Tetrahedron 66 (2010) 3897–3903

Contents lists available at ScienceDirect

Tetrahedron

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

Modular synthesis of ruthenium tripodal system with variable anchoring groups positions for semiconductor sensitization

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ARTICLE INFO

Article history:
Received 24 January 2010
Received in revised form 31 March 2010
Accepted 1 April 2010
Available online 7 April 2010

Keywords:
Tripods
Semiconductor nanoparticles
Titanium dioxide
Ruthenium(II) bipyridine

ABSTRACT

We describe an improved synthetic approach to access tripodal compounds with variable footprints and anchor groups. Two ruthenium(II) bipyridine tripodal complexes with three carboxylic acid groups in *meta* (**Ru-*m*-COOH**, **1**) and *para* (**Ru-*p*-COOH**, **2**) positions, and with large (180–250 Å^2) footprints were synthesized and bound to the surface of nanostructured TiO_2. Selected properties of **1** and **2** in solution and bound are reported.

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1. Introduction

Recent years have seen a surge in interest in the design of model dyes–linker–anchor molecules to study electron transfer across molecule-nanocrystalline semiconductor interfaces.[1] The molecule/metal oxide (MO_n) interface is important for the development of dye-sensitized solar cells, photocatalysts, sensors, and other devices. Dyes with tripodal linkers,[2,3] and other useful adamantyl-centered or tetrahedrally symmetrical molecules[4] have attracted much interest to interface redox-active or photo-active molecules with various surfaces (semiconductors, metals, nanoparticles, quantum dots etc.) because of the binding control that can be achieved through such linker units. More recently, we studied dye–dye interactions on the surface of semiconductor nanoparticles and other surfaces using large footprint tripods capped with pyrene.[5,6] This kind of molecule-tripodal linker models are also finding application as novel photochromic materials,[4a] and for the chemical modification of probes used for atomic force microscopy (AFM).[3d,4d] In general, the synthesis and purification of tripodal compounds are lengthy, proceed in low-yields, and it is difficult to vary the footprint sizes or the anchoring groups. Here we describe a more general approach to these kind of systems and an improved, three-steps synthesis of adamantyl-centered Ru(II) bipyridine complexes with large footprints and variable positions of the anchoring groups, shown in Figure 1. The larger footprints with

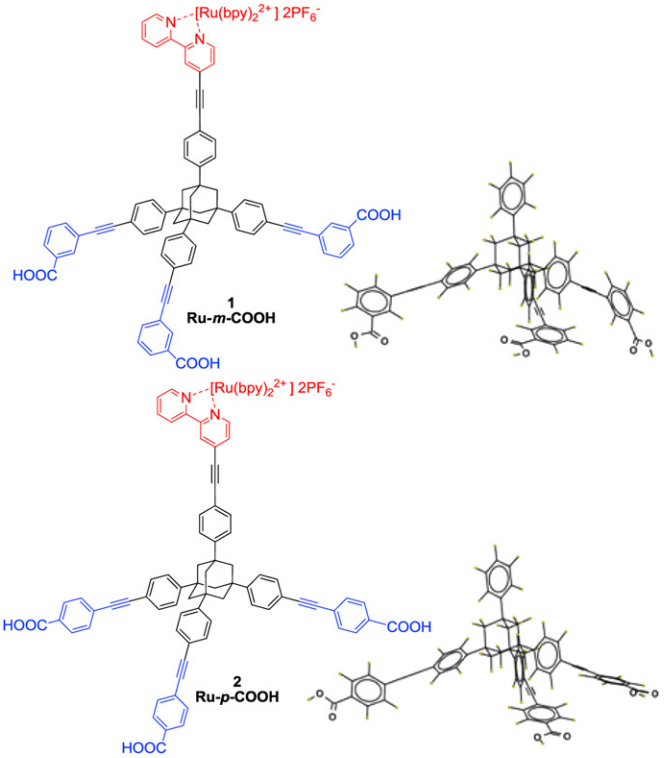

Figure 1. Structures and minimized geometry of the anchor units (Spartan '08) for **1** and **2**. The footprint area is ~180 Å^2 for **1** and ~250 Å^2 for **2**, estimated by selecting the three oxygens of the OH groups to define the plane.

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0040-4020/$ – see front matter Published by Elsevier Ltd.
doi:10.1016/j.tet.2010.04.005

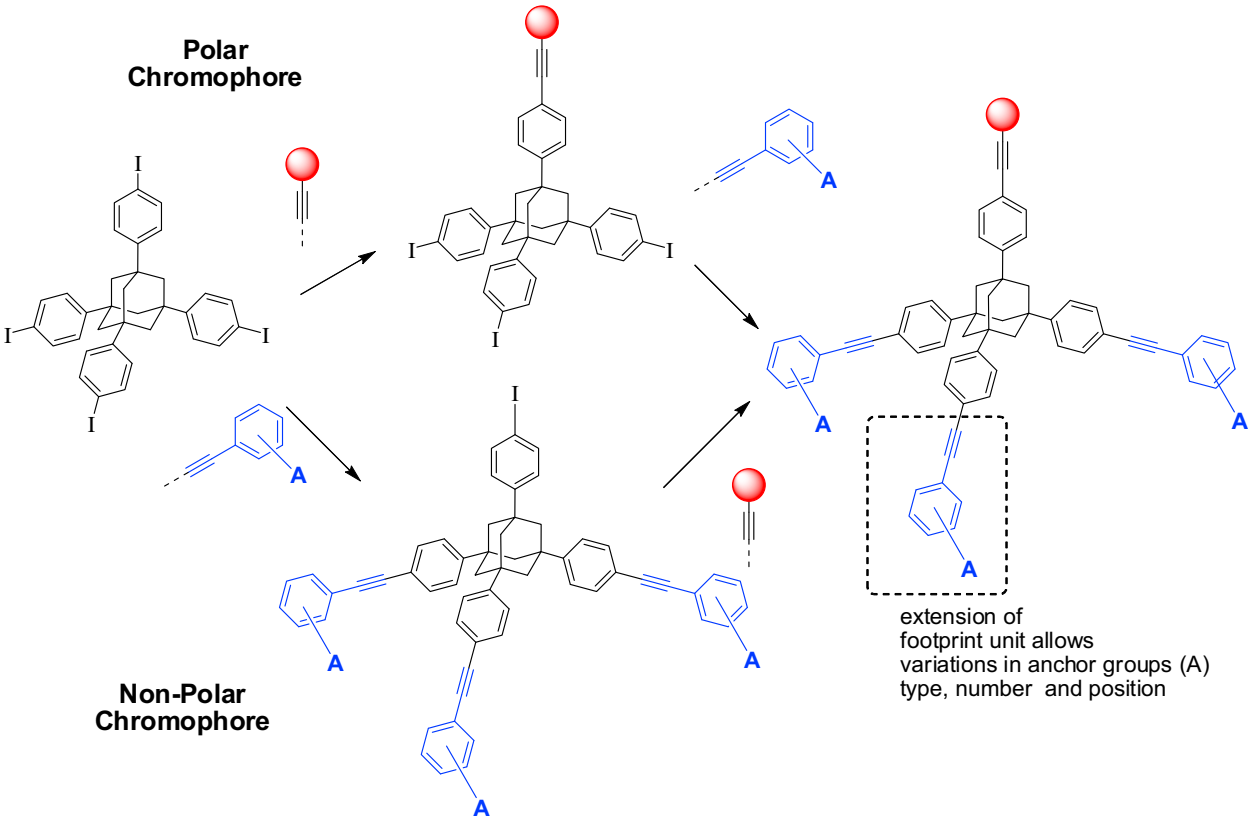
meta (**Ru-*m*-COOH**, **1**) and *para* (**Ru-*p*-COOH**, **2**) carboxylic acid anchoring groups were designed to compare the effect of different bite angles on planar, crystalline metal oxide semiconductor surfaces (TiO_2(110) and ZnO), and the effect of footprint sizes on injection and recombination dynamics on nanostructured metal oxide materials.

The synthesis of a tetrahedral compound with one branch different from the other three involves a low-yielding statistical step with a rather difficult separation of a crude mixture of mono-, di-, tri-, and tetra-substituted products. Based on the synthesis described in this paper and our previous work[5] we conclude that a good strategy, summarized in Scheme 1, is to add the chromophore (or ligand) first, when the chromophore (or ligand) is polar, and to add the anchor unit first, when the chromophore is non polar (for instance, 1-ethynyl-pyrene).[5] The separation by silica gel column chromatography of polar products formed in the statistical step was easier. Low conversions were preferred, because the formation of tri- and tetra-substituted products is avoided, and any unreacted starting material can be recycled. Hence, a ~1:1 ratio of the cross-coupling reagents **3** and 4-ethynyl-2,2′-bipyridine was used. In addition, the modular strategy illustrated in Scheme 1, involves two Sonogashira coupling reactions, and avoids the use of organolithium reagents as a way to introduce the anchoring units (i.e., metal–halogen exchange followed by carbon dioxide quenching, as in the older syntheses).[2] Finally, in this approach, the addition of the three anchoring units by a Pd-catalyzed cross coupling reaction allows controlling the footprint size, as well as the number, type and position of the functional groups that bind to the surface (groups A in Scheme 1).

2. Results and discussion

2.1. Synthesis

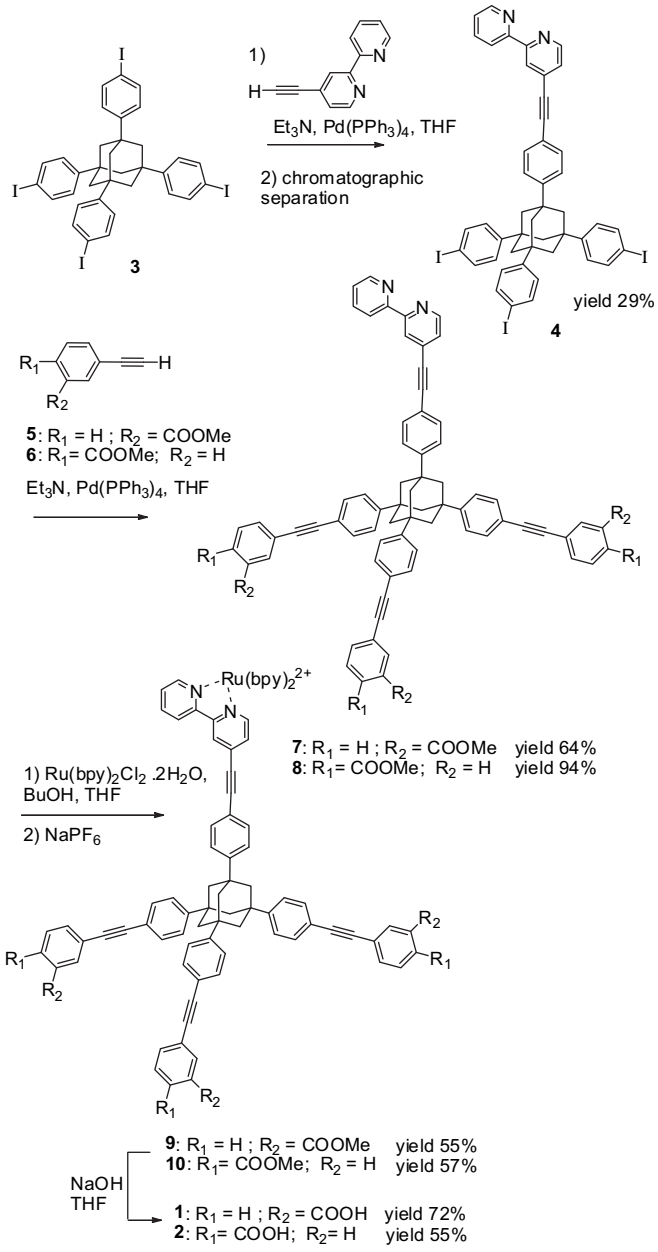
The three-step approach to **Ru-*m*-COOH** (**1**) and **Ru-*p*-COOH** (**2**) is shown in Scheme 2. The ligand unit 4-ethynyl-2,2′-bipyridine[7] was cross-coupled in Sonogashira conditions with 1,3,5,7-tetrakis(4-iodophenyl)adamantane **3**.[8] By using a nearly equimolar amount of **3** and 4-ethynyl-2,2′-bipyridine (1:0.8, respectively), mono-substituted **4** was the major cross-coupling product. A small amount of di-substituted product and mostly unreacted starting material **3**, which was recovered and recycled, were the other major products. Only traces of the tri- substituted derivative was isolated in this step, and no tetrasubstituted product was observed.



Scheme 1. Approaches to tripodal chromophoric compounds.

The products were separated by column chromatography, and **4** was isolated in 29% yield. Anchor groups 3- or 4-ethynylbenzoic acid methyl esters, **5** or **6**,[5,9] were cross-coupled with **4** to form **7** and **8**, respectively. Formation of the Ru(II) complexes **9** and **10**, followed by basic hydrolysis of the ester groups gave **1** and **2**, respectively. Total yields from **3** were modest (~10%) but the easier isolation of useful intermediate **4**, and the short synthetic path allowed the synthesis of the final products in half-gram amounts.

Esters **9** and **10** were soluble in THF, acetonitrile, and other organic solvents. Carboxylic acids **1** and **2**, however, were sparingly soluble in common organic solvents. We found (MS analysis) that the excess $HCl_{(aq)}$ used to precipitate the acid after the basic hydrolysis of the esters exchanged the PF_6^- counter ions with Cl^-, resulting in less soluble ruthenium(II) complexes. Compounds **1** and **2** were then dissolved in aqueous base in the presence of $NaPF_6$ in excess, and precipitated by cautious addition of dilute $HCl_{(aq)}$.



Scheme 2. Synthesis of **Ru-*m*-COOH** (**1**) and **Ru-*p*-COOH** (**2**).

The precipitate was filtered, washed with water, and dried in vacuo. After this step, both carboxylic acids products **1** and **2** were soluble in acetonitrile and THF. MS and elemental analyses indicated that **1** and **2** were Ru(II) complexes PF_6^- salts.

The hydrolysis of methyl esters **9** and **10** to carboxylic acids **1** and **2**, respectively, was monitored by ^1H, ^{13}C and DEPT NMR. The disappearance of the characteristic ^1H and ^{13}C signal of the methyl ester group (–OMe) in the final product was consistent with complete hydrolysis of the ester group. The carbonyl stretching band in the IR spectra shifted about 20 wave numbers to lower energies from ν(C=O)=1723 cm^{-1} for ester **9** to 1705 cm^{-1} for carboxylic acid **1**.

2.2. ^1H NMR

The formation of mono-substituted **4** in the coupling of 4-ethynyl-2,2′-bipyridine with **3** was monitored by ^1H NMR. In the spectrum of the tetrahedrally symmetric starting material, 1,3,5,7-tetrakis(4-iodophenyl)adamantane (**3**),[8] in Figure 2a, the two doublets were assigned to the eight aromatic protons (δ 7.68 and 7.21 ppm) in *ortho* to the *iodo*-substituted position on the four phenyl rings, and the Hc protons of the adamantane unit were observed as a singlet in the aliphatic region (δ 2.1 ppm, 12H).

In the spectrum of the isolated mono-substituted product **4**, in Figure 2b, a set of seven signals appeared in the aromatic region, which is characteristic of the bipyridyl ring (δ 7.3–8.7 ppm). Because of the lower symmetry of **4**, the twelve Hc protons of the adamantane unit split in two singlets (δ 2.0 and 2.1 ppm), and a new set of two doublets in the aromatic region (δ 7.5 and 7.4, He/f, 4H) was assigned to the phenyl group with the ligand unit. The chemical shift and coupling of the protons assigned to the *iodo*-substituted rings were unchanged.

2.3. Solution properties and binding studies

Selected properties of complexes **1** and **2** were studied in solution and bound to TiO_2 nanoparticle films, and are summarized

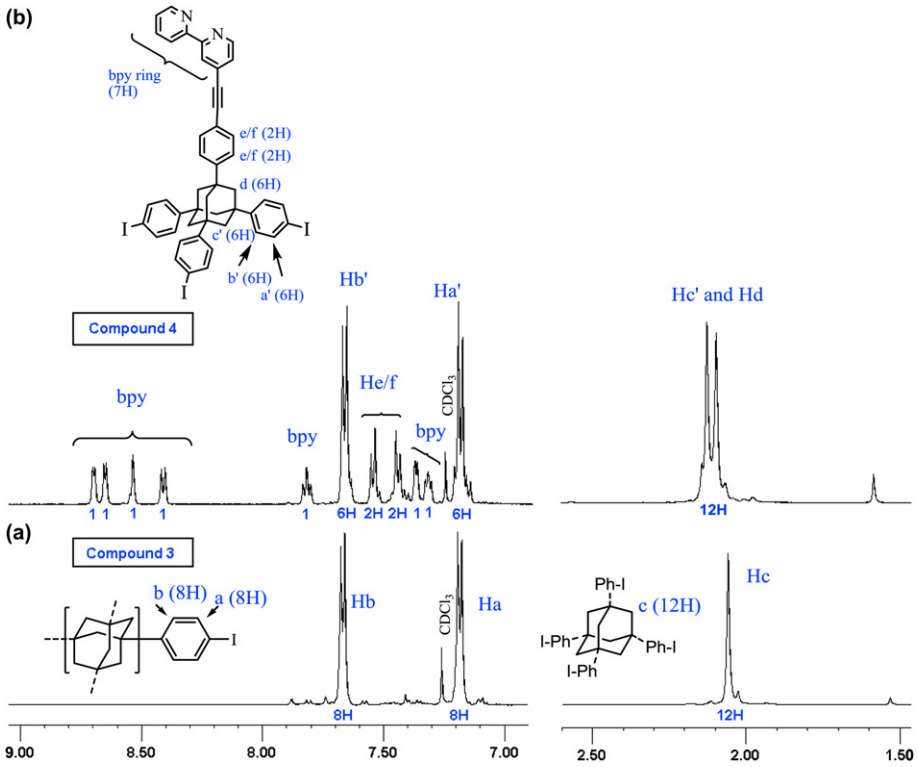


Figure 2. Selected region in the ^{1}H NMR spectra of **3** and **4** in $CDCl_3$. Expanded regions for the shown spectra are reported in the Supporting data.

in Table 1. The UV–vis absorption and fluorescence spectra of THF solutions of methyl esters **9**, **10**, and carboxylic acids **1** and **2** are shown in an overlay in Figure 3.

tripodal sensitizers with phenylenethynylene bridges.[10] The presence of the phenylenethynylene bridges resulted in $E_{1/2}$ $Ru^{III/II}$ waves in **9** and **10** that are shifted to slightly more positive

Table 1
Selected properties of esters **9**, **10**, acids **1**, **2**, and a reference Ru(II) complex[a]

Compound	λ_{max} (ε, $M^{-1}cm^{-1}$)	λ_{PL} (nm)	Φ_{PL} $\times10^{-2}$	$\nu_{as(C=O)}$ (cm^{-1})	$E_{1/2}$ $Ru^{III/II}$ (mV)[b]	$E_{1/2}$ $Ru^{2+/+}$ (mV)[b]	$E_{1/2}$ $Ru^{+/0}$ (mV)[b]	$E_{1/2}$ $Ru^{III/II*}$ (mV)[b]
$Ru(bpy)_3^{2+}$[c]	452	626			1260	−1340	−1520	−860
Ru-*m*-COOMe 9	462 (1.5×10^4)	643	4.8	1723	1365	−1435	−1555	−895
Ru-*p*-COOMe 10	463 (1.7×10^4)	644	5.6	1720	1330	−1346	−1648	−922
Ru-*m*-COOH 1	461 (1.5×10^4)	645	4.6	1705				
Ru-*p*-COOH 2	462 (1.6×10^4)	644	4.6	1701				

[a] All measurements were performed at room temperature.
[b] Data (±20 mV) were measured at a glassy carbon working electrode in 0.1 M Bu_4NPF_6/MeCN solution using Ag/AgCl as the reference electrode and Pt as the counter electrode.
[c] From Ref. 10.

All compounds exhibited the characteristic, broad MLCT band centered at 450 nm in their absorption spectra, and the fluorescence emission band at λ_{maxFL}=644 nm in their emission spectra. The key difference between the *meta* and the *para* tripods is the presence of intense π–π* transition bands at ~322 nm in the absorption spectra of *para* derivatives **10** and **2**, assigned to the conjugation effect of the –COOH anchoring units in *para* position. No shifts of the λ_{maxFL} in the emission spectra of **1**, **2**, **9**, and **10** were observed.

Esters **9** and **10** displayed semi-reversible $Ru^{III/II}$ reductions in acetonitrile solution, Figure 4 and Table 1. Both **9** and **10** exhibited $Ru^{III/II}$ reduction potentials at ~1.3 V vs Ag/AgCl that were, within experimental error, the same as those reported previously for potentials, compared to the reference compound $Ru(bpy)_3^{2+}$.[10] The excited state reduction potentials were nearly identical to those obtained for related bpy-based tripods.

The binding of **1** and **2** to TiO_2 (anatase) nanoparticle films on glass prepared according to literature procedures[11] was done by immersing the films in 0.5 mM THF solutions of acids **1** and **2** for one day. After that, the sensitized films were immersed in neat THF, with stirring, until no leaching of dyes was observed in the UV–vis absorption spectra of the solvent. Upon binding to TiO_2, fluorescence quenching was observed for both **1** and **2** (Fig. 5). The quenching of fluorescence is indicative of electron injection into the semiconductor.

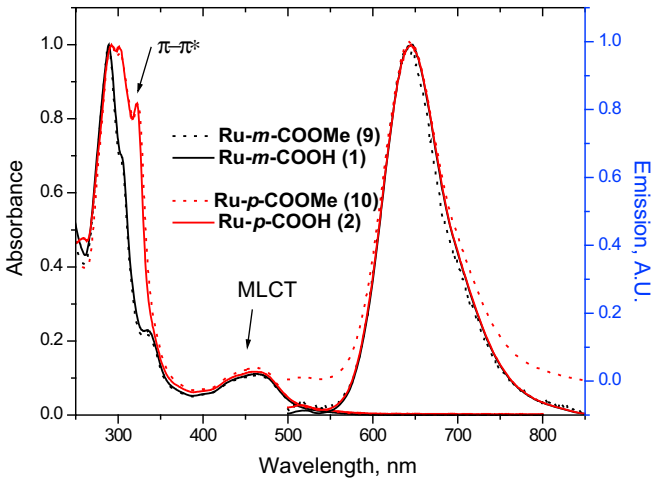


Figure 3. Normalized UV–vis spectra and fluorescence emission spectra (λ_{exc}=430 nm) of *meta* compounds (ester **9** (black dotted line) and carboxylic acid **1** (black solid line)), and *para* compounds (ester **10** (red dotted line) and carboxylic acid **2** (red solid line)) in THF solutions.

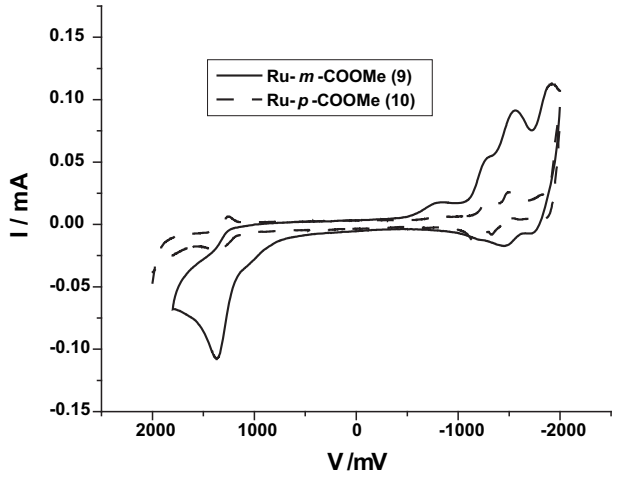


Figure 4. Cyclic voltammograms of solutions of esters **9** and **10** in MeCN and 0.1 M Bu_4NPF_6.

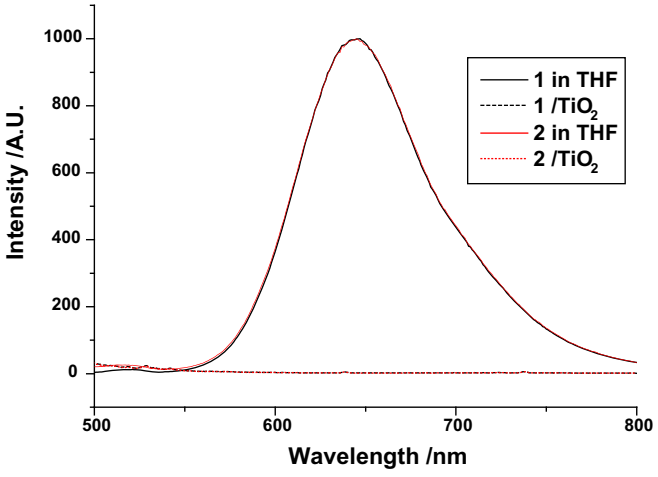


Figure 5. Fluorescence spectra of **1** and **2** in THF solution (solid lines) and bound to TiO_2 (dotted lines).

3. Conclusions

Tripod-shaped molecules are finding applications as surface probes and sensitizers for semiconductors,[2,6,10] for photochromic materials,[4a] and to develop new types of AFM tips.[3d,4d] A practical, three-step modular synthetic approach utilizing only Pd-catalyzed cross coupling reactions was developed. This method allows varying the position of the functional groups, as well as increasing the footprint sizes. Two ruthenium(II) bipyridine complexes with adamantane-centered linkers with *meta* (**Ru-*m*-COOH**, **1**) and *para* (**Ru-*p*-COOH**, **2**) carboxylic acid anchoring groups were synthesized and characterized through this method. The compounds exhibited spectral properties typical of ruthenium (II) bipyridine complexes and the quenching of fluorescence of **1** and **2** on anatase TiO_2 films is indicative of electron injection into the semiconductor. Photophysical studies of **1** and **2**, in solution and bound, including charge transfer kinetics on TiO_2 films, and binding studies of **1** and **2** on planar metal oxide surfaces are in progress.

4. Experimental

4.1. General

Reactions were carried out in flame-dried glassware and under nitrogen atmosphere. THF was distilled over sodium/benzophenone. Dichloromethane was distilled over calcium hydride. All reagents (1-bromoadamantane, 2,2′-bipyridine *N*-oxide, 3/4-bromo benzoic acid methyl ester, and ruthenium dipyridine dichloride dihydrate) were purchased commercially and used without further purification. The following compounds were prepared according to published literature procedures: 1,3,5,7-tetrakis(4-iodophenyl)adamantane,[8] methyl 4-ethynylbenzoate,[9] and methyl 3-ethynylbenzoate.[5,9] Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were acquired on a Varian INOVA 500 spectrometer operating at 499.896 MHz for ^{1}H, and 125.711 MHz for ^{13}C at room temperature in $CDCl_3$, THF-d_8 or acetone-d_6 as noted. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or $CDCl_3$ (δ 7.26 ppm), THF-d_8 (δ 1.73 ppm) or acetone-d_6 (δ 2.05 ppm) for ^{1}H, and $CDCl_3$ (δ 77.0 ppm), THF-d_8 (δ 25.37 ppm) or acetone-d_6 (δ 29.92 ppm) for ^{13}C. Flash column chromatography was performed on silica gel (230–400 mesh) while TLC on aluminum-backed silica gel plates (200 μm thick). Mass spectra were obtained by GC–MS or ESIMS. Data are reported for the molecule ion or protonated molecule ion. GC–MS was recorded from HP 6890 gas chromatograph with a HP 5973 MS detector. High resolution mass spectra were recorded on a high-resolution mass spectrometer (Agilent 6520 Q-TOF or Agilent 6340 Ion Trap with Electron Transfer Dissociation) in electron impact mode from Hunter College. Elemental analyses were determined by Perkin Elmer 2400 CHN Analyzers from Quantitative Technologies, Inc.

4.2. Spectroscopic measurements

Infrared (IR) spectra were obtained at room temperature on a Thermo Electron Corporation's Nicolet 6700 FT-IR spectrometer using ZnSe crystal for FT-IR-ATR or in KBr pellets. Absorption spectra were obtained at room temperature by a VARIAN Cary-500 spectrophotometer. Emission spectra were recorded at room temperature on a VARIAN Cary-Eclipse fluorescence spectrophotometer.

4.3. Electrochemistry

Cyclic voltammograms were obtained at room temperature under nitrogen using a voltammetric analyzer (CV-50 W from Bioanalytical System, Inc). The measurements were carried out with potential calibration using the ferricenium/ferrocene redox couple, i.e., E_0 (Fe^{3+}/Fe^{2+}) in CH_2Cl_2 as +0.45 V in 0.1 M Bu_4NPF_6

solution at room temperature under nitrogen. A glassy carbon electrode was used as the working electrode, Pt electrode as the counter electrode, and Ag/AgCl as the reference electrode. The excited state reduction potentials, $E_{1/2}(Ru^{III/II*})$, were calculated from the ground-state potentials and from the free energy in the thermally equilibrated MLCT excited-state, ΔG_{es}, according to Eq. 1:

$$E_{1/2}\left(Ru^{III/II^*}\right) = E_{1/2}\left(Ru^{III/II}\right) - \Delta G_{es} \quad (1)$$

ΔG_{es} was estimated by drawing a tangent line to the high-energy side of the corrected photoluminescence spectra.

4.4. Synthesis

*4.4.1. 1-(4-Ethynyl-2,2′-bipyridine)-3,5,7-tris-(4-iodophenyl)adamantane(**4**).* To a stirred solution of 1,3,5,7-tetrakis-(4-iodophenyl)-adamantane[8] (**3**, 1.5 g, 1.6 mmol) in THF (30 mL), 4-ethynyl-2,2′-bipyridine (0.23 g, 1.3 mmol), $Pd(PPh_3)_4$ (0.09 g, 0.08 mmol), and triethylamine (60 mL) were added. The reaction mixture was stirred for 2 days at 80 °C. The solution was concentrated in vacuo and partitioned between $CHCl_3$ and water. The organic layer was washed with water and brine several times, dried over anhydrous Na_2SO_4, and the solvent evaporated in vacuo. The crude mixture of products was separated by silica gel column chromatography (gradient from hexane to $CHCl_3$ and then THF) to yield **4**. The solid was triturated with MeOH/CH_2Cl_2 to yield **4** as a pale yellow solid (0.4 g, 29%). ^{1}H NMR ($CDCl_3$): 8.70–8.71 (d, 1H, J=3.9 Hz), 8.65–8.66 (d, 1H, J=4.9 Hz), 8.54 (s, 1H), 8.41–8.42 (d, 1H, J=8.0 Hz), 7.82–7.85 (dt, 1H, J=1.1, 7.8 Hz), 7.67–7.69 (d, 6H, J=8.3 Hz), 7.55–7.57 (d, 2H, J=8.3 Hz), 7.45–7.47 (d, 2H, J=8.3 Hz), 7.38–7.39 (dd, 1H, J=1.4, 5.0 Hz), 7.32–7.35 (dt, 1H, J=1.6, 6.5 Hz), 7.20–7.22 (d, 2H, J=8.6 Hz), 2.05 and 2.13 (two s, 12 H); ^{13}C NMR ($CDCl_3$) 156.2, 155.6, 149.9, 149.22, 149.19, 148.4, 137.5, 137.0, 132.5, 132.1, 127.1, 125.2, 124.0, 123.2, 121.2, 120.3, 93.8, 91.7, 87.1, 46.73, 46.70, 39.4, 39.1; HRMS(ESI$^+$-TOF) m/z: 995.9941 (calcd for $C_{46}H_{35}I_3N_2^+$=995.9934 found $[M]^+$); FT-IR (cm^{-1}) ν=3053, 2926, 2897, 2851, 2206, 1596, 1582, 1535, 1486, 1457, 1391, 1356, 1067, 1003, 894, 820, 791, 778, 744, 711, 661. Anal. Calcd for $C_{46}H_{35}I_3N_2$: C (55.44%); H (3.54%); N (2.81%). Found: C (55.22%); H (3.29%); N (2.78%).

*4.4.2. 1-(4-Ethynyl-2,2′-bipyridine)-3,5,7-tris-(3-carbomethoxyphenyl-4-ethynyl-phenyl)adamantane(**7**).* To a stirred solution of **4** (0.68 g, 6.8 mmol) in THF (14 mL), methyl 3-ethynylbenzoate[9,5] (0.87 g, 54.6 mmol), $Pd(PPh_3)_4$ (0.07 g, 0.02 mmol), and triethylamine (14 mL) were added. The reaction mixture was stirred under nitrogen for 2 days at 80 °C, and CH_2Cl_2 and water were added. The organic layer was washed with water and brine several times. The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. The crude product was purified by silica gel column chromatography (gradient from $CHCl_3$ to THF). The product **7** was eluted as the most polar component. Trituration in $CHCl_3$/MeOH yielded **7** as a white solid (0.48 g, 64%). ^{1}H NMR($CDCl_3$): 8.70–8.71 (d, 1H, J=4.0 Hz), 8.66–8.67 (d, 1H, J=5.0 Hz), 8.54 (s, 1H), 8.41–8.43 (d, 1H, J=8.0 Hz), 8.22 (s, 2H), 7.99–8.00 (d, 3H, J=7.8 Hz), 7.82–7.85 (dt, 1H, J=1.6, 7.8 Hz), 7.70–7.72 (d, 3H, J=7.8 Hz), 7.49–7.60 (m, 16H), 7.39–7.45 (m, 5H), 7.32–7.39 (t, 1H, J=6.5 Hz), 3.94 (s, 9H), 2.20 (s, 12H); ^{13}C NMR($CDCl_3$) 166.4, 156.2, 155.6, 150.1, 149.4, 149.19, 149.15, 137.0, 135.6, 132.7, 132.5, 132.1, 131.8, 130.4, 129.1, 128.5, 125.2, 125.1, 124.0, 123.8, 123.1, 121.1, 120.8, 120.2, 93.8, 90.2, 88.2, 87.0, 52.2, 46.7, 39.4, 39.3, 39.2; HRMS(ESI$^+$-TOF) m/z: 1092.4127 (calcd for $C_{76}H_{56}N_2O_6^+$ 1092.4138 found $[M]^+$); FT-IR (cm^{-1}) ν=3033, 2926, 2852, 2206, 1723, 1597, 1582, 1510, 1438, 1258, 1194, 1145, 1102, 1017, 989, 834, 793, 753. Anal. Calcd for $C_{76}H_{56}N_2O_6$: C (83.49%); H (5.16%); N (2.56%). Found: C (83.16%); H (4.80%); N (2.62%).

*4.4.3. 1-(4-Ethynyl-2,2′-bipyridine)-3,5,7-tris-(4-carbomethoxyphenyl-4-ethynyl-phenyl)adamantane(**8**).* To a stirred solution of **4** (0.37 g, 3.7 mmol) in THF (8 mL), methyl 4-ethynylbenzoate[9] (0.35 g, 22.1 mmol), $Pd(PPh_3)_4$ (0.02 g, 0.02 mmol), and triethylamine (8 mL) were added. The reaction mixture was stirred under nitrogen for 2 days at 80 °C, then CH_2Cl_2 and water were added. The organic layer was washed with water and brine several times. Then, the organic layer was evaporated in vacuo. The crude product was purified by column chromatography (gradient from $CHCl_3$ to THF). The product **8** was eluted as the most polar compound. Trituration in $CHCl_3$/MeOH yielded **8** as a pale yellow solid (0.38 g, 94%). ^{1}H NMR($CDCl_3$): 8.70–8.71 (d, 1H, J=3.9 Hz), 8.65–8.66 (d, 1H, J=4.8 Hz), 8.54 (s, 1H), 8.41–8.42 (d, 1H, J=8.0 Hz), 8.01–8.03 (d, 6H, J=8.2 Hz), 7.81–7.84 (t, 1H, J=7.4 Hz), 7.48–7.60 (m, 14H), 7.48–7.52 (t, 8H, J=8.5 Hz), 7.39–7.40 (d, 1H, J=4.6 Hz), 7.32–7.34 (t, 1H, J=5.7 Hz), 3.92 (s, 9H), 2.18 (s, 12H); ^{13}C NMR($CDCl_3$) 166.5, 156.2, 155.6, 150.0, 149.6, 149.2, 137.0, 132.5, 132.1, 131.9, 131.5, 129.5, 128.0, 125.2, 124.0, 123.2, 121.2, 120.7, 120.3, 93.8, 92.2, 88.6, 87.1, 52.2, 46.7, 39.4, 29.7; HRMS(ESI$^+$-TOF) m/z: 1092.4145 (calcd for $C_{76}H_{56}N_2O_6^+$ 1092.4138 found $[M]^+$) FT-IR (cm^{-1}) ν=2928, 2852, 2215, 1724, 1603, 1583, 1515, 1435, 1275, 1176, 1140, 1107, 1018, 856, 832, 793, 768. Anal. Calcd for $C_{76}H_{56}N_2O_6$: C (83.49%); H (5.16%); N (2.56%). Found: C (83.80%); H (4.82%); N (2.52%).

*4.4.4. Ruthenium(II) [1-(4-ethynyl-2,2′-bipyridine)]-3,5,7-tris-(3-carbomethoxyphenyl-4-ethynyl-phenyl)adamantane-bis(2,2′-bipyridine)$^{2+}$ bis-hexafluorophosphate(**9**).* To a stirred solution of **7** (0.55 g, 0.5 mmol) in THF(10 mL), ruthenium dipyridine dichloride dihydrate(0.3 g, 0.6 mmol), and butanol (5 mL) were added. The solution was refluxed under nitrogen overnight, then cooled to room temperature and filtered. The solid was washed with MeOH. $NaPF_6$ (1.2 g, 7.0 mmol) in water (10 mL) was added to the solution in one portion. An orange-red precipitate was filtered and washed with water. The complex was precipitated in THF/$CHCl_3$ as a bright orange-red solid (0.5 g, 55%) ^{1}H NMR-(acetone-d_6) 8.89–9.2 (m, 2H), 8.80–8.82 (d, 4 H, J=7.7 Hz), 8.16–8.21 (m, 6H), 8.12 (s, 3H), 8.05–8.07 (m, 5H), 7.96–8.00 (d, 3H, J=7.7 Hz), 7.77–7.78 (d, 5H, J=6.5 Hz), 7.68–7.70 (d, 6H, J=8.3 Hz), 7.52–7.65 (m, 17H), 3.91 (s, 9H), 2.25 (s, 12H); ^{13}C NMR(acetone-d_6) 166.6, 158.6, 158.2, 158.1, 157.8, 153.1, 152.8, 152.7, 151.4, 139.15, 139.07, 136.5, 133.6, 133.1, 133.0, 132.6, 131.8, 130.0, 129.8, 129.1, 128.9, 127.0, 126.9, 126.6, 125.8, 125.4, 124.8, 121.4, 119.8, 99.1, 91.2, 88.7, 86.5, 52.7, 47.2, 40.7, 40.5; HRMS(ESI$^+$-TOF) m/z: 753.2288 (calcd for $C_{96}H_{72}N_6O_6Ru^{2+}$ 753.2273 found $[M]^{2+}$); FT-IR (cm^{-1}) ν=2928, 2852, 2216, 1724, 1603, 1515, 1435, 1275, 1176, 1107, 1018, 832, 768; UV–vis (log ε)=215 (4.86), 243 (4.83), 289 (5.13), 331 (4.47), 462 (4.16). Anal. Calcd for $C_{96}H_{72}F_{12}N_6O_6P_2Ru$: C (64.18%); H (4.04%); N (4.68%). Found: C (64.44%); H (4.07%); N (4.43%).

*4.4.5. Ruthenium(II) [1-(4-ethynyl-2,2′-bipyridine)]-3,5,7-tris-(4-carbomethoxyphenyl-4-ethynyl-phenyl)adamantane-bis(2,2′-bipyridine)$^{2+}$ bis-hexafluorophosphate(**10**).* To a stirred solution of **8** (0.25 g, 0.2 mmol) in THF (10 mL), ruthenium dipyridine dichloride dihydrate (0.13 g, 0.2 mmol), and butanol (5 mL) were added. The solution was refluxed under nitrogen overnight. Then, the solution was cooled to room temperature and then filtered. The residue was washed with MeOH, and $NaPF_6$ (0.53 g, 3.1 mmol) in water (10 mL) was added to the solution in one portion. An orange-red precipitate formed. This was collected and washed with water. The complex was precipitated in THF/$CHCl_3$ to yield **10** as a bright orange-red solid (0.23 g, 57%). ^{1}H NMR(THF-d_8): 8.75–8.77 (2H), 8.63–8.65 (t, 4H, J=7.1 Hz), 8.03–8.08 (t, 5H, J=7.9 Hz), 7.99–8.01 (d, 6H, J=8.3 Hz), 7.91–7.92 (d, 1H, J=5 Hz), 7.82–7.89 (m, 5H), 7.56–7.69 (m, 16H), 7.54–7.55 (d, 6 H, J=8.4 Hz), 7.45–7.49 (m, 6H), 3.86 (s, 9H), 2.22 (s, 12H); ^{13}C NMR(acetone-d_6) 166.8, 158.6, 158.2, 158.1, 157.8, 153.2, 152.93, 152.86, 152.81, 152.7, 151.7, 139.2, 139.1, 133.6, 133.1, 132.7, 132.5,

130.8, 130.6, 130.5, 129.8, 129.1, 128.92, 128.88, 127.03, 126.95, 126.7, 125.8, 125.5, 121.3, 119.8, 99.1, 93.2, 89.1, 86.5, 86.2, 52.6, 47.2, 40.7, 40.5, 26.3; HRMS(ESI$^+$-TOF) m/z: 753.2299 (calcd for $C_{96}H_{72}N_6O_6Ru^{2+}$ 753.2273 found $[M]^{2+}$); FT-IR (cm^{-1}) ν=2927, 2852, 2212, 1720, 1603, 1515, 1437, 1277, 1177, 1108, 1018, 842, 768; UV–vis ($\log \varepsilon$)=234 (4.99), 292 (5.13), 301 (5.11), 463 (4.23). Anal. Calcd for $C_{96}H_{72}F_{12}N_6O_6P_2Ru$: C (64.18%); H (4.04%); N (4.68%). Found: C (64.37%); H (3.81%); N (4.80%).

*4.4.6. Ruthenium(II) [1-(4-ethynyl-2,2′-bipyridine)]-3,5,7-tris-(3-carboxylphenyl-4-ethynyl-phenyl)adamantane-bis(2,2′-bipyridine)$^{2+}$ bis-hexafluorophosphate(**1**).* To a stirred solution of **9** (0.06 g, 0.003 mmol) in THF (5 mL), NaOH (0.1 g, 2.6 mmol) in 5 mL of water was added dropwise. The mixture was stirred for 4 hr and then concentrated HCl was added to adjust the pH<2. The precipitate formed was filtered and precipitated in THF/MeOH to yield orange-red solid. (0.04 g, 72%) ^{1}H NMR(THF-d_8): 8.72–8.78 (2H), 8.62–8.67 (t, 4H, J=6.0 Hz), 8.13–8.17 (s, 3H), 8.04–8.11 (dd, 5H, J=7.6, 14.6 Hz), 7.96–8.00 (d, 3H, J=7.8 Hz), 7.87–7.91 (d, 1H, J=5.2 Hz), 7.78–7.86 (m, 5H), 7.67–7.70 (d, 5H, J=7.4 Hz), 7.60–7.65 (t, 8H, J=8.4 Hz), 7.53–7.57 (d, 6H, J=8.3 Hz), 7.44–7.50 (m, 9H), 2.22 (s, 12H); ^{13}C NMR(THF-d_8) 167.1, 158.4, 158.1, 158.04, 157.95, 157.9, 157.6, 153.0, 152.5, 152.44, 152.37, 151.3, 139.0, 138.9, 136.0, 133.7, 133.5, 133.1, 132.5, 130.2, 129.6, 129.5, 129.2, 128.9, 126.8, 126.7, 126.4, 125.5, 125.4, 124.7, 121.7, 120.1, 99.0, 91.0, 88.9, 86.6, 51.9, 47.5, 40.7, 40.5, 30.7; HRMS(ESI$^+$-TOF) m/z: 732.2057 (calcd for $C_{93}H_{66}N_6O_6Ru^{2+}$ 732.2038 found $[M]^{2+}$), FT-IR (cm^{-1})=2929, 2854, 2212, 1705, 1604, 1561, 1514, 1465, 1446, 1408, 1311, 1261, 1231, 1174, 1142, 1112, 992, 768, 732, 497, UV–vis ($\log \varepsilon$)=215 (4.94), 248 (4.85), 289 (5.13), 334 (4.49), 461 (4.18). Anal. Calcd for $C_{93}H_{66}F_{12}N_6O_6P_2Ru$: C (63.66%); H (3.79%); N (4.79%). Found: C (63.44%); H (4.02%); N (4.40%).

*4.4.7. Ruthenium(II) [1-(4-ethynyl-2,2′-bipyridine)]-3,5,7-tris-(4-carboxylphenyl-4-ethynyl-phenyl)adamantane-bis(2,2′-bipyridine)$^{2+}$ bis-hexafluorophosphate(**2**).* To a stirred solution of **10** (0.19 g, 0.1 mmol) in THF (5 mL), NaOH (0.33 g, 8.2 mmol) in 5 mL of water was added dropwise. The mixture was stirred for 4 hr and then concentrated HCl was added to adjust pH<2. The precipitated formed was filtered and precipitated from THF/MeOH to yield orange-red solid of **2** (0.1 g, 55%). ^{1}H NMR(THF-d_8): 8.74–8.78 (2H), 8.62–8.68 (t, 4H, J=6.6 Hz), 8.16 (s, 2H), 8.02–8.10 (dd, 5H, J=6.9, 14.0 Hz), 7.96–8.03 (m, 4H), 7.76–7.89 (m, 6H), 7.40–7.62 (m, 28H), 2.24 (s, 12H); ^{13}C NMR(acetone-d_6) 166.8, 158.4, 158.0, 157.9, 157.6, 152.8, 152.7, 152.61, 152.56, 151.5, 139.1, 139.0, 133.5, 133.1, 132.6, 132.4, 130.6, 130.4, 129.7, 129.0, 128.83, 128.78, 126.9, 126.6, 126.4, 125.7, 125.4, 99.0, 93.3, 89.1, 86.5, 52.6, 47.1, 40.5, 40.3; HRMS(ESI$^+$-TOF) m/z: 732.2047 (calcd for $C_{93}H_{66}N_6O_6Ru^{2+}$ 732.2038 found $[M]^{2+}$); FT-IR (cm^{-1})=2931, 2211, 1701, 1604, 1560, 1515, 1465, 1447, 1408, 1310, 1232, 1175, 1141, 1108, 1017, 765, 732, 496, UV–vis ($\log \varepsilon$)=212 (4.85), 292 (5.12), 310 (5.12), 323 (5.05), 462 (4.20). Anal. Calcd for $C_{93}H_{66}F_{12}N_6O_6P_2Ru$: C (63.66%); H (3.79%); N (4.79%). Found: C (63.95%); H (3.63%); N (4.35%).

4.4.8. Exchange of Cl^- with PF_6^-. Compounds **1** and **2** were redissolved in basic conditions with excess $NaPF_6$ and then precipitated by addition of dilute $HCl_{(aq)}$. The precipitate was filtered, washed with water, and dried in vacuo. After this step, both products **1** and **2** were soluble in acetonitrile and THF. The MS and elemental analysis were consistent with the formation of the hexafluorophosphate salts.

Acknowledgements

We are grateful to Dr. Sujatha Thyagarajan for her early contribution to the synthesis of **2**. This work was funded by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-FC02-01ER15256.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.04.005. This data include MOL files and InChiKeys of the most important compounds described in this article.

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