 ($-CH_2-(p$-Ar$C)-C\equiv C-Ar$), 171.2 (second generation $C{=}O$), 171.5 (first generation $C{=}O$), 171.6 (third generation $C{=}O$), 173.3 (fourth generation $C{=}O$). ^{31}P NMR (146 MHz, $CDCl_3$): δ 3.76 ($J_{P-Pt} = 2345$ Hz).

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