REYES & REYES
A B O G A D O S

SUPERINTENDENTE DE INDUSTRIA Y C

E. S. D.

REF: **Expediente 12-068-973**

TÍTULO SOLICITADO: **PROCESO PARA LA ELABORACIÓN DE COMPUESTOS ORGÁNICOS.**

PUBLICACIÓN: **Gaceta 653 de 28/09/2012, número de publicación 1487.**

PRIORIDAD: **EP 09174264.3 de 27/01/2009**

SOLICITANTE: **NOVARTIS AG.**

APODERADO: **CARLOS REINALDO OLARTE GARCIA.**

TRÁMITE: **SUSTENTACION DE OPOSICIÓN.**

JOSÉ LUIS REYES VILLAMIZAR, mayor de edad, identificado como aparece al pie de mi firma, abogado en ejercicio, titular de la tarjeta profesional número 44655 del Consejo Superior de la Judicatura, obrando en calidad de apoderado de la sociedad **TECNOQUIMICAS S.A.,** sociedad constituida y vigente de conformidad con las leyes colombianas, con domicilio en Cali, Valle, en ejercicio de lo dispuesto por el artículo 42 de la Decisión 486 de 2000, y por medio del presente escrito, procedo a sustentar y complementar la oposición presentada el 27 de diciembre de 2012, en los siguientes términos:

I. RATIFICACIÓN

Comedidamente me permito insistir en que la solicitud de la referencia, relacionada con procesos para la elaboración de un bloqueador de los receptores de angiotensina ARB (también denominado como antagonista de los receptores de angiotensina II o antagonista del receptor AT1), y a sales de los mismos, a intermediarios novedosos, y a los pasos del proceso, carece de los requisitos de

patentabilidad establecidos por la Decisión 486 y que como tal, no merece recibir el beneficio patentario.

- En relación con el "uso", tal como se observa en las reivindicaciones 14 y 15, se debe señalar que dicha pretensión resulta inaceptable a la luz de la Decisión 486 en tanto los "usos" son una categoría excluida del concepto de "Productos o Procedimientos" que establece el artículo 14 de la norma citada.

- En cuanto al reactivo de azida (reivindicaciones 3, 4, 8, 9 y 10), específicamente una azida de fórmula R7R8MN en donde M es boro o aluminio para la obtención de un compuesto de fórmula I (un tetrazol 5-sustituido) a partir de un compuesto de fórmula IV (que comprende un grupo nitrilo) es importante indicar que en el estado de la técnica se reporta el documento "Benzopyrones. 7. Synthesis and Antiallergic Activity of some 2-(5-Tetazolyl)chromones" publicado en el *Journal of medicinal Chemistry, 1972, Vol. 15, Nº 8. Pág 865* (**D1**), en el cual el mencionado grupo R corresponde a una benzopirona, y se puede obtener el **grupo tetrazol** mediante **la conversión** lenta **del grupo carbonitrilo** por reacción con una **azida de sodio** y cloruro de amonio en DMF.

- De lo anterior, resulta evidente que en ambos casos la fabricación del grupo tetrazol se logra mediante el tratamiento de un compuesto R-CN con una azida, en consecuencia, la utilización de este tipo de reactivos azidicos, en especial los de fórmula R7R8MN, carece de novedad por obra de lo revelado en el artículo antes señalado.

- En cuanto a la ausencia de nivel inventivo del proceso reivindicado en la solicitud actual, tenemos que se revelan con anterioridad procesos de ciclación a partir de carbonitrilos o ciano con alquil estaño-azidas tal como lo demuestra el documento WO94/07872 (**D2**) publicado el 14 de abril de 1994, perteneciente a Abbott Laboratories y el documento WO9314086 (**D3**) publicado el 22 de julio de 1993 perteneciente a Syntex Inc.

- También los documentos EP 0 796 852 "Process for preparation of 5-substituted tetrazoles" del 24 de septiembre de 1997 (**D4**) y EP 0 120 483 "(1H-tetrazol-5-yl)-2(1H)-quinolinones" de octubre 3 de 1984 (**D5**) detallan el uso de Azida de Sodio con una amina, característica que el solicitante

describe como desventajosa por la volatilidad y riesgo de explosión de los vapores y propone entonces el uso de compuestos órgano-metalo azidicos de fórmula (R1) (R2) BN3 y (R1) (R2) Al N3, que coinciden con el reactivo R7R8MN revelado en la solicitud en cuestión.

- En el estado del arte se encuentran múltiples ejemplos de solicitudes en las que para obtener un grupo **tetrazol** se usan compuestos de tipo nitrilo o ciano y **azidas**, lo que nos demuestra que al menos desde 1984 este procedimiento es ampliamente conocido y que dados los inconvenientes provocados por las azidas, han permitido y han conducido obviamente a los expertos en síntesis a la búsqueda de reactivos que protejan el medio ambiente y que permitan obtener procesos más limpios.

- Los compuestos azidos órgano-boranos y azido Aluminanos se reportan desde 1954 como lo detalla la siguiente referencia bibliográfica: "Gas Phase Synthesis, Structure, and Dissociation of Boron Triazide" *J. Phys. Chem. 1995, 99, 6294- 6300* **(D6)**, describe la síntesis de borano-azidas a partir de diboranos con HN3, y detallada.

- Pretender proteger la obtención de antagonistas del receptor de angiotensina II mediante el proceso descrito, si bien es cierto no se ha encontrado una descripción textual del mismo, se debe tener en cuenta que éste proceso no reúne el requisito de nivel inventivo ya que al igual que los documentos citados como anterioridades la fabricación del grupo tetrazol se lleva en condiciones similares, es decir, que se hace reaccionar un compuesto de tipo nitrilo con una azida adecuada para obtener un R-tetrazol.

- La patente europea EP 1714963 publicada el 25 de octubre de 2006, revela por su parte compuestos de la fórmula II, con lo cual afecta la novedad del compuesto de fórmula III de la solicitud colombiana en trámite, en especial la reivindicación 12. Por su partem la patente europea EP1533305 publicada el 25 de mayo de 2005 afecta la novedad del compuesto IV revelado en la solicitud colombiana en trámite, especialmente en la reivindicación 13.

- Los intermediarios relacionados a los compuestos III y IV carecen de novedad y a su vez el procedimiento de obtención carece de nivel inventivo puesto que

usa reactivos convencionales y reconocidos en el estado de la técnica para convertir un grupo nitrilo en tetrazoles 5-sustituidos.

II. COMPLEMENTO DE INFORMACIÓN

En complemento a lo anterior, y esta vez refiriéndonos a la reacción de desprotección del grupo carboxilo presente en el compuesto de formula III a través de un haluro de organoaluminio, tal y como se presenta en las reivindicaciones 1, 2, 3, 4, 6, 7, 10, 11, 12, 14 y 15, existen documentos que con anterioridad revelan el uso de estos compuestos como agentes deprotectores de estos grupos carboxílico en la forma de esteres, veamos:

- La publicación científica "Tripodal pyrene chromophores for semiconductor sensitization: new footprint design[1]" publicada el 18 de mayo de 2007 revela:

> lower yields. The last step involved the hydrolysis of the methyl ester 7a, since carboxylic acids are needed to form strong bonds to the metal oxide semiconductor surface.[33] Bases such as NaOH could not be used, since the silicon center is readily attacked by nucleophiles. The use of weak bases,[34] hard acid-soft nucleophile systems,[35] or mild conditions involving Me_3SiCl[36] resulted in partial fragmentation

- Por su parte la publicación "Synthesis and Controlled Radical Polymerization of Multifunctional Monomers" publicada en junio de 2004, revela:

> The preparation of esters can be classified into two main categories: (1) carboxylate activation[185] with a good leaving group and (2) nucleophilic displacement of a carboxylate on an alkyl halide or sulfonate. The latter approach is generally not suitable for the preparation of esters if the halide or tosylate is sterically hindered, but there has been some success with simple secondary halides[183] and tosylates (ROTs, DMF, K_2CO_3, 69-93 % yield).[184]
>
> An ester has two sites that can be potentially attacked by a nucleophile. In general, the approach of cleaving ester groups can be employed under acidic, basic or hydrogenolytic conditions.[185]

Estas dos publicaciones, hacen referencia a las condiciones en cuanto a la desprotección o hidrólisis del grupo éster para liberar el carboxilo.

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[1] Sujatha Thyagarajan, Aiping Liu, Olumide A. Famoyin, Massimiliano Lambertoy and Elena Galoppini. S. Thyagarajan et al. / Tetrahedron 63 (2007) 7550–7559.

- La publicación "Recent Developments in chemical deprotection of ester functional groups" de Salomon Et al[2], que en el ISR realizado por la OMPI para la equivalente internacional de la solicitud colombiana en cuestión, se clasifica como un documento que por sí solo afecta la novedad de la reivindicación 14, por mencionar explícitamente haluros de organoaluminio para la conversión de esteres en el ácido libre, que en suma con lo mencionado con las publicaciones anteriores, son evidencia suficiente para demostrar que cualquier persona medianamente versada en la síntesis química podría seleccionar este tipo de compuestos organometálicos (con características básicas débiles) para realizar los pasos concernientes a la deprotección o hidrólisis del grupo éster del compuesto de la fórmula III de la solicitud en cuestión, y que por lo tanto su utilización no puede solventar novedad, ni mucho menos nivel inventivo alguno.

Por todo lo anterior, le solicito Señor Superintendente, que analice los argumentos citados con el rigor y detenimiento habituales y que decrete, además de la negación de la solicitud en comento, el archivo del citado expediente.

III. ANEXOS.

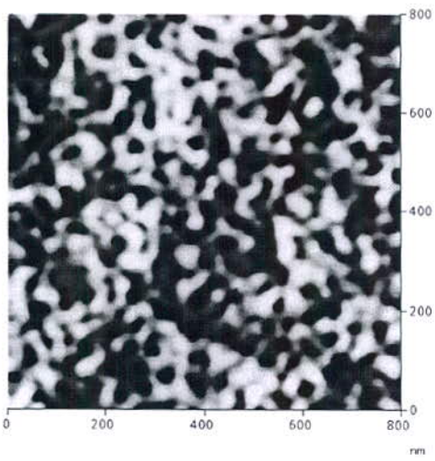
- Publicación "Synthesis and Controlled Radical Polymerization of Multifunctional Monomers" publicada en junio de 2004, Portada pág 29 y 30.
- La publicación científica "Tripodal pyrene chromophores for semiconductor sensitization: new footprint design" publicada el 18 de mayo de 2007.

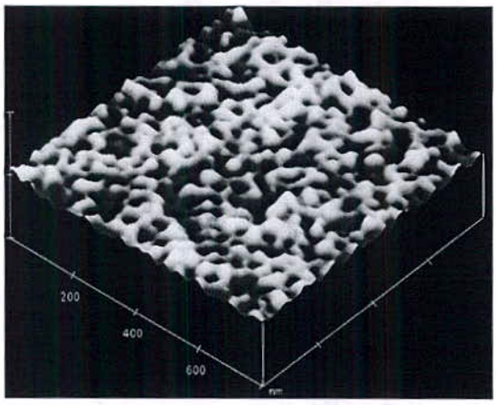
Señor Superintendente,

JOSE LUIS REYES VILLAMIZAR
C.C. 79.152.473 de Usaquén
T.P. 44655 del C. S de la J.

[2] Salomon, C.J.; Mata, E.G.; Mascaretti, O.A. Tetrahedron Lett., 1993, 49, 3691.

Synthesis and Controlled Radical Polymerization of Multifunctional Monomers





Meizhen Yin

Technischen Universität Dresden

June 2004

use in nucleotide synthesis.[179] Ethers are formed and removed under a wide variety of conditions. Some of the ethers that have been used extensively to protect alcohols include substituted methyl ethers, substituted ethyl ethers, substituted benzyl ethers and various silyl ethers.

Among ethers, silyl ethers are the most frequently used protective groups for the alcohol function.[180] The selective cleavage of numerous silyl derivatives has been investigated.[181] This stems largely from the fact that their reactivity (both formation and cleavage) can be modulated by a suitable choice of substituents on the silicon atom. Both steric and electronic effects are the basic controlling elements that regulate the ease of cleavage in multiply functionalized substrates. In planning selective deprotection, the steric environment around the silicon atom, as well as the environment of the protected molecular framework, must be considered. Electron-withdrawing substituents on the silicon atom increase its susceptibility toward basic hydrolysis, but decrease its sensitivity toward acid. For some of the more common silyl ethers, such as trimethylsilyl (TMS), triethylsilyl (TES), *t*-butyldimethylsilyl (TBDMS), triisopropylsilyl (TIPS), *t*-butyldiphenylsilyl (TBDPS), the stability toward acid increases in the order: TMS < TES < TBDMS < TIPS < TBDPS, and the stability toward base increase in the order: TMS < TES < TBDMS ~TBDPS < TIPS. One of the properties that have made silyl groups so popular is the fact that they are easily cleaved by fluoride ion, which is attributed to the high affinity that fluoride ion has for silicon.

- **Carbonates**

Organic carbonates are also used as protective groups and can be cleaved by basic hydrolysis, but are generally much less susceptible than esters because of the resonance effect of the second oxygen. In general, carbonates are cleaved by taking advantage of the properties of the second alkyl substituent (e.g., zinc reduction of the 2,2,2-trichloroethyl carbonate). The reagents used to introduce the carbonate onto alcohols react readily with amines as well. As expected, basic hydrolysis of the resulting carbamate is considerably more difficult than hydrolysis of a carbonate.

2.3.2.3. Protection of carboxyl groups

Carboxylic acids are protected for a number of reasons: (1) to mask the acidic proton so that it does not interfere with base-catalyzed reactions, (2) to mask the carbonyl group to prevent

nucleophilic addition reactions, and (3) to improve the handling of the molecule in question (e.g., to make the compound less water soluble, to improve its NMR characteristics, or to make it more volatile so that it can be analyzed by gas chromatography).

Besides stability to a planned set of reaction conditions, the protective group must also be removed without affecting other functionalities in the molecule. For this reason, a large number of protective groups for acids have been developed that are removed under a variety of conditions, even though most can be readily cleaved by simple hydrolysis. Hydrolysis is an important means of deprotection, and the rate of hydrolysis is, of course, dependent upon steric and electronic factors that help to achieve different deprotection in polyfunctional substrates. These factors are also important in the selective protection of compounds containing two or more carboxylic acids.[182]

- **Esters**

A wide range of methods is available for the protection of carboxyl functions by means of methyl, ethyl, substituted methyl and ethyl, *t*-butyl, allyl, benzyl, substituted benzyl, diphenyl methyl and silyl esters among others.

The preparation of esters can be classified into two main categories: (1) carboxylate activation with a good leaving group and (2) nucleophilic displacement of a carboxylate on an alkyl halide or sulfonate. The latter approach is generally not suitable for the preparation of esters if the halide or tosylate is sterically hindered, but there has been some success with simple secondary halides[183] and tosylates (ROTs, DMF, K_2CO_3, 69-93 % yield).[184]

An ester has two sites that can be potentially attacked by a nucleophile. In general, the approach of cleaving ester groups can be employed under acidic, basic or hydrogenolytic conditions.[185]

Available online at www.sciencedirect.com
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Tetrahedron
Tetrahedron 63 (2007) 7550–7559

Tripodal pyrene chromophores for semiconductor sensitization: new footprint design

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Received 26 March 2007; revised 11 May 2007; accepted 14 May 2007
Available online 18 May 2007

Abstract—Large footprint tripodal linkers for metal oxide nanoparticle sensitization, substituted with pyrene as the dye, and three COOR binding groups in *para* or *meta* position, were prepared to study the effect of the anchoring group position and of the footprint size on the sensitization processes. Two tripods based on tetraphenylsilane, (1-pyrenyl-4-ethynyl-phenyl)-tris(4-carbomethoxyphenyl-4-ethynyl-phenyl)silane, and (1-pyrenyl-4-ethynyl-phenyl)-tris(4-(4-methoxybenzyloxycarbonyl)phenyl-4-ethynyl-phenyl)silane, decomposed during hydrolysis, while the tetraphenyladamantane derivative, 1-(1-pyrenyl-4-ethynyl-phenyl)-3,5,7-(3-carbomethoxyphenyl-4-ethynyl-phenyl)-adamantane, was chemically stable and was readily converted into the corresponding acid and bound to TiO_2 films. The FT-IR-ATR spectrum of 1-(1-pyrenyl-*p*-ethynyl-phenyl)-3,5,7-(3-carboxyphenyl-4-ethynyl-phenyl)adamantane bound to TiO_2 nanoparticles showed bands characteristic of carboxylate bidentate bonds. The UV–vis absorption and fluorescence emission in THF solution at room temperature were typical of pyrenes substituted with oligophenyleneethynylene linkers.

1. Introduction

TiO_2 nanoparticle thin films with anchored chromophores or redox active group are used in dye-sensitized solar cells and other devices.[1] Linkers that connect a chromophore to the semiconductor are useful to control the distance and orientation with respect to TiO_2 nanoparticle surfaces for interfacial electron transfer studies.[2,3] In particular, tripodal linkers with three anchoring groups (COOH, PO_3H) have been used by us[4] and by others[5] to bind Ru–bpy complexes and other groups to the surface of semiconductor nanoparticles. In this paper we describe a methodology that allows varying the type and position of the anchoring groups on the tripodal linker as well as the footprint area (Fig. 1).

In the previously reported procedure, the starting material, tetrakis-1,3,5,7-(*p*-iodophenyl)adamantane (**1**), was converted into linker **2**, with fixed footprint size and having

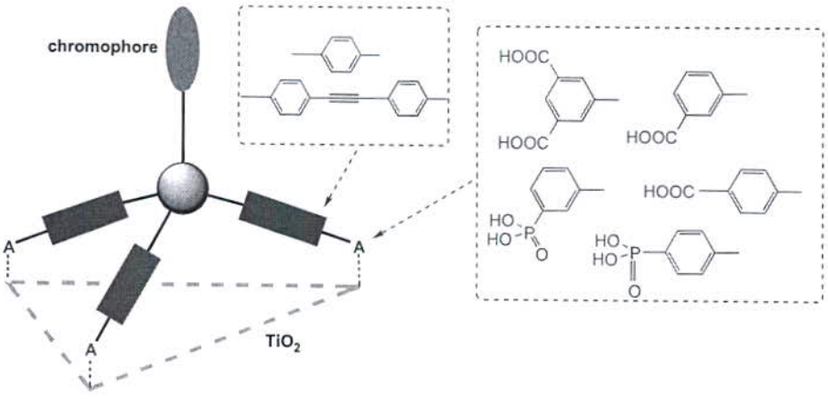

Figure 1. Schematic representation of the strategy: footprint size and possible anchoring group modifications.

Keywords: Tripods; Pyrene; Semiconductor nanoparticles; Sensitization; Titanium dioxide.
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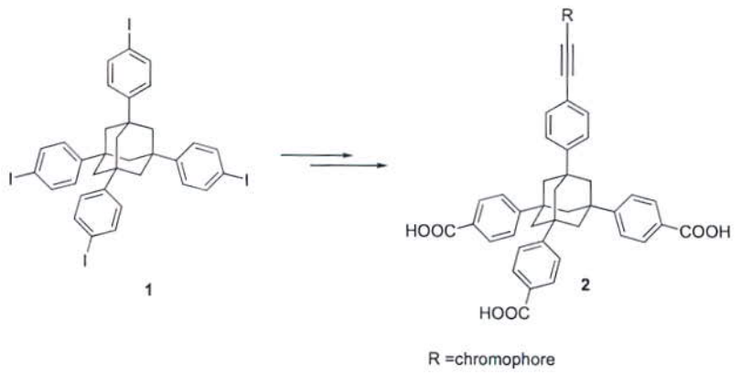
doi:10.1016/j.tet.2007.05.055



Scheme 1. Multistep synthesis of tripodal sensitizers.[6,7]

the COOH groups on the phenyl rings in *para* position (Scheme 1).[6,7]

The possibility to modify the anchoring unit, however, is important to achieve strong binding from all three anchoring groups on a variety of surfaces. The binding process influences most applications, including interfacial charge transfer and excimer effect studies. Also, the use of different semiconductors (TiO_2, ZnO), crystal structures (anatase, wurtzite), and morphologies (nanoparticles, nanowires) requires a more versatile approach to vary the type and position of the anchoring groups.[1a] For instance, preliminary theoretical calculations indicate that, in a tripodal linker, COOH anchoring groups in *meta* position (rather than in *para*, as in **2**, Scheme 1) may enhance the binding of the molecule to TiO_2 anatase (001) by all three legs of the tripods, because of the more favorable angle for surface anchoring.[8] The synthesis of varying tripodal anchoring units will complement ongoing computational studies aiming at matching anchoring groups with various semiconductor surfaces.[8] A comparison between footprint sizes for various tripodal linkers is shown in Figure 2.

Secondly, tripods with larger footprints can find use to study dye–dye interactions on the surface of semiconductors, a phenomenon that influences numerous interfacial processes.

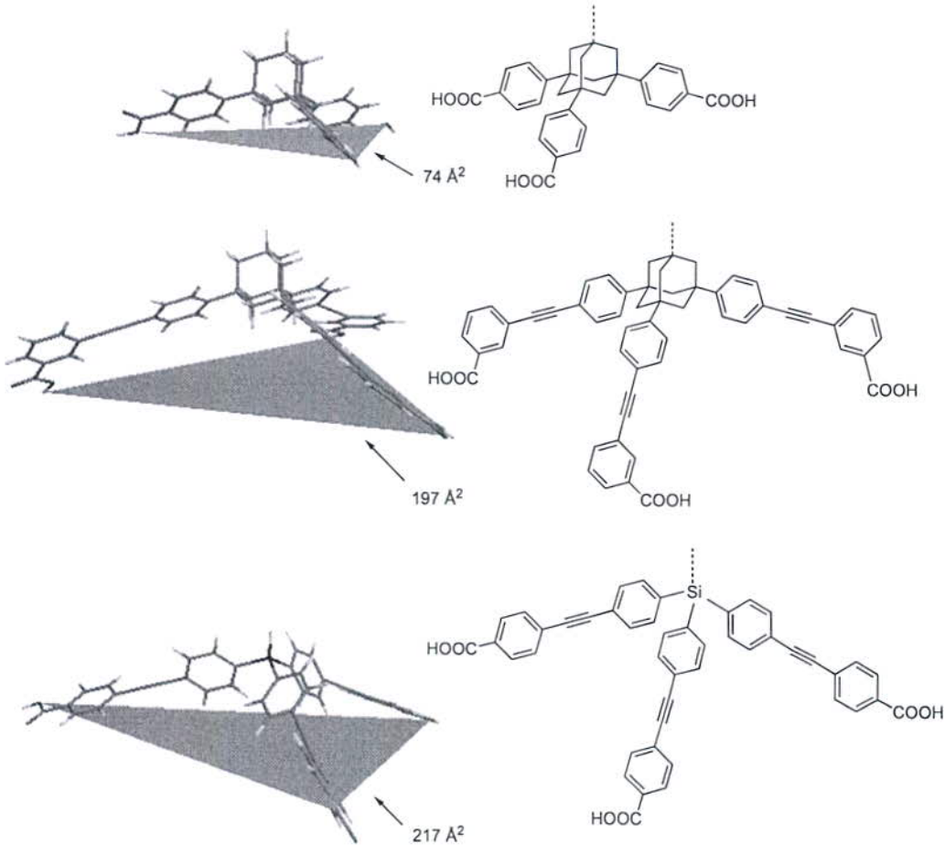


Figure 2. Comparison between the footprint size of various tripodal linkers.

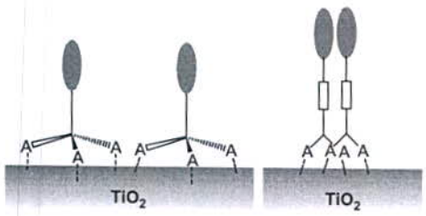


Chart 1.

The study of aggregation effects is important, because of the increasing interest in organic dyes that possess useful properties, such as porphyrins,[9] coumarins,[10,11] perylenes,[12] and other organic chromophores.[13–16] Through structural modifications it is possible to tune the position of the excited state energy level relative to the conduction band edge of the semiconductor, to widen the range of spectral absorption, and to increase the extinction coefficient. Also, organic dyes are excellent model systems for fundamental studies of charge injection and recombination processes at the molecule–nanoparticle interface.[4b,17]

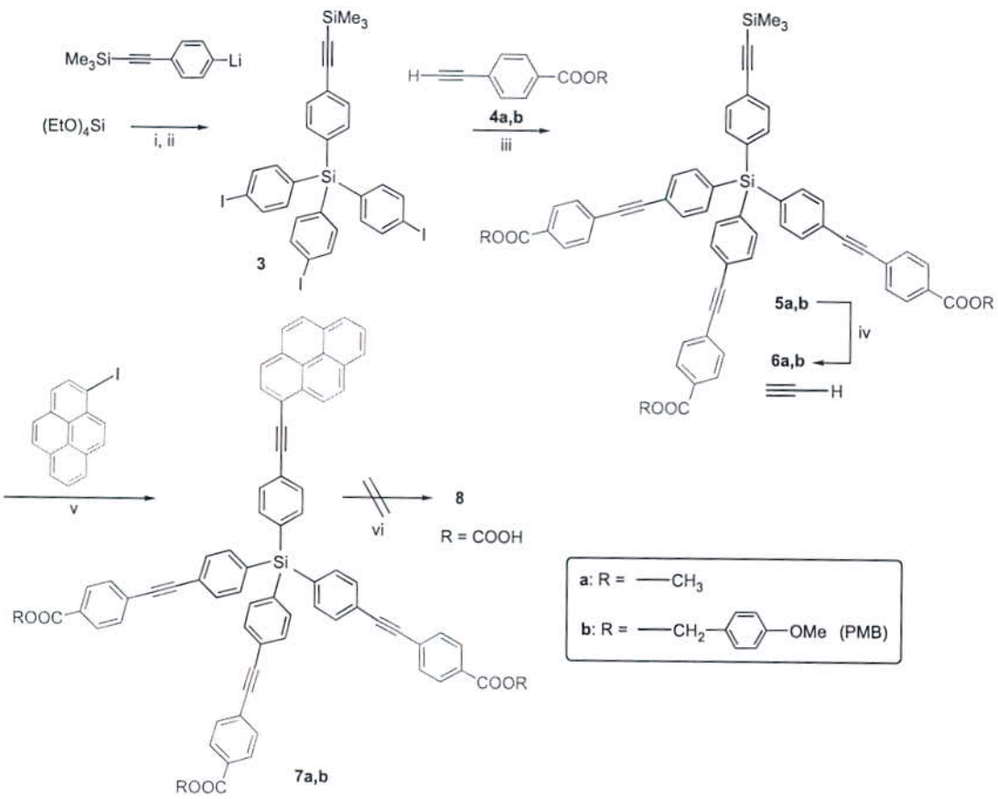
Organic dyes containing π-conjugated systems tend to stack through π–π interactions on the surface of the semiconductor,[18] resulting in shifts in the absorption spectra and formation of excimers. Aggregation on TiO_2 influences most applications, and usually decreases the performance of solar cells through a variety of mechanisms.[19,20] Strategies employed to prevent it include the use of lipophilic coadsorbates,[19,21] substitution with bulky group,[12a,12d,22] and encapsulation of the dye in a guest.[23–25] There are examples, however, in which aggregation results in good efficiencies.[26] For instance, our studies of closely stacked pyrene-substituted rigid rods suggest that pyrene excimer could be a very effective sensitizer.[27] The spacing of dyes on the surface of semiconductors by using large tripods could be useful to study excimer and monomer effects as shown in Chart 1.

Finally, the footprint of the adamantane tripod **2** is ~0.7 nm^2. Extension of each 'leg' by a phenylethynyl unit, for instance, results in a fourfold increase of the footprint area (Fig. 2). Model dyes having larger footprint area but with similar distance of the Ru-chromophore from the semiconductor will allow to study whether the binding area influences the rates of injection or recombination.

2. Results and discussion

2.1. Synthesis

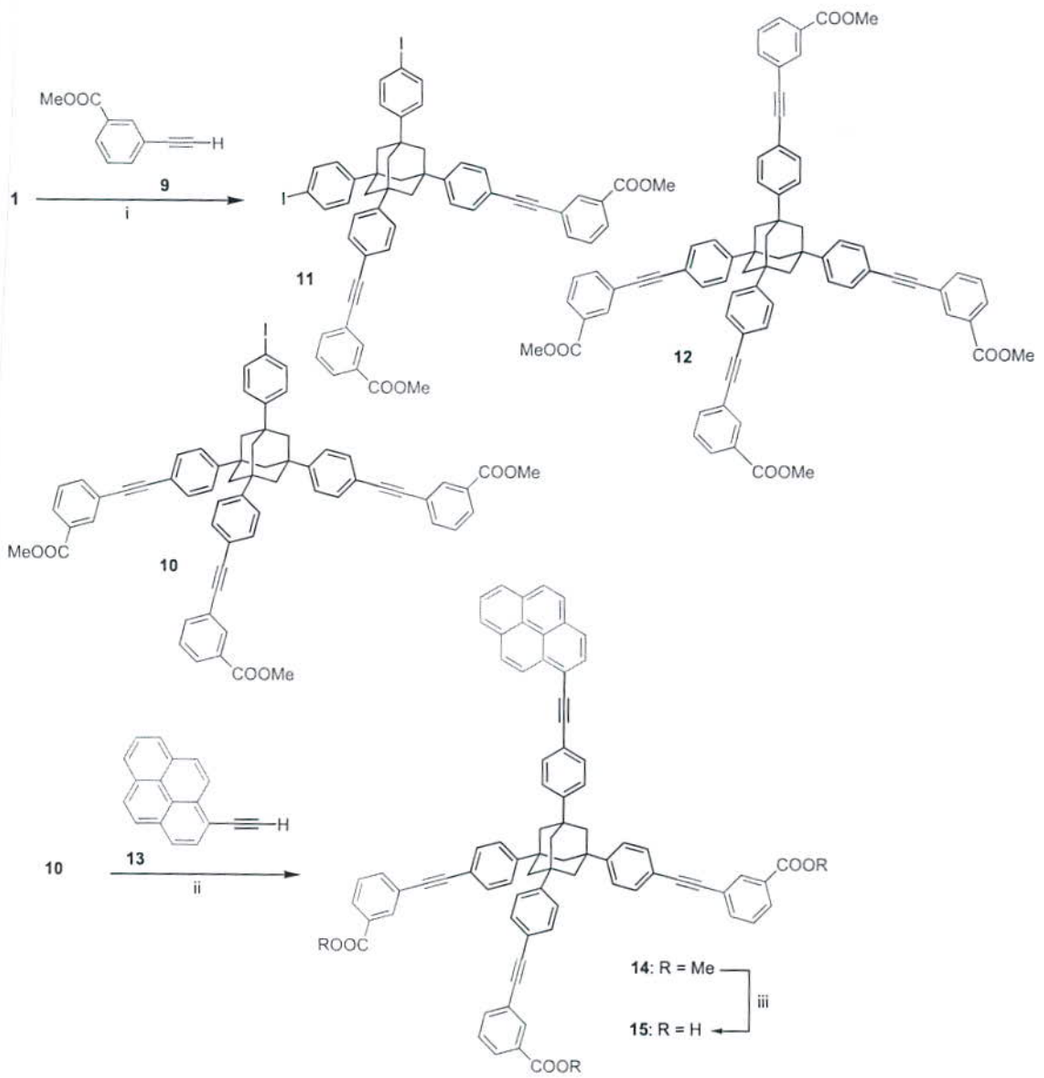
In this paper we describe the synthesis of silicon- and adamantane-centered tripods with larger footprints and variable position of the anchoring groups (Fig. 2). Pyrene was selected as the chromophore to make comparisons with the reported pyrene-substituted rigid rods.[27] Silicon-centered tripods **7a** and **7b**, in Scheme 2, were prepared by modifying



Scheme 2. Reagents and conditions: (i) 1,4-diiodobenzene, *n*-BuLi, Et_2O, −78 °C, 44%; (ii) Et_2O, −78 °C, 33%; (iii) $Pd(dba)_2$, PPh_3, CuI, $(i\text{-}Pr)_2NEt$, THF, rt, **5a** 69%, **5b** 75%; (iv) TBAF, AcOH, THF, rt, **6a** 90%, **6b** 52%; (v) *Sonogashira*: $Pd(dba)_2$, PPh_3, CuI, $(i\text{-}Pr)_2NEt$, THF, rt, **7a** 66%, **7b** 76%. *Suzuki*: (a) $(Me_3Si)_2NLi$, THF, −78 °C, (b) B-MeO-9-BBN, −78 °C, (c) 1-iodopyrene, $Pd(PPh_3)_4$, THF, rt, **7a** 41%; (vi) see text for details.

the procedure developed by Tour and Yao for the synthesis of 'Si-caltrops'.[28] This route permits to extend the footprint of 'Si-caltrop' **3**[28] by adding the anchoring unit (in blue) in a Pd-catalyzed[29] cross-coupling step, in this case a methyl- or 4-methoxy-benzyl-4-ethynyl-benzoate (**4a** and **4b**). The PMB ester **4b** was prepared by esterification of 4-trimethylsilylethynyl-benzoic acid[30] with 4-methoxybenzyl alcohol followed by deprotection with TBAF. The chromophore was introduced via a Sonogashira[31] coupling reaction of terminal alkyne **6a** with 1-iodopyrene at room temperature to form **7a** in 66% yields. A Suzuki-type[32] cross-coupling between iodopyrene and ethynylboronate from **6a** gave lower yields. The last step involved the hydrolysis of the methyl ester **7a**, since carboxylic acids are needed to form strong bonds to the metal oxide semiconductor surface.[33] Bases such as NaOH could not be used, since the silicon center is readily attacked by nucleophiles. The use of weak bases,[34] hard acid-soft nucleophile systems,[35] or mild conditions involving Me_3SiCl[36] resulted in partial fragmentation of **7a**. We then prepared ester **7b**, since the COOPMB group is readily hydrolyzed by trifluoroacetic acid, and the end of the hydrolysis is conveniently indicated by a color change.[37] Decomposition of **7b**, however, occurred within minutes, most likely by the same mechanism described for the decomposition of tetraphenylsilanes by acids.[38] In conclusion, esters **7a** and **7b** had limited chemical stability, could not be converted into carboxylic acid **8** in satisfactory amounts for the binding study, and attempts to directly bind the esters to metal oxide surfaces did not succeed.

Although there are numerous protecting groups and methodologies for ester hydrolysis, the instability of Si-tripods on the surface of the semiconductor to acids, bases, or electrolytes would be a major limitation to the photoelectrochemical studies of sensitized films alone or in working solar cells. This convinced us to modify the adamantane tripods, because of their proven stability. The first synthesis of such compounds, **15**, is shown in Scheme 3.



Scheme 3. Reagents and conditions: (i) $Pd(PPh_3)_2Cl_2$, CuI, $(i\text{-}Pr)_2NEt$, THF, rt, **10** 22%, **11** 28%, **12** 7%; (ii) $Pd_2(dba)_3$, $(o\text{-tolyl})_3P$, Et_3N, THF, 60 °C, 38%; (iii) NaOH aq, THF, rt, 83%.

The starting material, tetrakis-1,3,5,7-(*p*-iodophenyl)adamantane **1**, was prepared in ~50% yields and multigram amounts from 1-bromoadamantane, following a two-step procedure published by Mathias and Reichert.[7] Sonogashira cross-coupling of **1** with *m*-ethynyl-benzoate **9**,[39] produced a mixture of the product, **10**, together with the di-ester **11** (28%), tetra-ester **12** (7%), and a small amount of unreacted **1**. Compound **10** was isolated in 22% yield after repeated silica gel chromatography columns with hexanes/ethylacetate. Cross-coupling of **10** with ethynylpyrene **13** yielded methyl ester **14** in 38% yield. The overall yield of **14** from **1** was ~8%. This methyl ester was readily hydrolyzed with base to the corresponding acid **15** as a pale yellow solid.

2.2. Solution properties and binding

The UV–vis absorption spectra of **7a** and **14** in THF solutions, Figure 3a, displayed a pattern similar to that observed in other phenylethynylpyrenes,[40] with absorption spectra red-shifted with respect to the spectrum of pyrene.[41]

The extended π-conjugation in **7a** and **14** resulted in a 20-nm red shift of the longer wavelength band and higher extinction coefficients (ε_{393}=36,567 $M^{-1}\,cm^{-1}$) when compared to pyrene (ε_{372} ~200 $M^{-1}\,cm^{-1}$).[27a] The bands at 325 nm were assigned to the π,π* transitions of the *p*-phenyleneethynylene units. The UV–vis absorption spectrum of **15** bound to TiO_2 is shown in Figure 3b. Only the lowest energy vibronic band is observable for **15**/TiO_2 as bands below 380 nm are covered by the absorption of the semiconductor.

The fluorescence emission spectra of **7a** and **14** in THF solutions are shown in Figure 4a. In both cases the emission λ_{max} are red-shifted compared with those of pyrene.[41] Furthermore, **7a** and **14** exhibited almost quantitative fluorescence quantum yields compared to pyrene (Φ_{Fl} ~0.9). Similar effects, shorter excited state lifetimes (τ ~2 ns) and quantum yields close to unity, have been observed in 1-phenylethynyl-pyrenes[27a,40] and were attributed to a switching in the order of the two lowest singlet-lying states of pyrene upon substitution with phenyleneethynylene groups.[27a] The quenching of fluorescence of **15** on anatase TiO_2 films (Fig. 4b) indicates efficient electron injection into the semiconductor. In conclusion, the solution photophysical properties of **14** are similar to those observed for

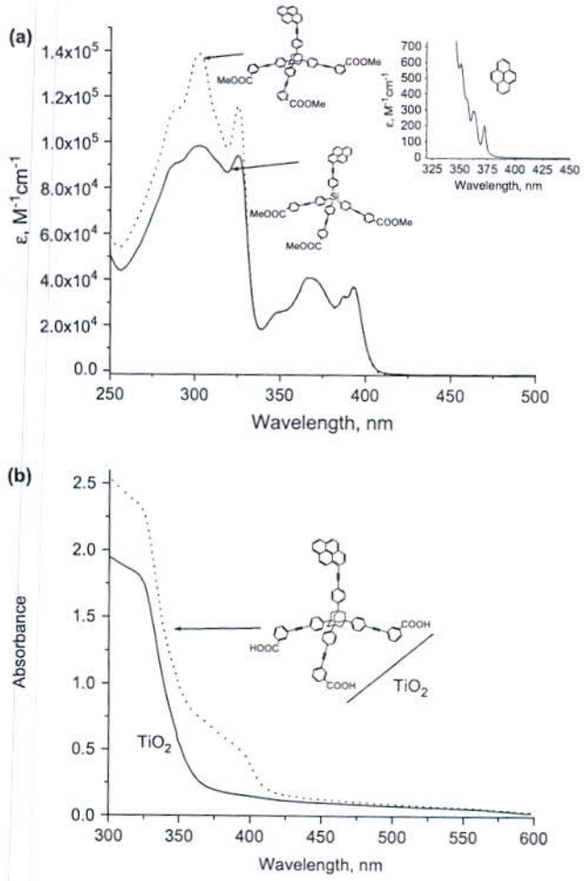


Figure 3. (a) Absorption spectra of **7a** (solid line) and **14** (dotted line) in THF. Inset: absorption spectrum of pyrene in THF. (b) Absorption spectrum of **15** bound to TiO_2/glass (dotted line) and the reference TiO_2/glass (solid line).

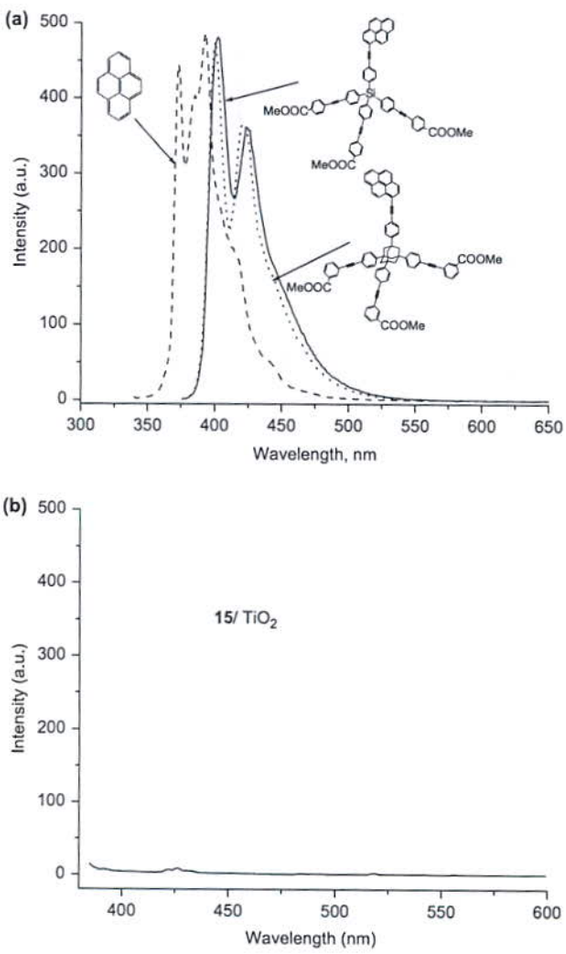


Figure 4. (a) Normalized fluorescence emission spectra of **7a** (solid line), **14** (dotted line), and pyrene (dashed line) in solution. In all the cases, the solvent was THF. λ_{ex}=360 nm (for **7a** and **14**) and 335 nm (for pyrene). (b) Fluorescence quenching of **15** bound to TiO_2. λ_{ex}=380 nm.

the rigid rod pyrene derivatives[27a] that aggregate on the surface of nanoparticles. Comparisons of aggregation effects and solar cell efficiency between such rigid rod compounds and **15** bound to metal oxide surfaces are in progress.

The binding was done by immersing the films in 0.5 mM solutions of **15** in THF. Base (pH 11), acid (pH 1) pretreated TiO_2 films (see Section 4) were employed, as well as non-pretreated films, as we observed that pretreatment of the film does influence the coverage.[4,27] In this case, the highest coverage was obtained when the films were pretreated with base and the data of **15**/TiO_2 reported here were obtained on such films. The fluorescence emission of **15**/TiO_2 was fully quenched, indicating that binding results in electron injection in the semiconductor. The binding mode of **15** to TiO_2 through the COOH groups was characterized by FT-IR-ATR. Figure 5 shows the FT-IR-ATR spectra of **15** neat (as powder) and bound to TiO_2. The free carboxylic acid **15** shows an intense band at 1697 cm^{-1} characteristic of the carbonyl asymmetric $\nu_{(C=O)}$ stretch in carboxylic acids, and the $\nu_{(C-OH)}$ stretch at 1257 cm^{-1}. Upon binding to TiO_2, the $\nu_{(C=O)}$ and $\nu_{(C-OH)}$ stretching modes disappear with the appearance of broad bands at ~1555 cm^{-1}, in the carboxylate (CO_2^-) region. The observed spectral changes are consistent with carboxylate derivatives bound to TiO_2 surfaces through bidentate binding modes as in Figure 5.[27a,42,43] The disappearance of the C=O band suggests that **15** binds to TiO_2 through carboxylate bonds, rather than ester-type bonds and that no detectable free acid is present.

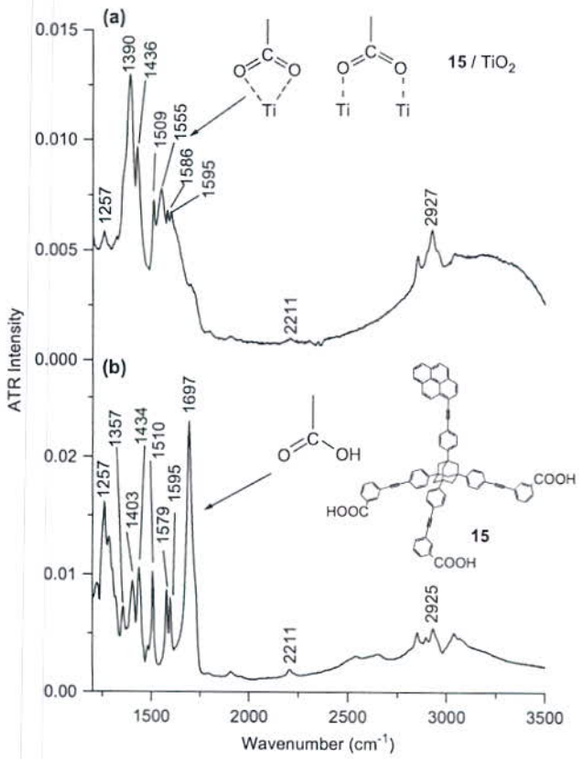


Figure 5. FT-IR-ATR spectra of (a) **15** bound to TiO_2 (pH 11 pretreated) and (b) **15** in the solid state. The broad band observed at ~3000 cm^{-1} for the TiO_2 bound **15** is assigned to absorbed moisture on the film.

3. Conclusions

Silicon- and adamantane-centered tripodal pyrene sensitizers (**7a**, **7b**, and **14**) were synthesized and characterized. By adding the anchoring unit in a cross-coupling step we were able to vary the position of the functional groups, as well as increase the footprint size. The tripods based on tetraphenylsilane, **7a**, and **7b**, decomposed during hydrolysis, while the tetraphenyladamantane derivative was chemically stable and was readily converted into the corresponding acid, **15**, and bound to TiO_2 films. The compounds exhibited spectral properties typical of phenyleneethynylene-substituted pyrenes. The quenching of fluorescence of **15** on anatase TiO_2 films indicates efficient electron injection into the semiconductor. Pyrene tripods, with their characteristic excimer and exciplex emission spectra are good models for photophysical and electron transfer studies at nanoparticle interfaces. Photophysical studies of excimer and exciplex effects, solar cells studies, and a comparison with previously reported pyrene rigid rods[27] are in progress.

4. Experimental

4.1. Metal oxide thin film preparation

Colloidal anatase TiO_2 films were prepared by a previously described sol–gel technique[44] that produces mesoporous films of approximately 10 μm thickness, and that consist of nanoparticles with an average diameter of ~20 nm. Briefly, the films were prepared by casting the colloidal solutions by the doctor blade technique onto cover glass slides (VWR Scientific) over an area of 1×2 cm^2, followed by sintering at ~450 °C for 30 min. *Binding of* ***15***. Basic or acidic pretreatment of the TiO_2 films was tested, as well as non-pretreated films, but higher coverages were obtained when the films were pretreated by immersion in a pH 11 aqueous NaOH solution for 5 min, heated at 150 °C for 30 min, and cooled to 80 °C prior to immersion in the dye solution. The sensitization of the films was accomplished by overnight (~10–12 h) immersion in 0.5 mM THF solutions of **15** at room temperature. The sensitized films were thoroughly rinsed and immersed into pure THF until desorption of weakly bound sensitizer molecules was no longer detected by UV–vis.

4.2. Spectroscopy

Fourier-transform infrared attenuated total reflectance (FT-IR-ATR) measurements were collected on a Thermo Electron Corporation's Nicolet 6700 FT-IR spectrometer using ZnSe crystal. Solution UV–visible absorption measurements were acquired on a VARIAN Cary-500 spectrophotometer, in THF (Acros, spectroscopic grade). **15**/TiO_2 films were placed diagonally in a 1 cm^2 cuvette in air while recording the spectra. Fluorescence emission spectra were obtained with a VARIAN Cary-Eclipse fluorescence spectrophotometer using THF as solvent for **7a**, and **14** in a four-way transparent 1 cm^2 cuvette (λ_{ex}=360 nm). Fluorescence quantum yields for the samples (Φ_{Fl}) were performed in THF solutions deaerated by freeze-pump-thaw, using the optically dilute technique with pyrene as the reference (Φ_{Py}=0.72 in acetonitrile)[45], λ_{ex}=360 nm, using Eq. 1.

$$\Phi_{Fl} = (A_{Py}/A_s)(I_s/I_{Py})(\eta_s/\eta_{Py})^2 \Phi_{Py} \quad (1)$$

where 's' refers to the samples, 'Py' refers to reference pyrene, A is the absorbance at the excitation wavelength, I is the integrated emission area, and η is the solvent refraction index.

4.3. Synthesis

4.3.1. General. NMR spectra were obtained on a Varian INOVA 500 spectrometer operating at 499.896 MHz for ^{1}H, 125.711 MHz for ^{13}C and collected at ambient probe temperature using $CDCl_3$ as solvent unless otherwise mentioned. The chemical shifts δ are reported in parts per million relative to the residual $CHCl_3$ peak at 7.27 ppm. Coupling constants (J) are reported in Hertz with a precision of ±0.1 Hz. The ^{1}H spectra were referenced to tetramethylsilane and the ^{13}C spectra are referenced to the central line of the solvent. Melting points were measured with a Fisher melting point apparatus. High- or low-resolution mass spectra (HRMS-FAB or LRMS-FAB) were obtained at a commercial facility (Michigan State University Mass Spectrometry Facility). GC/MS data were obtained on a HP 6890 gas chromatograph with a HP 5973 MS detector. Major ions are recorded to unit mass with the percentage of the strongest peak given in parenthesis.

4.3.2. Materials. Tetrahydrofuran (THF) was purchased anhydrous (Acros) and then distilled under nitrogen from sodium benzophenone ketyl. Et_3N and $(i\text{-Pr})_2NEt$ were distilled from KOH under nitrogen prior to use. Bulk grade hexane was distilled prior to use for column chromatography. Ethyl acetate was HPLC grade and used without further purification. Flash chromatography was carried out using 230–600 mesh silica gel (Sorbent Technologies). Thin-layer chromatography was performed using aluminum backed silica gel TLC plates (Sorbent Technologies) and visualization with UV light. The following compounds were prepared according to the published literature procedures: 1,3,5,7-tetrakis (4-iodophenyl)adamantane **1**,[7] tris(4-iodophenyl)-(4′-(trimethylsilylethynyl)phenyl)-silane **3**,[28] methyl 4-ethynylbenzoate **4a**,[39] 1-iodopyrene,[46] methyl 3-ethynylbenzoate **9**,[39] and 1-ethynylpyrene **13**.[47]

4.3.3. Methods. All air and moisture sensitive reactions were carried out under nitrogen or argon atmosphere, in glassware that had been oven-dried and flamed under vacuum, and using anhydrous solvents. Standard workup procedures involved extractions with the indicated organic solvent, washing the combined extracts with brine, drying over Na_2SO_4, and removal of solvent in vacuo on a rotary evaporator.

4.3.4. *p*-Methoxybenzyl-4-ethynylbenzoate 4b. To 4-trimethylsilylethynyl-benzonate-4-methoxy-benzylester[30] (0.039 g, 0.12 mmol) in THF (3 mL) was added TBAF (0.18 mL, 0.18 mmol, 1.0 M in THF). The resulting brown solution was stirred for 1 h at room temperature and then poured into water. After standard workup with ether (3×5 mL), column chromatography with hexanes/ethyl acetate (90/10) afforded 0.026 g of **4b** as a colorless solid (86%). $R_{f\mathbf{4b}}$=0.41. Mp 66–69 °C. ^{1}H NMR ($CDCl_3$) δ 8.02 (2H, d, J=8.5 Hz), 7.54 (2H, d, J=8.5 Hz), 7.39 (2H, d, J=8.5 Hz), 6.93 (2H, d, J=9.0 Hz), 5.31 (2H, s), 3.83 (3H, s), 3.23 (1H, s). ^{13}C NMR ($CDCl_3$) δ 165.8, 159.7, 132.0, 130.3, 130.2, 129.5, 127.9, 126.7, 114.0, 82.8, 80.0, 66.8, 55.3. IR (cm^{-1}): 3271, 2959, 2157, 1695, 1455, 1314. LRMS (FAB) calcd for $C_{17}H_{14}O_3$ (M^+): 266.09, found 266.20.

4.3.5. (4-Trimethylsilylethynyl-phenyl)-tris(4-carbomethoxyphenyl-4-ethynyl-phenyl)silane 5a. A flask was charged with **3** (0.39 g, 0.48 mmol), **4a** (0.48 g, 3 mmol), $Pd(dba)_2$ (0.040 g, 0.07 mmol), PPh_3 (0.074 g, 0.28 mmol), CuI (0.027 g, 0.14 mmol), $(i\text{-Pr})_2NEt$ (3 mL), and THF (7 mL). The reaction mixture was stirred for 3 days at room temperature under nitrogen. Then the reaction mixture was poured into distilled water and filtered to remove the solid. After standard workup with ether (3×15 mL) the crude product was purified by silica gel column chromatography with hexanes/ethyl acetate (88/12) to afford 0.3 g of **5a** as a white solid (69%). $R_{f\mathbf{5a}}$=0.68. Mp 176–178 °C. ^{1}H NMR ($CDCl_3$) δ 8.01 (6H, d, J=8.5 Hz), 7.58 (6H, d, J=8.5 Hz), 7.55 (6H, d, J=8.5 Hz), 7.51 (6H, d, J=7.5 Hz), 7.27 (4H, m), 3.91 (9H, s), 0.24 (9H, s). ^{13}C NMR ($CDCl_3$) δ 166.5, 136.2, 136.0, 134.0, 133.4, 131.6, 131.4, 131.1, 129.6, 129.5, 127.7, 124.9, 124.4, 104.6, 96.0, 92.0, 90.0, 52.3, −0.1. IR (cm^{-1}): 2957, 2157, 1721, 1435, 1144. HRMS (FAB) calcd for $C_{59}H_{46}O_6Si_2$ (MH^+): 907.2912, found 907.2916.

4.3.6. (4-Trimethylsilylethynyl-phenyl)-tris(4-(*p*-methoxybenzyloxycarbonyl)phenyl-4-ethynyl-phenyl)silane 5b. A flask was charged with **3** (0.078 g, 0.096 mmol), **4b** (0.1 g, 0.38 mmol), $Pd(dba)_2$ (0.01 g, 0.017 mmol), PPh_3 (0.021 g, 0.081 mmol), CuI (7 mg, 0.036 mmol), $(i\text{-Pr})_2NEt$ (5 mL), and THF (10 mL). The reaction mixture was stirred for 2 days at room temperature under nitrogen, then poured into distilled water and filtered. After standard workup of the filtrate with ether (3×10 mL) the crude residue was purified by silica gel column chromatography with hexanes/ethyl acetate (80/20) to give 0.088 g of **5b** as a brown sticky solid (75%). $R_{f\mathbf{5b}}$=0.33. Mp 66–68 °C. ^{1}H NMR ($CDCl_3$) δ 8.05 (6H, d, J=9.0 Hz), 7.60–7.49 (22H, m), 7.41 (6H, d, J=9.0 Hz), 6.94 (6H, d, J=9.0 Hz), 5.32 (6H, s), 3.83 (9H, s), 0.27 (9H, s). ^{13}C NMR ($CDCl_3$) δ 165.9, 159.7, 136.2, 136.0, 134.0, 131.6, 131.4, 131.2, 131.1, 129.8, 129.6, 127.9, 127.8, 127.7, 124.9, 124.4, 114.0, 104.7, 96.0, 92.0, 90.0, 66.8, 55.3, −0.1. IR (cm^{-1}): 2955, 2156, 1715, 1305, 1144. HRMS (FAB) calcd for $C_{80}H_{64}O_9Si_2$ (M^+): 1224.4090, found 1224.4096.

4.3.7. (4-Ethynyl-phenyl)-tris(4-carbomethoxyphenyl-4-ethynyl-phenyl)silane 6a. A solution of **5a** (0.233 g, 0.257 mmol) in THF (10 mL) was stirred at room temperature. A mixture of TBAF (1.33 mL, 1.33 mmol, 1.0 M in THF) and acetic acid (0.075 mL, 1.33 mmol, 17.4 mol/L) was added dropwise to the solution. The solution was stirred for 45 min after the addition was completed. The reaction mixture was poured into water and after usual workup with ether (4×15 mL), the crude was purified by silica gel column chromatography with hexanes/ethyl acetate (70/30) to afford 0.181 g of **6a** as a white solid (90%). $R_{f\mathbf{6a}}$=0.59. Mp 140–143 °C. ^{1}H NMR ($CDCl_3$) δ 8.01 (6H, d, J=8.0 Hz), 7.58 (6H, d, J=8.5 Hz), 7.55 (6H, d,

J=7.5 Hz), 7.53–7.48 (10H, m), 3.91 (9H, s), 3.14 (1H, s). ^{13}C NMR ($CDCl_3$) δ 166.5, 136.2, 136.1, 134.0, 133.9, 131.7, 131.6, 131.2, 129.7, 129.5, 127.7, 124.4, 123.9, 92.0, 90.0, 83.3, 78.6, 52.3. IR (cm^{-1}): 2949, 2144, 1721, 1489, 1191. HRMS (FAB) calcd for $C_{56}H_{38}O_6Si_2$ (M^+): 834.2438, found 834.2437.

4.3.8. (4-Ethynyl-phenyl)-tris(4-(*p*-methoxybenzyloxycarbonyl)phenyl-4-ethynyl-phenyl)silane 6b. A mixture of TBAF (0.36 mL, 0.36 mmol, 1.0 M in THF) and acetic acid (21 μL, 0.36 mmol) was added to a solution of **5b** (0.088 g, 0.072 mmol) in THF (2 mL) under nitrogen, stirred for 1 h, and then poured into water. The mixture was washed with water (2×5 mL). After usual workup with dichloromethane (3×5 mL), silica gel column chromatography of the solid crude with hexanes/ethyl acetate (80/20) afforded 0.0428 g of **6b** as a yellow sticky solid (52%). $R_{f\mathbf{6b}}$=0.19. Mp 72–76 °C. ^{1}H NMR ($CDCl_3$) δ 8.05 (6H, d, J=8.0 Hz), 7.60–7.53 (22H, m), 7.41 (6H, d, J=8.5 Hz), 6.94 (6H, d, J=9.0 Hz), 5.32 (6H, s), 3.83 (9H, s), 3.17 (1H, s). ^{13}C NMR ($CDCl_3$) δ 165.9, 159.7, 136.2, 134.8, 133.9, 131.6, 131.5, 131.2, 131.1, 130.2, 129.8, 129.6, 127.9, 127.7, 124.4, 123.9, 114.0, 92.0, 90.1, 83.3, 78.6, 66.8, 55.3. IR (cm^{-1}): 2925, 2156, 1714, 1305, 1143. HRMS (FAB) calcd for $C_{77}H_{56}O_9Si$ (MH^+): 1153.3730, found 1153.3767.

4.3.9. (1-Pyrenyl-4-ethynyl-phenyl)-tris(4-carbomethoxyphenyl-4-ethynyl-phenyl)silane 7a. *Sonogashira*: A flask was charged with **6a** (0.031 g, 0.037 mmol), 1-iodopyrene[46] (0.023 g, 0.072 mmol), $Pd(dba)_2$ (3 mg, 0.005 mmol), PPh_3 (4 mg, 0.015 mmol), CuI (3 mg, 0.018 mmol), (i-Pr)$_2$NEt (5 mL), and THF (10 mL). The reaction mixture was stirred at room temperature for 2 days under nitrogen and then poured into water. After usual workup with ether (3×25 mL) the crude product was purified by silica gel column chromatography with hexanes/ethyl acetate (80/20) to afford 0.025 g of **7a** as a pale yellow solid (66%). $R_{f\mathbf{7a}}$=0.38. Mp 135–138 °C. ^{1}H NMR ($CDCl_3$) δ 8.65 (1H, d, J=9.0 Hz), 8.23–8.18 (4H, m), 8.13 (1H, d, J=8.0 Hz), 8.10 (1H, d, J=8.5 Hz), 8.05 (2H, d, J=9.0 Hz), 8.01 (6H, d, J=7.5 Hz), 7.75 (2H, d, J=8.0 Hz), 7.61–7.58 (20H, m), 3.92 (9H, s). ^{13}C NMR ($CDCl_3$) δ 166.5, 136.3, 136.2, 134.0, 133.3, 132.0, 131.6, 131.4, 131.3, 131.2, 131.1, 131.0, 129.8, 129.7, 129.5, 128.5, 128.3, 127.7, 127.2, 126.3, 125.8, 125.7, 125.4, 125.3, 124.6, 124.5, 124.4, 124.3, 117.4, 94.8, 92.0, 90.2, 90.0, 52.3. IR (cm^{-1}): 2925, 2255, 1721, 1434, 1190. HRMS (FAB) calcd for $C_{72}H_{46}O_6Si$ (MH^+): 1035.3143, found 1035.3139. *Suzuki*: A solution of **6a** (0.28 g, 0.33 mmol) in THF (15 mL) was cooled to −78 °C with stirring. Lithium bis(trimethylsilyl) amide (0.36 mL, 0.36 mmol, 1.0 M in hexane) was added dropwise to the solution via a syringe pump (1.96 mL/h). The resulting pale yellow solution was stirred at −78 °C for 30 min, followed by the addition of B-methoxy-9-BBN (0.36 mL, 0.36 mmol, 1.0 M in hexane), dropwise via a syringe pump (1.96 mL/h). The solution was stirred for 2 h after the addition was completed and then transferred via cannula to a second flask containing a mixture of $Pd(PPh_3)_4$ (0.129 g, 0.11 mmol) and 1-iodopyrene (0.14 g, 0.04 mmol) in THF (15 mL) at room temperature. The reaction mixture was refluxed for 2 days, then allowed to cool to room temperature and poured into water. After workup with ether (3×25 mL), purification by silica gel column chromatography with hexanes/ethyl acetate (80/20) gave 0.14 g of **7a** as a pale yellow solid (41%).

4.3.10. (1-Pyrenyl-4-ethynyl-phenyl)-tris(4-(*p*-methoxybenzyloxycarbonyl)phenyl-4-ethynyl-phenyl)silane 7b. A flask was charged with **6b** (0.030 g, 0.026 mmol), 1-iodopyrene (0.128 g, 0.039 mmol), $Pd(dba)_2$ (1 mg, 0.002 mmol), PPh_3 (2 mg, 0.007 mmol), CuI (0.7 mg, 0.004 mmol), (i-Pr)$_2$NEt (10 mL), and THF (5 mL). The reaction mixture was stirred at room temperature for 24 h under nitrogen, and then poured into water. After usual workup with dichloromethane (2×5 mL), purification by silica gel column chromatography of the crude residue with hexanes/ethyl acetate (70/30) gave 0.028 g of **7b** as a brown sticky solid (76%). $R_{f\mathbf{7b}}$=0.59. Mp 66–69 °C. ^{1}H NMR ($CDCl_3$) δ 8.68 (1H, d, J=8.5 Hz), 8.26–8.20 (4H, m), 8.17–8.12 (2H, m), 8.09–8.05 (9H, m), 7.77 (2H, d, J=8.0 Hz), 7.64–7.59 (19H, m), 7.41 (6H, d, J=8.5 Hz), 6.94 (6H, d, J=8.5 Hz), 5.32 (6H, s), 3.83 (9H, s). ^{13}C NMR ($CDCl_3$) δ 166.2, 159.9, 138.0, 136.6, 136.5, 136.2, 134.3, 133.5, 131.8, 131.7, 131.5, 131.4, 131.3, 131.2, 130.4, 130.0, 129.9, 129.2, 128.7, 128.6, 128.2, 128.0, 127.5, 126.8, 126.5, 126.0, 125.7, 125.6, 124.9, 124.8, 124.7, 124.5, 117.7, 95.0, 92.3, 90.4, 90.3, 67.0, 55.5. IR (cm^{-1}): 2955, 2156, 1714, 1514, 1246. HRMS (FAB) calcd for $C_{93}H_{64}O_9Si$ (M^+): 1352.4320, found 1352.4328.

4.3.11. 1-(4-Iodophenyl)-3,5,7-(3-carbomethoxyphenyl-4-ethynyl-phenyl)adamantane 10. A flask was charged with **1** (0.25 g, 0.27 mmol), **9** (0.44 g, 2.73 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 0.008 mmol), CuI (2.4 mg, 0.013 mmol), (i-Pr)$_2$NEt (10 mL), and THF (5 mL). The reaction mixture was stirred for 2 days at room temperature under nitrogen, then poured into distilled water, and filtered. After standard workup of the filtrate with dichloromethane (3×10 mL) the crude residue was purified by silica gel column chromatography with hexanes/ethyl acetate (80/20) to give 0.039 g of **10** as a white solid (22%). $R_{f\mathbf{10}}$=0.14. Mp 88–92 °C. ^{1}H NMR ($CDCl_3$) δ 8.25 (2H, s), 8.03 (2H, d, J=6.5 Hz), 7.73–7.68 (5H, m), 7.59–7.57 (7H, m), 7.50–7.46 (8H, m), 7.29–7.22 (4H, m), 3.97 (9H, s), 2.16 (12H, two s). ^{13}C NMR ($CDCl_3$) δ 166.4, 149.4, 148.6, 137.5, 135.7, 132.7, 131.8, 131.7, 130.4, 129.2, 128.5, 127.2, 125.1, 123.7, 120.8, 90.1, 88.2, 52.3, 46.7, 39.3, 39.1, 29.7. IR (cm^{-1}): 2923, 2208, 1723, 1509, 1257. HRMS (FAB) calcd for $C_{64}H_{49}IO_6$ (MH^+): 1041.2649, found 1041.2659. Also isolated were **11** and **12** both as white solids. Compound **11**: 0.074 g (28%). $R_{f\mathbf{11}}$=0.17. Mp 83–85 °C. ^{1}H NMR ($CDCl_3$) δ 8.23 (2H, s), 8.01 (2H, d, J=7.5 Hz), 7.72–7.68 (5H, m), 7.55 (4H, d, J=8.0 Hz), 7.47–7.42 (8H, m), 7.22 (3H, d, J=8.5 Hz), 3.95 (6H, s), 2.11 (12H, two s). ^{13}C NMR ($CDCl_3$) δ 166.4, 149.2, 148.5, 137.4, 135.6, 132.7, 131.7, 130.4, 129.1, 128.5, 127.1, 125.1, 125.0, 123.7, 120.8, 90.1, 88.2, 52.3, 46.7, 46.6, 39.2, 39.0, 29.6. IR (cm^{-1}): 2924, 2206, 1720, 1508, 1255. LRMS (FAB) calcd for $C_{54}H_{42}I_2O_4$ (MH^+): 1009.1, found 1009.3. Compound **12**: 0.021 g (7%). $R_{f\mathbf{12}}$=0.11. Mp 97–99 °C. ^{1}H NMR ($CDCl_3$) δ 8.23 (4H, s), 8.00 (8H, d, J=7.5 Hz), 7.73 (8H, d, J=7.5 Hz), 7.57 (4H, d, J=8.5 Hz), 7.51 (4H, d, J=8.0 Hz), 7.44 (4H, t, J=8.0 Hz), 3.95 (12H, s), 2.19 (12H, s). ^{13}C NMR ($CDCl_3$) δ 166.4, 149.4, 135.7, 132.7, 131.8, 130.4, 129.1, 128.5, 125.2, 123.8, 120.8, 90.2, 88.2, 52.3, 46.8, 39.3. IR (cm^{-1}): 2925, 2204, 1720, 1501, 1249.

LRMS (FAB) calcd for $C_{74}H_{56}O_8$ (M^+): 1072.3, found 1072.2.

4.3.12. 1-(1-Pyrenyl-4-ethynyl-phenyl)-3,5,7-(3-carbomethoxyphenyl-4-ethynyl-phenyl)adamantane 14. A flask was charged with **10** (0.068 g, 0.065 mmol), 1-ethynylpyrene **13**[47] (0.030 g, 0.130 mmol), $Pd_2(dba)_3$ (0.030 g, 0.032 mmol), (*o*-tolyl)$_3$P (0.060 g, 0.196 mmol), Et_3N (10 mL), and THF (20 mL). The reaction mixture was stirred at 60 °C for 24 h under nitrogen, then cooled, poured into distilled water, and filtered. After usual workup with dichloromethane (3×10 mL) the residue was purified by silica gel column chromatography using hexanes/ethyl acetate (80/20) to give 0.028 g of **14** as a pale yellow solid (38%). R_{f14}=0.28. Mp 130–134 °C. ^{1}H NMR ($CDCl_3$) δ 8.69 (1H, d, J=9.0 Hz), 8.24–8.00 (14H, m), 7.75–7.72 (5H, m), 7.59–7.51 (9H, m), 7.46–7.43 (8H, m), 3.86 (9H, s), 2.12 (12H, two s). ^{13}C NMR ($CDCl_3$) δ 166.4, 149.5, 149.3, 135.7, 132.7, 131.9, 131.8, 131.7, 131.3, 131.2, 131.1, 130.4, 129.6, 129.3, 129.2, 128.5, 128.3, 128.1, 127.3, 126.2, 125.7, 125.6, 125.3, 125.2, 125.1, 124.5, 124.3, 123.8, 121.5, 120.9, 117.9, 95.0, 90.2, 88.6, 88.2, 52.3, 52.1, 46.8, 39.4, 39.3. IR (cm^{-1}): 2923, 2208, 1721, 1510, 1257. HRMS (FAB) calcd for $C_{82}H_{58}O_6$ (MH^+): 1139.4309, found 1139.4315.

4.3.13. 1-(1-Pyrenyl-4-ethynyl-phenyl)-3,5,7-(3-carboxyphenyl-4-ethynyl-phenyl)adamantane 15. To methyl ester **14** (0.02 g, 0.017 mmol) in THF (4 mL) was added 1.0 N NaOH (1 mL) and the solution was stirred at room temperature overnight. The basic aqueous layer was extracted with dichloromethane, followed by the dropwise addition of 1.0 N HCl. Upon acidification, a precipitate was formed. This was filtered to afford **15** as a pale yellow solid (0.018 g, 83%). Mp 250–255 °C. ^{1}H NMR (THF) δ 8.69 (1H, d, J=9.0 Hz), 8.28–7.98 (14H, m), 7.73–7.66 (5H, m), 7.58–7.56 (9H, m), 7.48–7.45 (8H, m), 2.27 (12H, two s). ^{13}C NMR (THF) δ 167.3, 150.1, 149.6, 137.2, 135.8, 133.7, 133.2, 132.9, 132.6, 132.4, 131.9, 131.1, 130.4, 129.1, 128.7, 128.5, 128.0, 127.6, 127.2, 126.7, 125.8, 125.6, 125.3, 125.1, 125.0, 124.7, 124.4, 124.0, 122.9, 121.8, 118.6, 94.9, 91.4, 89.0, 88.6, 48.3, 45.4, 39.9, 38.7. IR (cm^{-1}): 3038, 2925, 2211, 1697, 1510, 1257. HRMS (FAB) calcd for $C_{79}H_{52}O_6$ (MH^+): 1097.3839, found 1097.3848.

Acknowledgements

Support of this research by the National Science Foundation, NIRT-0303829 is gratefully acknowledged.

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