Pergamon

Tetrahedron Letters 41 (2000) 7419–7421

TETRAHEDRON LETTERS

Synthesis of a molecular tripod to anchor molecular coordination compounds to semiconductor nanoparticles

Wenzhuo Guo, Elena Galoppini,* Gunilla Rydja and Gianluca Pardi

Rutgers University, Chemistry Department, 73 Warren Street, Newark, NJ 07102, USA

Received 24 May 2000; accepted 15 July 2000

Abstract

A 1,3,5,7-tetraphenyladamantane derivative having three arms terminating with carboxylic acids and a fourth substituted with a 9,10-phenanthrolinyl ligand was prepared as a new kind of molecular linkage to study dynamics of electron injection at the interface of TiO_2 nanoparticles. © 2000 Published by Elsevier Science Ltd.

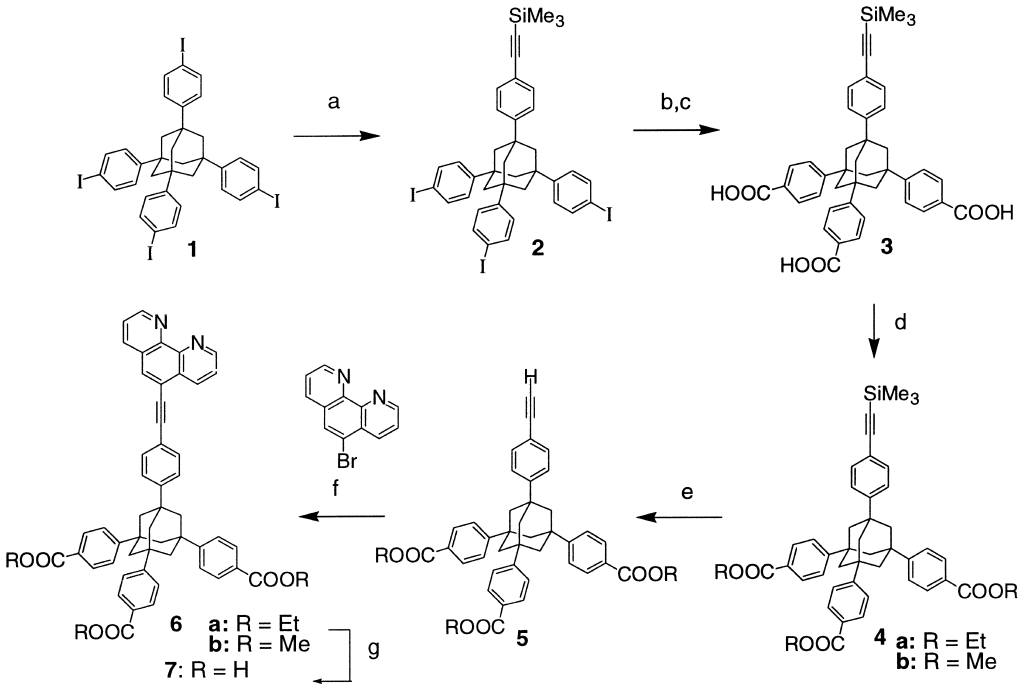
Solar cells that convert sunlight into electricity by sensitization of wide bandgap n-type semiconductor nanoparticles with dyes, usually Ru(II) polypyridyl coordination compounds, have been studied since the early 1970s.[1] The dyes are anchored to metal oxide semiconductor surfaces, for instance TiO_2, through the reaction of one or two carboxylic acid groups present on a bpy ligand with surface hydroxyl groups.[2] A highly promising and yet relatively unexplored area in this field is the development of new rigid linkages to study dynamics of remote electron injection at the interface of semiconductors nanoparticles.[1a,3] We have now developed new molecular linkages that act as rigid scaffolds for the dye and hold it at fixed distance with respect to the semiconductor surface. These are molecules having the shape of a tripod, with three rigid-rod arms terminating with carboxylic acids and a fourth substituted with a metal-binding ligand, such as phenanthroline or bipyridine. Structural, optical and electrochemical properties of the tripods will be tuned by changing one or more of their three components: core, arms and sensitizer.

In this paper we describe the synthesis of the first model compound, **6** (Scheme 1). The starting material, tetraiodide **1**, was readily prepared from 1-bromoadamantane, following a clever two-step procedure developed by Mathias and coworkers.[4] Sonogashira cross-coupling[5] of

* Corresponding author.

0040-4039/00/$ - see front matter © 2000 Published by Elsevier Science Ltd.
PII: S0040-4039(00)01187-4

1 with trimethylsilylacetylene at room temperature produced a mixture of monosubstituted **2**† together with the disubstituted product and unreacted **1**. Since separation by silica gel column chromatography at this stage was lengthy, the two following steps (carboxylation and esterification) were performed directly on the mixture and the esters were easily separated to afford **4**† in 18–20% yield from **1**.[6] The alkynyl group was deprotected with tetrabutylammoniumfluoride (TBAF), followed by a Suzuki-type coupling[7] with 5-bromo-9,10-phenanthroline to yield **6a**†, a solid material that is soluble in numerous organic solvents.[8]



Scheme 1. *Reagents and conditions*: (a) $Me_3SiC{\equiv}CH$ (1.5 equiv.), $Cl_2Pd(PPh_3)_2$, CuBr, $(i\text{-}Pr)_2NH$, benzene, rt, 30%. (b) 1. *t*-BuLi; 2. CO_2. (c) H^+, H_2O. (d) DCC, DMAP, EtOH (R = Et) or CH_2N_2 (R = Me). (e) TBAF, CH_3CN, rt, 95%. (f) 1. $(Me_3Si)_2NLi$, −78°C; 2. 9-BBN, −78°C; 3. $Pd(PPh_3)_4$, THF, reflux, 30%. (g) KOH, EtOH, 90%

† *Selected data for* **2**: ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 7.65 (d, J = 8.5, 6 H), 7.44 (d, J = 8.5, 2 H), 7.34 (d, J = 8.5, 2 H), 7.17 (d, J = 8.5, 6 H), 2.05 and 2.04 (two s, 12 H, $C\underline{H}_2$), 0.24 (s, 9 H, $Si\underline{Me}_3$); ^{13}C NMR δ_C (125 MHz, $CDCl_3$): 149.04, 148.45 (PhI), 137.46 (PhI), 132.05, 127.13 (PhI), 124.91, 121.13, 104.85 ($PhC{\equiv}\underline{C}SiMe_3$), 94.07 ($Ph\underline{C}{\equiv}CSiMe_3$), 91.68 ($\underline{C}$–I), 46.64 ($\underline{C}H_2$ and $\underline{C}$–Ph–I), 39.17 ($\underline{C}$–Ph–C≡C), 39.01 ($\underline{C}H_2$), 0.00 ($Si\underline{Me}_3$). **4**: ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 8.03 (d, J = 8.5, 6 H), 7.54 (d, J = 8.5, 6 H), 7.46 (d, J = 8.0, 2 H), 7.40 (d, J = 8.0, 2 H), 4.37 (q, J = 7.0, $OC\underline{H}_2CH_3$, 6 H), 2.19 and 2.17 (two s, 12 H, $C\underline{H}_2$), 1.39 (t, J = 7.0, $OCH_2C\underline{H}_3$, 9 H), 0.25 (s, 9 H, $Si\underline{Me}_3$); ^{13}C NMR δ_C (125 MHz, $CDCl_3$): 166.27 ($\underline{C}OOEt$), 153.65 ($\underline{C}$–COOEt), 148.99, 132.00, 129.68 ($\underline{Ph}COOEt$), 128.53 ($\underline{Ph}COOEt$), 124.94 ($\underline{Ph}COOEt$), 124.79, 121.11 ($\underline{C}$–C≡C–$SiMe_3$), 104.82 ($C{\equiv}\underline{C}SiMe_3$), 93.98 ($\underline{C}{\equiv}CSiMe_3$), 60.77 ($O\underline{C}H_2CH_3$), 46.52 ($\underline{C}H_2$ and $\underline{C}$–Ph–COOEt), 39.46 ($\underline{C}H_2$), 39.15 ($\underline{C}$–Ph–C≡C), 14.33 ($OCH_2\underline{C}H_3$), 0.43 ($Si\underline{Me}_3$). **6a**: ^{1}H NMR δ_H (500 MHz, $CDCl_3$): 9.25 (m, 1 H), 9.21 (m, 1 H), 8.84 (m, 1 H), 8.25 (m, 1 H), 8.11 (m, 1 H), 8.05 (d, J = 8.5, 6 H), 7.75 (m, 1 H), 7.65 (m, 3 H), 7.56 (m, 8 H), 4.38 (q, J = 7.0, $OC\underline{H}_2CH_3$, 6 H), 2.23 (broad s, 12 H, $C\underline{H}_2$), 1.40 (t, J = 7, $OCH_2C\underline{H}_3$, 9 H); ^{13}C NMR δ_C (125 MHz, $CDCl_3$): 166.35 ($\underline{C}OOEt$), 153.59 ($\underline{Ph}COOEt$), 150.85, 150.61, 149.62, 146.03, 145.87, 135.74, 134.69, 131.89 ($\underline{Ph}C{\equiv}C$), 130.58, 129.75 ($\underline{Ph}COOEt$), 128.63 ($\underline{Ph}COOEt$), 128.21, 127.99, 125.25 ($\underline{Ph}C{\equiv}C$), 124.97 ($\underline{Ph}COOEt$), 123.44, 123.32, 120.61, 119.91, 95.15 ($C{\equiv}\underline{C}$Phena), 85.79 ($\underline{C}{\equiv}C$Phen), 60.88 ($O\underline{C}H_2CH_3$), 46.63 ($\underline{C}H_2$), 46.57 ($\underline{C}$–Ph–COOEt), 39.53 ($\underline{C}H_2$), 39.34 ($\underline{C}$–Ph–C≡C), 14.30 ($OCH_2\underline{C}H_3$).

The $Ru(bpy)_2$ complexes of both **6** and **7** were formed upon treatment with $RuCl_2(bpy)_2 \cdot 2H_2O$ and their photoelectrochemical studies will be published elsewhere. Although the yields of the first and last step are modest (total yield from **1** is 5–7%), compound **6** was prepared in sufficient quantities (100 mg scale) for the application of interest, and the same route was applied to other substrates such as tetraphenylmethane derivatives. To the best of our knowledge, this is the first example of a systematic synthesis aiming to differentiate one of the arms of tetrahedral molecules, which have been recently employed in the synthesis of branched polymers,[4,9] dendrimers and in crystallographic studies.[10] In summary, the tripod-shaped molecules in Scheme 1 may be of interest to researchers studying molecule/semiconductor systems as well as other areas of materials chemistry.

Acknowledgements

This work was supported in part by a grant from the Petroleum Research Fund (ACS-PRF 35081-G5) and the Rutgers Research Council. E.G. thanks Professor Gerald Meyer for insightful discussions and for providing the experimental procedure for 5-bromo-9,10-phenanthroline. G.R. thanks the CHUST program sponsored by the Royal Institute of Chemical Engineering, Stockholm, Sweden.

References

1. (a) Meyer, G. J. *J. Chem. Educ.* **1997**, *74*, 652. (b) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (c) Grätzel, M. *Heterogeneous Photochemical Electron Transfer*; CRC: Boca Raton, FL, 1989. (d) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (e) Kamat, P. V. *Chem. Rev.* **1993**, *93*, 267. (f) Gerischer, H. *Photochem. Photobiol.* **1972**, *16*, 243.
2. It is presumed that the carboxylic (or carboxylate) groups bind through ester bonds or non-covalent interactions.
3. (a) Stipkala, J. M.; Heimer, T. A.; Livi, K. J. T.; Meyer, G. *J. Chem. Mater.* **1997**, *9*, 2341. (b) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Meyer, G. *J. Inorg. Chem.* **1997**, *36*, 2.
4. Eichert, V. R.; Mathias, L. J. *Macromolecules* **1994**, *27*, 7015.
5. Sonogashira, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed. Pergamon: Oxford, UK, 1991; Vol. 3, pp. 551–561.
6. The separation of the mixture was difficult because of the presence of **1**. When the reaction was repeated in the presence of an excess of trimethylsilylacetylene, the crude contained mono-, di- and triethynylsubstituted products, but not **1**, and the separation was easy. In this case, however, the yield of **2** was lower. The di- and trialkynyl derivatives of **1** are also of interest for our studies and have been isolated.
7. (a) Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, *29*, 2631. (b) Soderquist, T. A.; Matos, K. *Tetrahedron Lett.* **1995**, *36*, 2401. (c) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.
8. Sonogashira coupling was used to prepare 5-trimethylsilylethynyl-9,10-phenanthroline (Boatin, R. H.; Rapoport, H. *J. Org. Chem.* **1986**, *51*, 5320), but repeated attempts to use these conditions with **5** and 5-bromo-9,10-phenanthroline resulted exclusively in the dimerization of **5**.
9. (a) Wilson, L. M.; Griffin, A. C. *J. Mater. Chem.* **1993**, *3*, 991. (b) Braun, D.; Keller, C.-C.; Roth, M. D.; Schartel, B.; Voigt, M.; Wendorff, J. H. *J. Prakt. Chem.* **1997**, *339*, 708.
10. (a) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1461 and references therein. (b) Galoppini, E.; Gilardi, R. *Chem. Commun.* **1999**, 173.