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Tripodal pyrene chromophores for semiconductor sensitization: new footprint design

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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

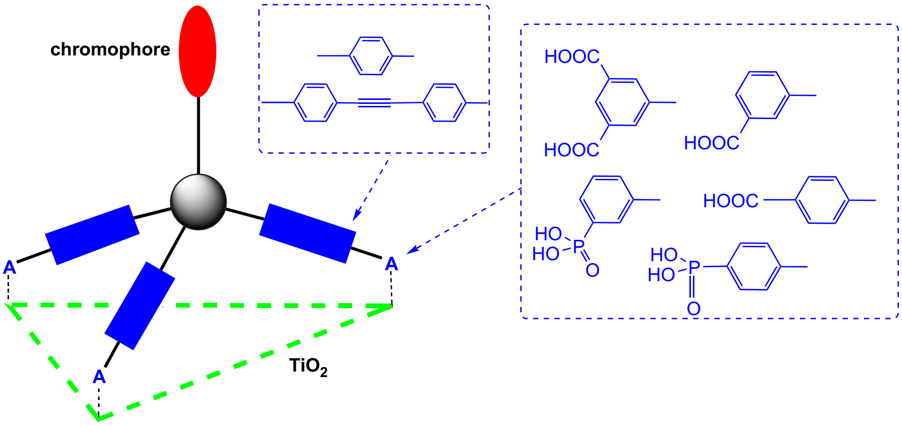

Figure 1. Schematic representation of the strategy: footprint size and possible anchoring group modifications.

Keywords: Tripods; Pyrene; Semiconductor nanoparticles; Sensitization; Titanium dioxide.

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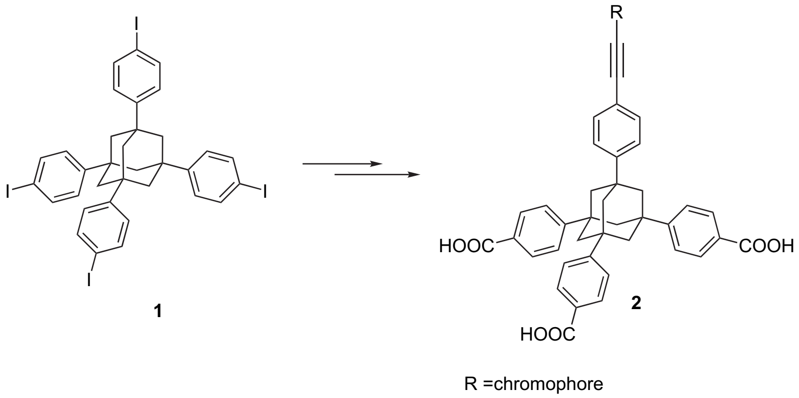


Scheme 1. Multistep synthesis of tripodal sensitizers.[6,7]

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.

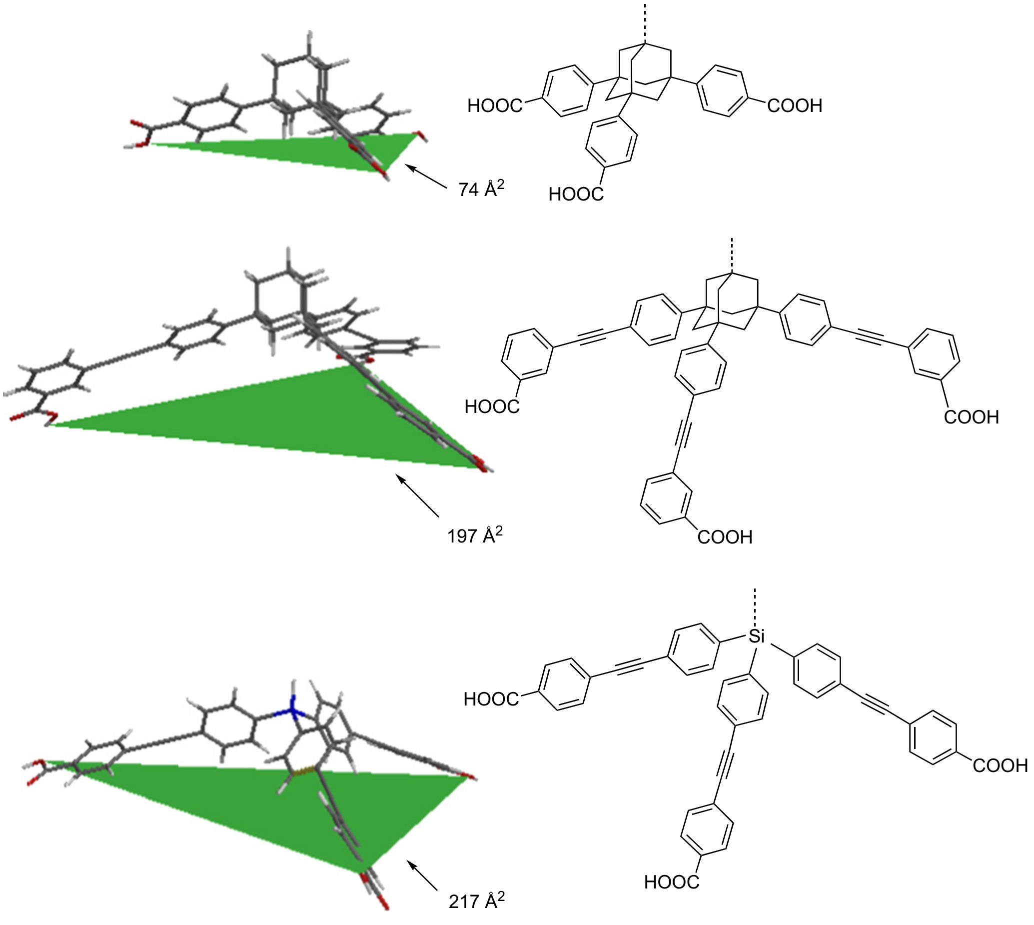


Figure 2. Comparison between the footprint size of various tripodal linkers.

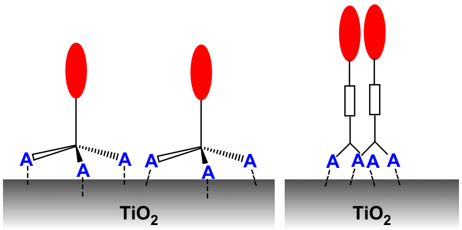


Chart 1.

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]

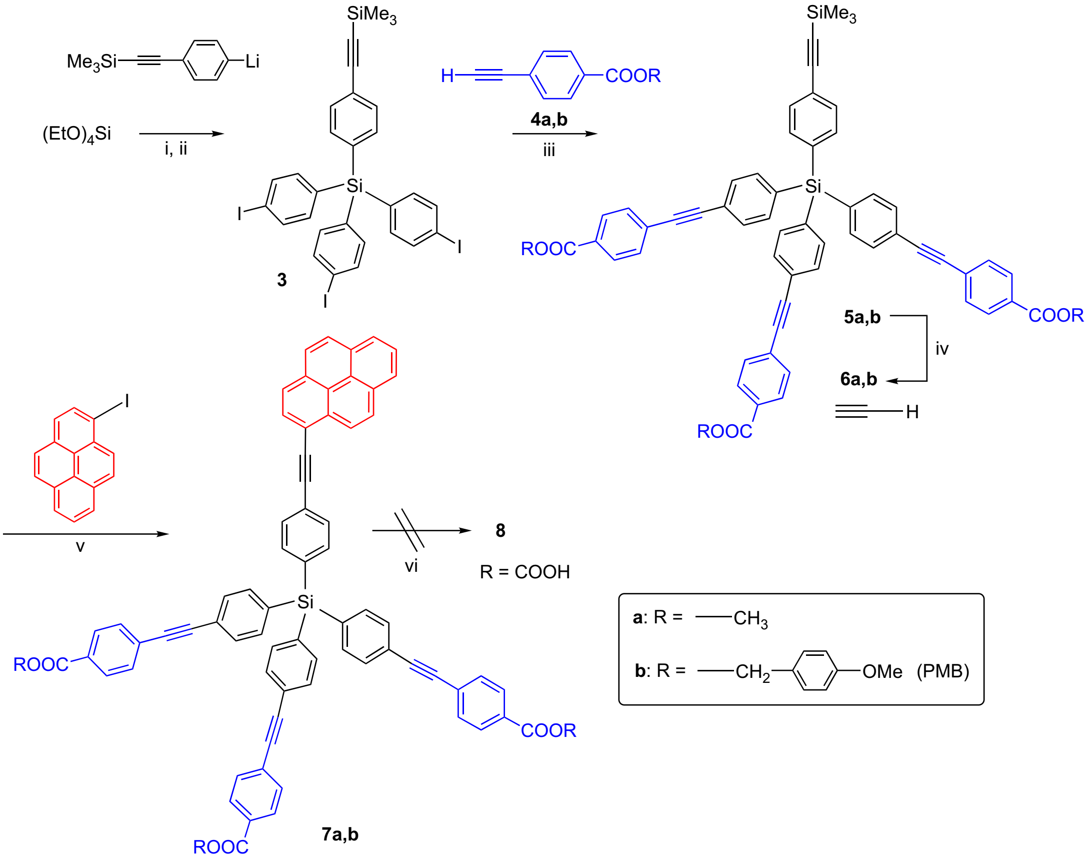
Organic dyes containing π-conjugated systems tend to stack through π–π interactions on the surface of the semiconductor,[18] resulting in shifts in the absorption spectra and formation of excimers. Aggregation on TiO_2 influences most applications, and usually decreases the performance of solar cells 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

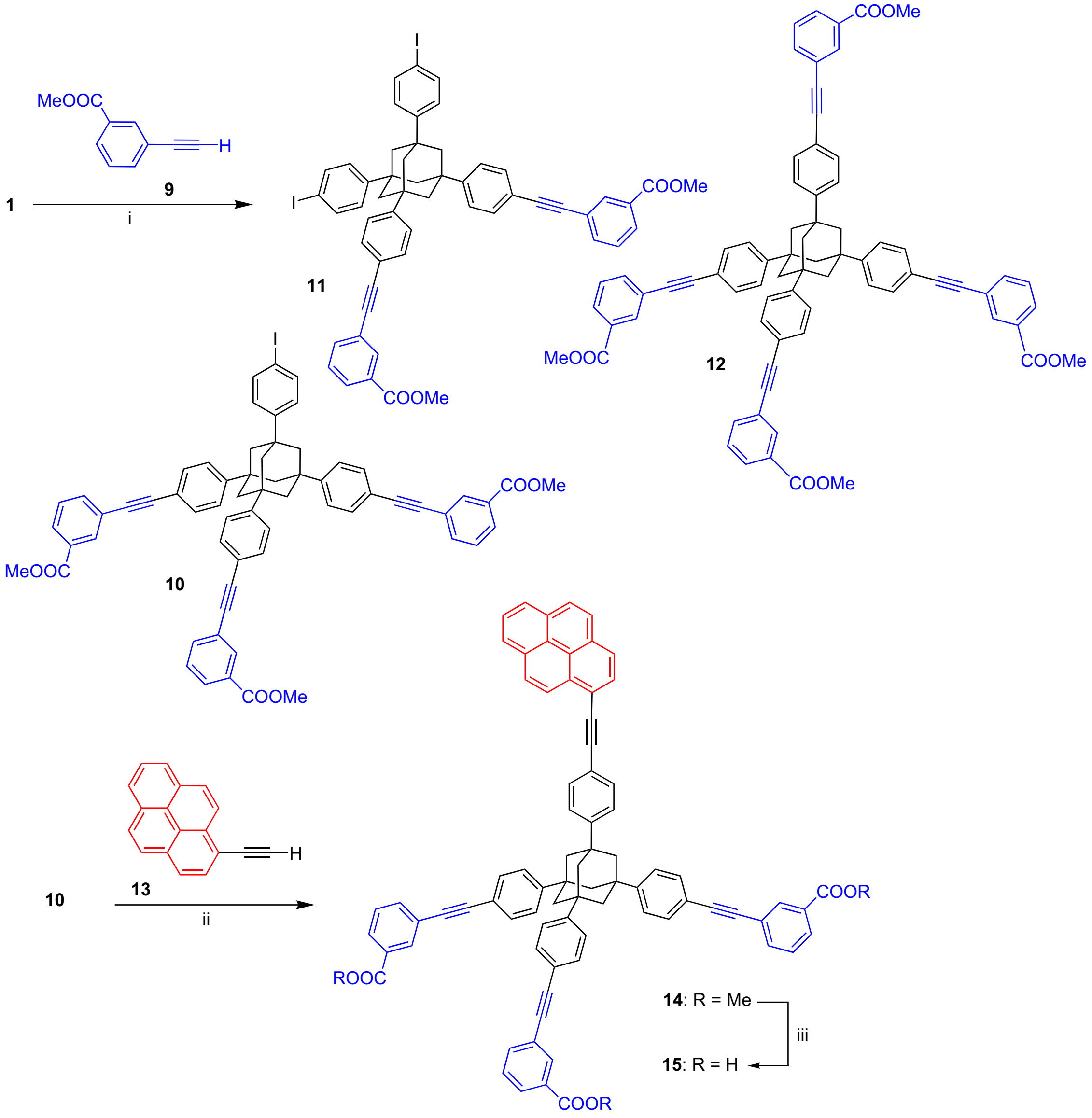
In this paper we describe the synthesis of silicon- and adamantane-centered tripods with larger footprints and variable position of the anchoring groups (Fig. 2). Pyrene was selected as the chromophore to make comparisons with the reported pyrene-substituted rigid rods.[27] Silicon-centered tripods **7a**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

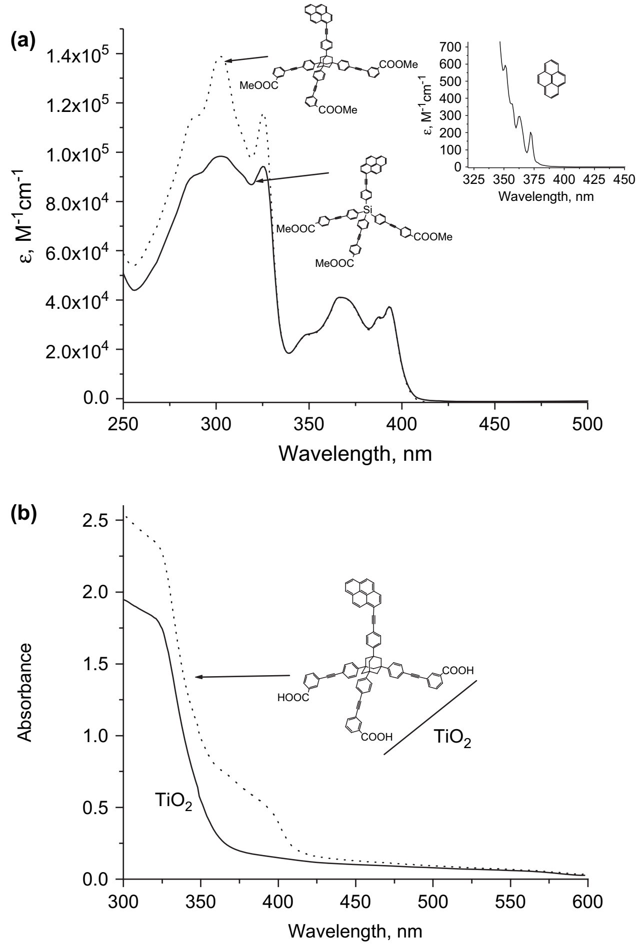


Figure 3. (a) Absorption spectra of **7a** (solid line) and **14** (dotted line) in THF. Inset: absorption spectrum of pyrene in THF. (b) Absorption spectrum of **15** bound to TiO_2/glass (dotted line) and the reference TiO_2/glass (solid line).

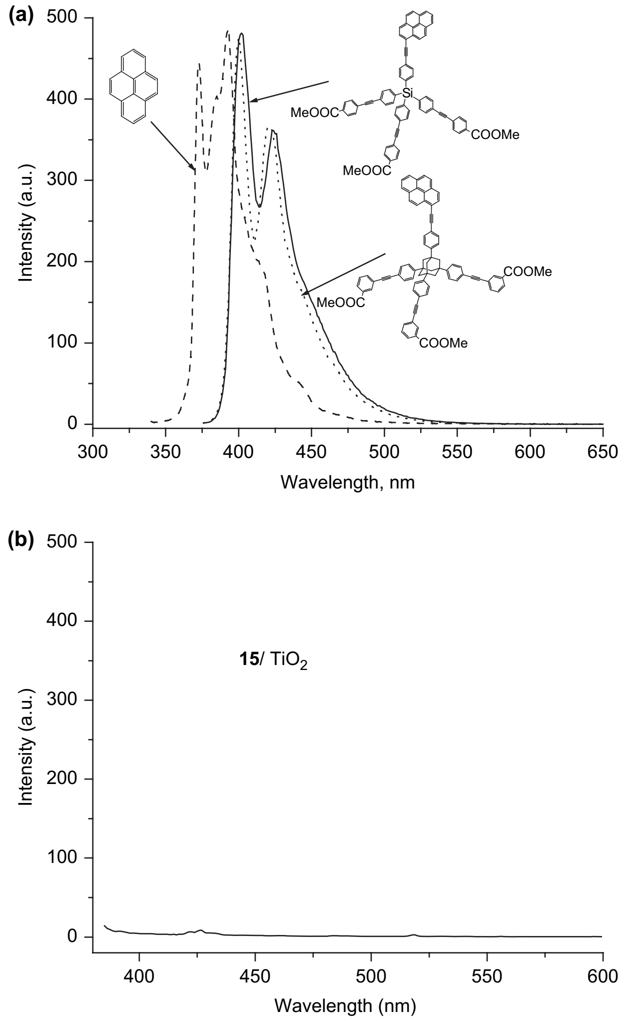


Figure 4. (a) Normalized fluorescence emission spectra of **7a** (solid line), **14** (dotted line), and pyrene (dashed line) in solution. In all the cases, the solvent was THF. λ_{ex}=360 nm (for **7a** and **14**) and 335 nm (for pyrene). (b) Fluorescence quenching of **15** bound to TiO_2. λ_{ex}=380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

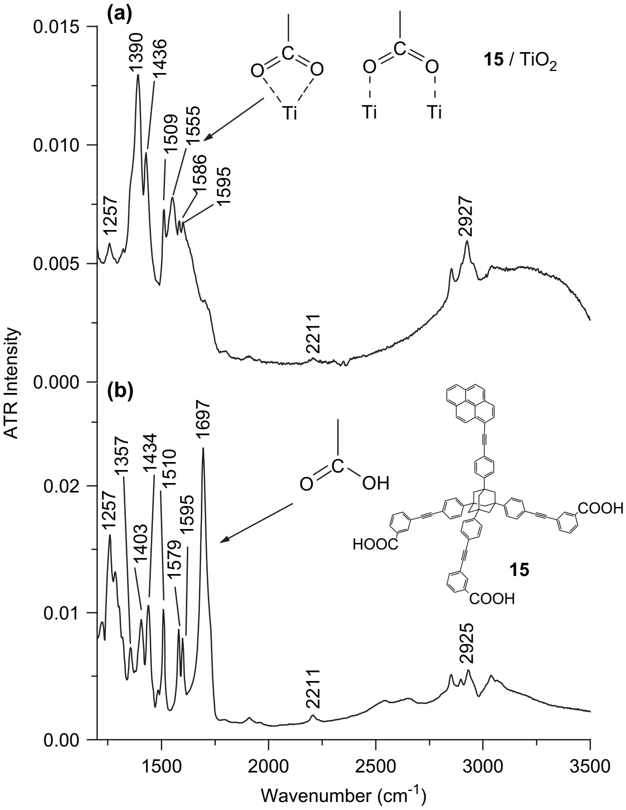


Figure 5. FT-IR-ATR spectra of (a) **15** bound to TiO_2 (pH 11 pretreated) and (b) **15** in the solid state. The broad band observed at ~3000 cm^{-1} for the TiO_2 bound **15** is assigned to absorbed moisture on the film.

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.

$$\Phi_{\rm Fl} = \left(A_{\rm Py}/A_{\rm s}\right)\left(I_{\rm s}/I_{\rm Py}\right)\left(\eta_{\rm s}/\eta_{\rm Py}\right)^2\Phi_{\rm Py} \quad (1)$$

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$_3$)$_2$Cl$_2$ (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%). $R_{f\mathbf{14}}$=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.

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