solution (5.0 g; 25 wt%; Aldrich), ultra-purified water (4.67 g; Millipore), and methanol (5.625 g, 175.55 mmol; Fluka, p.a.). Double-three ring (D3R) containing solutions were prepared by dissolving Aerosil 130 (0.193 g, 3.21 mmol) in aqueous tetraethylammonium hydroxide (5.0 g; 35 wt%; Aldrich), ultra-purified water (0.146 g; Millipore), and ethanol (1.817 g, 39.5 mmol; Fischer & Rintelen, puriss.). All solutions were stirred for 30 min and then heated at 70 °C for 18 h. The clear solutions were then filtered through a polyether sulfone membrane (Nalgene) with a pore width of 0.2 μm before being injected into the mass spectrometer.

The mass spectra were recorded with a Fisons VG Platform II instrument with a quadrupole analyzer. The sample was injected directly through a Rheodyne valve. Skimmer cone voltages were varied between 30 and 100 V. In order to obtain an independent verification of the findings, a second series of experiments was carried out on a quadrupole mass spectrometer (Hewlett Packard HP MS-Engine 5989B), fitted with an Analytica of Brandford ESI-source. The solutions were injected by direct infusion and measured with an ESI voltage of 3640 V, a flow rate of 40 μLmin^{-}, a desolvation temperature of 150 °C, a CapEx voltage of −133 V, and a skimmer voltage of −31.5 V.

^{29}Si NMR spectra were recorded with an AMX 400 Bruker spectrometer operating at 79.483 MHz. Samples containing D_2O for the deuterium locking frequency were placed in a 10-mm PTFE NMR tube liner without a glass sample tube to minimize the silicon background from the glass. The pulse sequence used to acquire the spectra was a ^{29}Si{^{1}H} inverse-gated experiment with a waltz16 composite pulse program for proton decoupling. Generally for the ^{29}Si determination a 13.6 μs pulse with a 8 s relaxation delay was used between each acquisition. The number of acquisitions ranged from 15000 to 30000 depending on the concentration of the solutions.

Received: May 8, 2000 [Z 15088]

---

[1] a) J. A. Dirksen, T. A. Ring, *Chem. Eng. Sci.* **1991**, *46*, 2389–2427; b) E. Matijevic, *Chem. Mater.* **1993**, *5*, 412–426.

[2] a) T. Løver, W. Henderson, G. A. Bowmaker, J. M. Seakins, R. P. Cooney, *J. Mater. Chem.* **1997**, *8*, 1553–1558; b) F. Sobott, S. A. Schunk, F. Schüth, B. Brutschy, *Chem. Eur. J.* **1998**, *4*, 2353–2359; c) D. A. Loy, J. P. Carpenter, S. A. Yamanaka, M. D. McClain, J. Greaves, S. Hobson, K. J. Shea, *Chem. Mater.* **1998**, *10*, 4129–4140; d) S. Cristoni, L. Armelao, S. Gross, E. Tondello, P. Traldi, *Rapid Commun. Mass Spectrom.* **2000**, *14*, 662–668.

[3] A. V. McCormick, A. T. Bell, *Catal. Rev. Sci. Eng.* **1989**, *31*, 97–127.

[4] C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic Press, Boston, **1990**.

[5] a) R. Murugavel, A. Voigt, M. G. Walawalkar, H. W. Roesky, *Chem. Rev.* **1996**, *96*, 2205–2236; b) F. J. Feher, D. A. Newman, J. F. Walzer, *J. Am. Chem. Soc.* **1989**, *111*, 1741–1748.

Stepwise Assembled Photoactive Films Containing Donor-Linked Fullerenes**

Chuping Luo, Dirk M. Guldi,* Michele Maggini, Enzo Menna, Simonetta Mondini, Nicholas A. Kotov, and Maurizio Prato

The construction of molecular devices such as photoelectrochemical cells for use in solar energy conversion is a very useful but challenging task.[1] Most common problems relate to the interfacial diffusion of the donor and acceptor molecules or the lack of semiconductor materials with large band gaps that give an efficient light response in the visible region.[2, 3]

Herein we present the supramolecular organization of donor-linked fullerenes as a viable alternative for the assembly of photoactive indium tin oxide (ITO) electrodes which exhibit an efficient generation of photocurrent.[4] The fundamental advantage of the fabrication of these tailored architectures is the control that can be exerted at a molecular level over the thickness and composition of the assembled films.[5] Equally important is the specific alignment and the orientation of the incorporated donor–acceptor systems so as to facilitate the electron transfer among adjacent layers.[6] Thus, the efficiency of the generated photocurrents is expected to depend on the cooperative interaction of these individual parameters (film thickness, alignment, and orientation).

In the following we describe the layer-by-layer deposition of a positively charged fulleropyrrolidinium ion (**1**) and a series of positively charged ruthenium(II)–polypyridyl–fullerene donor–acceptor dyads (**2** and **3**, the counterion is PF_6^- in both cases, Scheme 1) on solid substrates (quartz or semiconducting ITO electrodes). The ruthenium(II)–polypyridyl complexes employed show a marked red-shift in their absorption maxima while maintaining a high photopotential.[7, 8] Both parameters are essential in order to guarantee an elevated monochromatic photon-to-current conversion efficiency at longer wavelength. More importantly, the use of

---

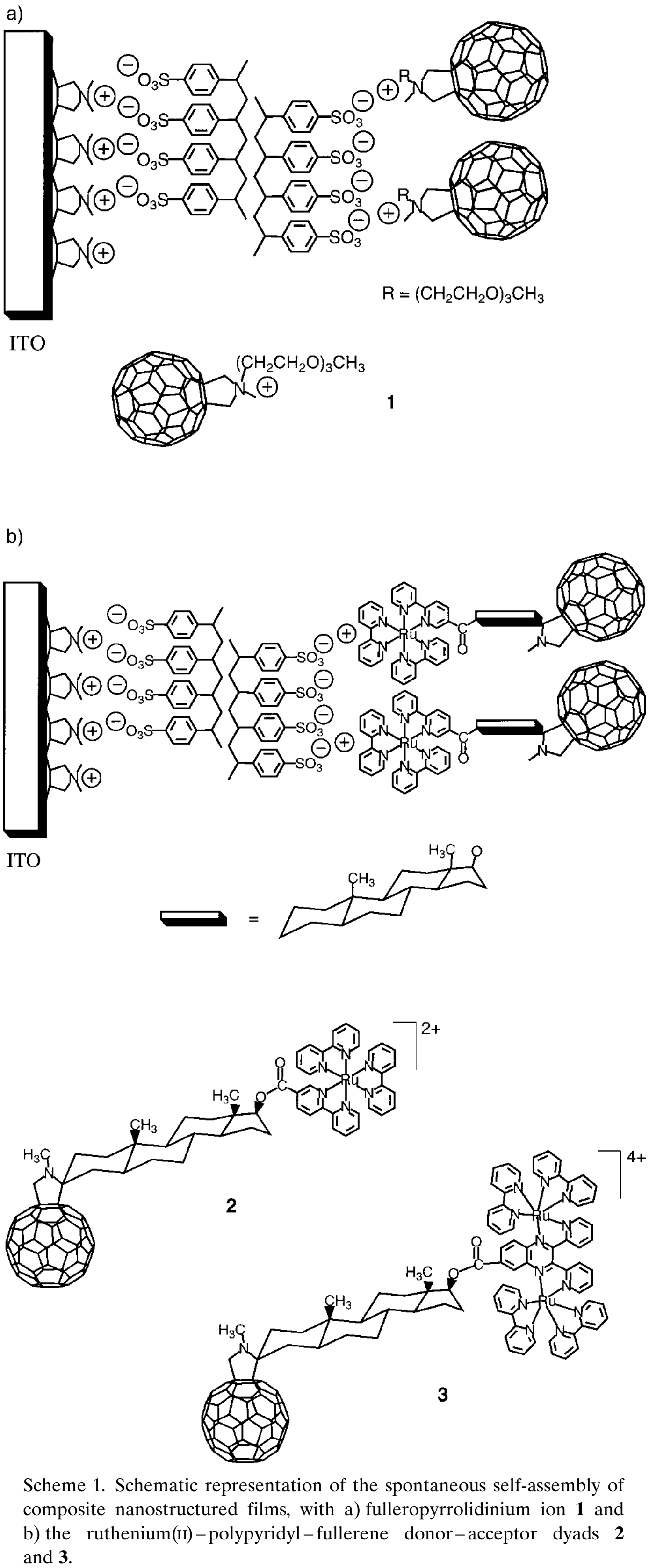
[*] Dr. habil. D. M. Guldi, Dr. C. Luo
Radiation Laboratory, University of Notre Dame
Notre Dame, IN 46556 (USA)
Fax: (+1) 219-631-8068
E-mail: guldi.1@nd.edu

Prof. M. Maggini, Dr. E. Menna, Dr. S. Mondini
Dipartimento di Chimica Organica, Universita' di Padova
Via Marzolo 1, 35131 Padova (Italy)

Prof. N. A. Kotov
Chemistry Department, Oklahoma State University
Stillwater, OK, 74078 (USA)

Prof. M. Prato
Dipartimento di Scienze Farmaceutiche
Università di Trieste
Piazzale Europa, 1, 34127 Trieste (Italy)

[**] This work was supported by the Office of Basic Energy Sciences of the Department of Energy and by MURST (no. 9803194198). This publication is document NDRL-4166 from the Notre Dame Radiation Laboratory. We thank Prof. Janos H. Fendler and Dr. T. Cassagneau (Clarkson University) for helpful discussions during the initial phase of the experiments. N.A.K. acknowledges the NSF for a CAREER award (CHE-9876265).



Scheme 1. Schematic representation of the spontaneous self-assembly of composite nanostructured films, with a) fulleropyrrolidinium ion **1** and b) the ruthenium(II)–polypyridyl–fullerene donor–acceptor dyads **2** and **3**.

covalently attached donor–acceptor systems (such as in dyads **2** and **3**) is sought to avoid the commonly encountered phase separation and, thereby, ensure stable donor–acceptor interfaces.

The synthesis of pyrrolidinium salt **1**-PF_6[9] and the tris(2,2'-bipyridine)ruthenium(II)–C_{60} dyad (**2**)[7] have already been reported. Dyad **3** was prepared by following a similar synthetic protocol[8] as for dyad **2**, but with a 2,3-bis(2-pyridyl)quinoxaline moiety used as the bridging ligand to coordinate the two metal centers.

The key step in the deposition of the C_{60}-based materials involves the coverage of the substrate surface with a negatively charged material. This was achieved in two separate steps, namely, by anchoring a poly(diallyldimethylammonium) chloride (PDDA chloride) layer to the hydrophilic surface, followed by the adsorption of a sodium poly(styrene-4-sulfonate) (PSS) coating. The subsequent deposition of the fullerene derivatives became possible through uniformly directed Coulombic forces and short-range van der Waals forces that govern the physisorption process between opposite charged ions.[5] For example, charge attraction is operative between the negative sulfonate groups and the pyrrolidinium cation in **1** and the ruthenium(II) complexes in **2** and **3**. After this modifiction, the hydrophobic fullerene core covers the surface of the modified electrode and this can then be coated with another dyad layer by making use of the hydrophobic interactions.[12]

The regularities of the stepwise deposition procedure were monitored by recording the UV/Vis absorption spectra of the resulting films after each deposition step. It should be noted that neither the PDDA layer nor the PSS layers exhibit strong absorption characteristics in the range monitored. The pyrrolidinium ion, on the other hand, was unequivocally identified in the monolayer from a set of maxima at 226, 260, and 336 nm. A solution of the same pyrrolidinium salt in dichloromethane exhibits transitions at 218, 257, and 330 nm, which is in excellent agreement with the monolayered films. Up to 20 individual coating runs were performed to obtain a sufficiently absorbing electrode. Repeated absorption patterns were evident in the absorption spectra of the deposited films on quartz. The linear dependence noted here is a meaningful criterion that indicates the satisfactory and uniform stacking of individually deposited films.

The linearity of the multilayer growth has also been confirmed by monitoring the ellipsometric thickness of the films (Figure 1). The increment of the deposition cycle of PSS and **1** is equal to 4.3 nm, which corresponds to the adsorption of 2–3 monolayers of **1** and a layer of PSS, whose thickness is typically 0.5–1 nm. The layer-by-layer pattern of the film growth can be clearly seen in the images (not shown) obtained by atomic force microscopy (AFM). The morphologies of PDDA/PSS and PDDA/PSS/**1** layers as observed in the AFM images are significantly different. PDDA/PSS forms a fairly flat surface with occasional pores. After adsorption of the pyrrolidinium salt **1**, the roughness of the surface decreases, while the fine-grained structure of the fullerene layer appears. Importantly, the surface becomes uniformly covered with characteristic 20-50-nm large 2D aggregates assembled in a continuous uniform film. No troughs can be observed in the entire area surveyed. A similar regularity and quality of the surface are expected for those formed with the other fullerene derivatives discussed below.

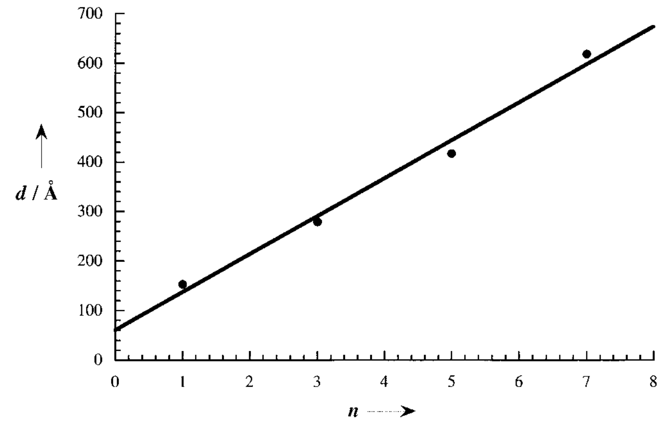


Figure 1. Ellipsometric thickness d of layers of **1** assembled on a silicon wafer.

The deposition of **1** onto a hydrophilic ITO electrode instead of quartz was carried out through the same sequence of steps and its progression was monitored by means of absorption spectroscopy. The low transparency of ITO in the UV region limited the film analysis to the wavelength region greater than 350 nm. All films (that is, on quartz and ITO) were found to be mechanically and chemically stable in air, but were kept in the dark prior to their photochemical investigation. It is worth noting that most films deposited by the Langmuir–Blodgett technique have a high environmental instability, especially those that contain fullerenes.[10]

In the next step the photoactivity spectra of one, five, and ten self-assembled monolayers of **1** on ITO were measured. The most important observation is that the photocurrent responded linearly at most wavelengths to the number of monolayers (Figure 2). This result is of extreme importance since it underlines the benefit of the supramolecular organization, rather than the adsorption of the photosensitizer (that is, the fulleropyrrolidinium ion) on mesoporous substrates, such as nanostructured TiO_2 or SnO_2.[3, 11] In addition, the photoactivity spectrum follows unequivocally the absorption spectrum of the pyrrolidinium salt.

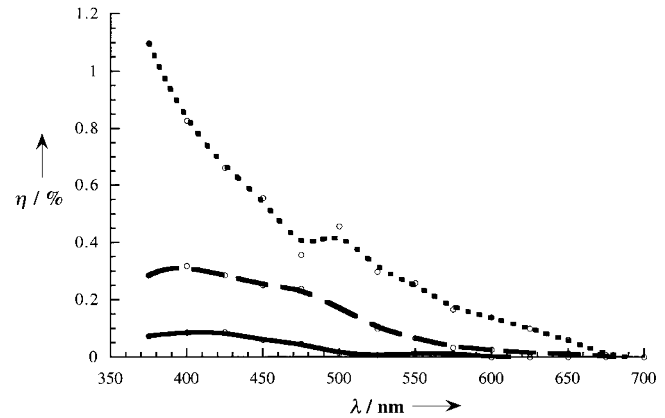


Figure 2. Photon-to-current conversion efficiency η of one (——), five (– – –), and ten (- - - -) self-assembled monolayers of the pyrrolidinium ion **1** on an ITO electrode; the efficiency was determined from the following expression $\eta\,[\%] = I_{SC}/I_{inc} \times 1240/\lambda\ [nm] \times 100]$ (I_{SC} = short-circuit photocurrent; I_{inc} = light intensity incident on the electrode).

To probe the direction of the photocurrent observed (hole or electron transport) we added various concentrations first of an electron acceptor (methylviologen) and second of a sacrificial electron donor (ascorbic acid) to the electrolyte solution. In the case of methylviologen, a concentration-dependent decrease in the photocurrent was noted (Table 1).

Table 1. Photocurrent I (measured at 400 nm) of a modified ITO electrode covered with ten layers of fulleropyrrolidinium ion **1** upon adding various concentrations c of an electron donor (ascorbic acid) and electron acceptor (methylviologen).

Quencher	c [mM]	I [nA]
methylviolgen	0	9.0
	5.8	5.2
	10.3	4.0
ascorbic acid	0	10
	6.6	58
	13.4	65

This relationship suggests that the electron acceptor competes efficiently with the modified ITO electrode to accept an electron from the photoexcited fullerene moiety. This proposal leads to the assumption that the addition of a sacrificial electron donor, such as ascorbic acid, should result in a net increase in the photocurrent. In fact, a significant enhancement (Table 1) was observed relative to the methylviologen case and also to that when there was no additive. We can conclude from these trends that the electron transfer into the ITO conduction band evolves from the fullerene excited state.

The promising features of the above-described system stimulated us to extend our investigation to the ruthenium–fullerene dyads **2** and **3**. The substantially red-shifted absorption maxima, which extend far into the visible region, in these dyads are expected to improve the light-harvesting properties of the modified electrodes. The maxima of the metal-to-ligand charge transfer (MLCT) transitions of dyad **2** and **3** lie at 460 and 640 nm, respectively. The strongest absorption of the fullerene moiety, on the other hand, is in the near visible region (around 335 nm).

The successive layer-by-layer deposition of **2** and **3** either onto quartz or ITO was monitored by absorption spectroscopy by using procedures similar to that used for **1**. Now, both absorption patterns, namely, that of the fullerene core (220, 260, and 335 nm) and that of the ruthenium(II)–polypyridyl complex fragments (**2**: 290 and 460 nm; **3**: 286, 408, 520, and 640 nm), were useful probes. Figure 3a displays the UV/Vis absorption spectrum of a quartz substrate covered with two to ten monolayers of **3**. Regardless of the origin, the absorption of both moieties (fullerene and ruthenium(II)–polypyridyl complex fragments) increased linearly with the number of layers. Figure 3b displays plots of the absorbance at 284 and 641 nm as a function of the number of monolayers of **3**.

Various attempts to use just the ruthenium complexes without the fullerene unit failed. Although noticeable amounts of the ruthenium complexes were assembled, subsequent immersion of the ruthenium-covered electrode into the PSS solutions led to a nearly quantitative dissolution

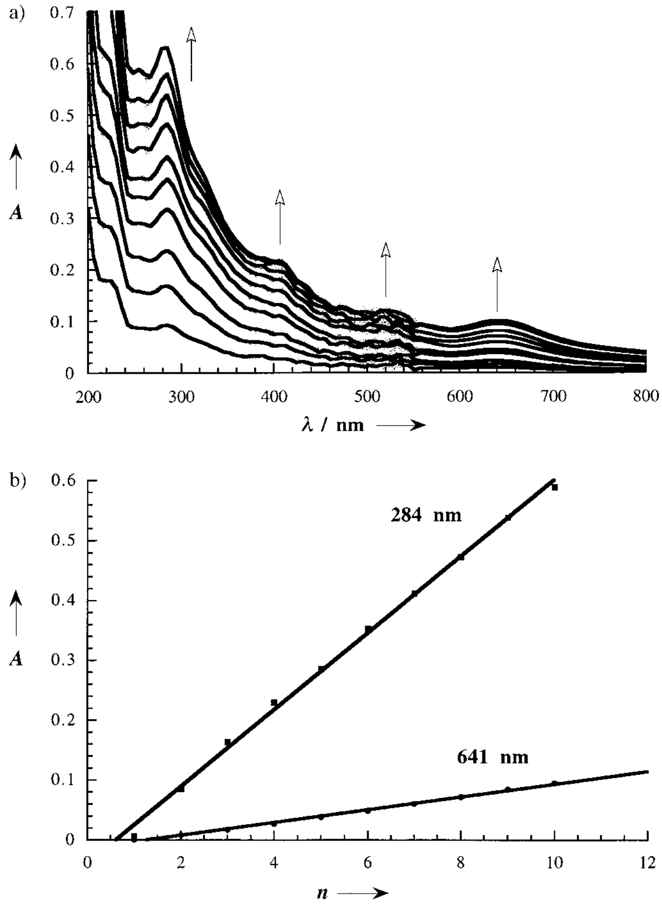


Figure 3. a) UV/Vis absorption spectra of a quartz substrate covered with two to ten monolayer films of the ruthenium(II)–polypyridyl–fullerene donor–acceptor dyad **3**. b) Plots of the absorbance at 284 and 641 nm as a function of the number of monolayers of **3**.

of the water-soluble complexes. Also, placement of a reference fulleropyrrolidine (that is, a compound with no positive charge on the nitrogen atom) was unsuccessful. Therefore, in **2** and **3** only the presence of the positive charges in combination with the adequate balance between the hydrophobic (fullerene) and the hydrophilic part (ruthenium complex fragment), opens the opportunity for the described assembly approach.[12]

It is noteworthy that the photocurrent followed exactly the trend established for the pyrrolidinium salt **1**. In particular, the photoactivity spectra are in good agreement with the ground-state absorption features of both ruthenium(II)–polypyridyl complexes. For example, the photocurrent of dyad **2** reaches a maximum at around 475 nm, while electrodes covered with dyad **3** showed a maximum between 600 and 625 nm, as well as another much stronger maximum at 400 nm.[13] The photocurrent ratio (I_{400nm}/I_{600nm}) of **3** is a good reflection of the ground-state absorption (A_{400nm}/A_{600nm}) both in solution and in the deposited film. Besides the observation that **3** is photoactive over practically the entire UV/Vis region, the response between 300 and 400 nm is enhanced by a factor of three relative to **2**.

The efficiency of these electrodes was studied as a function of the number of layers. In particular, modified ITO electrodes with a coverage of 1, 5, 10, and 20 layers of **2** or **3** were investigated. From these experiments a tendency was observed which is analogous to that summarized for the fulleropyrrolidinium salt namely, a progressive intensification of the photocurrent occurs with increasing numbers of layers. Furthermore, measurements over a time interval of 200 seconds gave rise to a repeatable and almost stable photocurrent in the case of **3**. For **2**, on the other hand, we found an exponential decay of about 25% during the first 20 seconds, followed then by a nearly steady-state current. All the films investigated responded uniformly to the repeatedly applied "light on/light off" intervals.

In summary, layer-by-layer deposition can be used as a viable alternative for the fabrication of photoactive films containing covalently linked donor–acceptor systems by using simple electrostatic attraction between oppositely charged moieties. Not only is the stability of the film remarkable, as a consequence of the strong adhesion of adjacent layers, but the layer-by-layer deposition technique can be performed in a systematic and controlled manner as monitored by the ground-state absorption and ellipsometry data on the modified electrode. Most significantly, the photocurrent response of the chemically modified electrodes increases with increasing film thickness (that is, with increasing number of assembled monolayers). No doubt, these characteristics point to the potential of these modified electrodes for materials and devices that have practical applications, such as solar energy conversion. Thus, this work provides a significant improvement over alternative approaches in which a single self-assembled monolayer on, for example, a gold electrode is employed.

Currently, we are intensifying our efforts to obtain a picture at molecular resolution, by means of AFM, of the modified fullerene ITO electrodes after each deposition step, that is, of the PDDA, PDDA/PSS, and PDDA/PSS/fullerene dyad. We are also pursuing ways to vary the polymeric PSS matrix with a view for improving the conductance between the aqueous environment and the ITO electrode and thereby obtaining higher efficiencies of the modified ITO electrodes.

Received: 10 February, 2000 [Z14679]

---

[1] V. Balzani, *Supramolecular Photochemistry*, D. Reidel, Dordrecht, **1987**; F. L. Carter, *Molecular Electronic Devices*, Dekker, New York, **1987**; M. A. Fox, M. Channon, *Photoinduced Electron Transfer*, Elsevier, Amsterdam, **1988**; E. Pelizzetti, M. Schiavello, *Photochemical Conversion and Storage of Solar Energy*, Kluwer, Dordrecht, **1997**.

[2] J. H. Fendler, I. Dekany, *Nanoparticles in Solids and Solutions*, Kluwer, Dordrecht, **1996**; P. V. Kamat, D. Meisel, *Semiconductor Nanoclusters*, Elsevier, Amsterdam, **1997**; J. H. Fendler, *Nanoparticle and Nanostructured Films*, WILEY-VCH, Weinheim, **1998**.

[3] P. V. Kamat, *Chem. Rev.* **1993**, *93*, 267; A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49.

[4] For other examples of fullerene photovoltaics, see N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, *Science* **1992**, *258*, 1474; L. Ouali, V. V. Krasnikow, U. Stalmach, G. Hadziioannou, *Adv. Mater.* **1999**, *11*, 1515; H.-L. Wang, D. W. McBranch, V. I. Klimov, R. Helgeson, F. Wudl, *Chem. Phys. Lett.* **1999**, *315*, 173; J. F. Nierengarten, J. F. Eckert, J. F. Nicoud, L. Ouali, V. Krasnikov, G. Hadziioannou, *Chem. Commun.* **1999**, 617; H. Imahori, H. Yamada, Y. Nishimura, I. Yamazaki, Y. Sakata, *J. Phys. Chem. B* **2000**, *104*, 2099; for a review, see H. Imahori, Y. Sakata, *Eur. J. Org. Chem.* **1999**, 2445.

[5] For leading references on layer-by-layer assembly, see M. Ahlers, W. Müler, A. Reichert, H. Ringsdorf, J. Venzmer, *Angew. Chem.* **1990**, *102*, 1310; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1269; J. H. Fendler, F. C. Meldrum, *Adv. Mater.* **1995**, *7*, 607; S. W. Keller, S. A. Johnson, E. S. Brigham, E. H. Yonemoto, T. E. Mallouk, *J. Am. Chem. Soc.* **1995**, *117*, 12879; G. Decher, *Science* **1997**, *277*, 1232; X. Zhang, J. Shen, *Adv. Mater.* **1999**, *11*, 1139; N. A. Kotev, T. Haraszti, L. Turi, G. Zavala, R. E. Geer, I. Dékány, J. H. Fendler, *J. Am. Chem. Soc.* **1997**, *119*, 6821.

[6] For previous reports on self-assembled fullerene layers using electrostatic interactions, see G. Decher, *Nachr. Chem. Tech. Lab.* **1993**, *41*, 793; H. Hong, D. Davidov, C. Kallinger, U. Lemmer, J. Feldmann, E. Harth, A. Gügel, K. Müllen, *Synth. Met.* **1999**, *102*, 1487.

[7] M. Maggini, D. M. Guldi, S. Mondini, G. Scorrano, F. Paolucci, P. Ceroni, S. Roffia, *Chem. Eur. J.* **1998**, *4*, 1992.

[8] D. M. Guldi, M. Maggini, E. Menna, G. Scorrano, F. Paolucci, M. Marcaccio, P Ceroni, S. Roffia, *Chem. Eur. J.* submitted; M. Maggini, D. M. Guldi in *Molecular and Supramolecular Photochemistry Vol. 4* (Eds.: V. Ramamurthy, K. S. Schanze), Marcel Dekker, New York, **2000**, p. 149.

[9] T. Da Ros, M. Prato, M. Carano, P. Ceroni, F. Paolucci, S. Roffia, *J. Am. Chem. Soc.* **1998**, *120*, 11645.

[10] C. A. Mirkin, W. B. Caldwell, *Tetrahedron* **1996**, *52*, 5113; L. Leo, G. Mele, L. Valli, G. Vasapollo, D. M. Guldi, G. Mascolo, *Langmuir* **2000**, 4599.

[11] C. P. Luo, C. H. Huang, L. B. Gan, D. J. Zhou, W. S. Xia, Q. K. Zhuang, Y. L. Zhao, Y. Y. Huang, *J. Phys. Chem.* **1996**, *100*, 16685; P. V. Kamat, M. Gevaert, K. Vinodgopal, *J. Phys. Chem. B* **1997**, *101*, 4422; M. Kocher, T. K. Daubler, E. Harth, E. Harth, U. Scherf, A. Gügel, D. Neher, *Appl. Phys. Lett.* **1998**, *72*, 650; P. V. Kamat, S. Barazzouk, K. G. Thomas, S. Hotchandani, *J. Phys. Chem.* **2000**, *104*, 4014.

[12] N. A. Kotov, *Nanostruct. Mater.* **1999**, *12*, 789.

[13] The photon-to-current conversion efficiency at 475 nm of a single monolayer of dyads **2** and **3** in the absence of any sacrificial electron donor are 0.0784 and 0.0833 %, respectively.

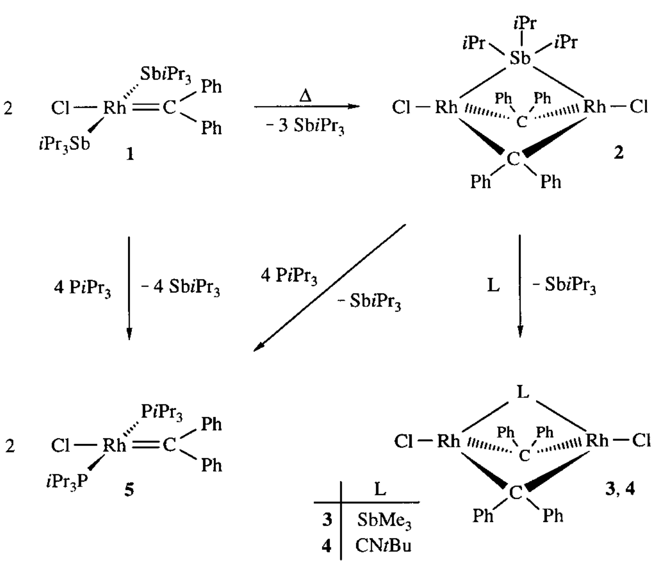
Breaking the Rule: Synthesis and Molecular Structure of Dinuclear Rhodium Complexes with Bridging and Semibridging Trialkylphosphane Ligands[**]

Thomas Pechmann, Carsten D. Brandt, and
Helmut Werner[*]

In memory of John Osborn

Tertiary phosphanes PR_3 with R = alkyl or aryl belong like CO to the most well-known ligands in coordination chemistry.[1] While with regard to CO not only numerous metal complexes with *terminal* but also with *bridging* carbonyl ligands have been reported, the same is not true for tertiary phosphanes. Textbooks on Inorganic Chemistry[2] as well as corresponding monographs and reviews[3] mention without exception that tertiary phosphanes (and tertiary arsanes AsR_3 and stibanes SbR_3 as well) behave exclusively as terminal coordinated ligands.

Recently, we have begun to illustrate that this postulate may need to be modified by showing that the thermal reaction of the square-planar precursor **1** leads to the dinuclear complex **2** from which the related compounds **3** and **4** were obtained by exchange of the bridging Sb*i*Pr$_3$ ligand for $SbMe_3$ and CN*t*Bu (Scheme 1).[4] However, attempts to substitute the stibane by a tertiary phosphane failed. Treatment of **2** with P*i*Pr$_3$ did not afford $[Rh_2Cl_2(\mu\text{-P}i\text{Pr}_3)(\mu\text{-CPh}_2)_2]$ but gave the mononuclear complex **5** by displacement of the stibane *and* cleavage of the carbene bridges. Now we have found that replacing one of the chloro ligands in **2** by acetylacetonate (acac) changes the reactivity of the stibane-bridged dinuclear compound dramatically and turns the dream of the isolation of a transition metal complex with $M(\mu\text{-PR}_3)M$ as a molecular unit into reality.



Scheme 1.

The dinuclear compound **6**, obtained from **2** and an equimolar amount of [Tl(acac)] , reacts with PMe_3 in the molar ratio of 1:1 in pentane/diethyl ether to give the substitution product **7** (Scheme 2). After recrystallization from acetone, red-brown crystals of **7** were isolated in 82 % yield. The ^{31}P NMR spectrum of **7** (in C_6D_6) displays a doublet of doublets at $\delta = -36.4$ with $^{31}P-^{103}Rh$ coupling constants of 147.5 and 81.4 Hz, indicating that the PMe_3 ligand is not linked to one of the metal centers in a terminal fashion. For the dirhodium compound $[(acac)Rh(\mu\text{-CO})\{\mu\text{-C}(p\text{-Tol})_2\}_2Rh(acac)(PMe_3)]$, which is formed by stepwise reaction of $[(acac)Rh(\mu\text{-Sb}i\text{Pr}_3)\{\mu\text{-C}(p\text{-Tol})_2\}_2Rh(acac)]$ with PMe_3 and CO and which contains a *terminal* Rh–PMe_3 bond,[5] the $^{31}P-^{103}Rh$ coupling constants of the signal observed in the ^{31}P NMR spectrum at $\delta = -5.2$ are 129.7 and 7.6 Hz, respectively. The ^{31}P NMR resonance signals for the PMe_3 ligand of other

---

[*] Prof. Dr. H. Werner, Dipl.-Chem. T. Pechmann,
Dipl.-Chem. C. D. Brandt
Institut für Anorganische Chemie der Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4605
E-mail: helmut.werner@mail.uni-wuerzburg.de

[**] This work was supported by the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie. We thank in particular Dr. J. Wolf and Dr. U. Herber, Universität Würzburg, for valuable advice and discussions.