Synthesis of “Molecular Landers”

André Gourdon

Groupe Electronique Moléculaire, CEMES, CNRS UP 8011,
B.P. 4347, 29 Rue Jeanne Marvig, F-31055 Toulouse Cedex, France
Fax: (internat.) + 33-5/62 25 79 99
E-mail: gourdon@cemes.fr

Received July 3, 1998

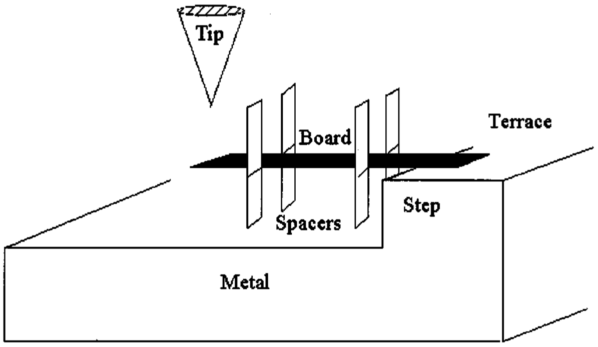
Keywords: Arenes / Ladder / Molecular devices / Electron transport / Scanning tunnelling microscopy

PAHs (molecular landers), 17.7 to 30 Å long, devised for the study of electron transport along a single molecular wire in an STM tip–molecule–electrode experiment, have been obtained by Diels–Alder cycloadditions of benzadiyne to two cyclopentadienone precursors. They comprise a polyaromatic molecular board with a terminal fluoranthene group for chemisorption (and electrical contact) on a metallic diatomic terrace, and 4 to 8 3,5-di-*tert*-butylphenyl spacers. As a result of steric crowding, these spacers are held in such a conformation that the phenyl rings are nearly perpendicular to the main board plane and maintain the molecular wire 6.8 Å above the metallic surface.

Introduction

Molecular systems capable of allowing fast, reliable, long-distance electron transport are an essential requisite for future applications in molecular electronics. In order to design and synthesize the optimal molecules for this purpose, it is very important to have an understanding of the parameters that control this phenomenon. Although theoretical investigations of the conductance and transparence of long molecular wires between two metallic electrodes have recently been published,[1] an experimental study of electron transport decay with increasing molecular length and with different types of molecules has yet to be carried out. Along these lines, only two electrode−molecule−electrode experiments have been described to date: one using a gapless (“metallic”) single-wall nanotube,[2] while in the other a benzene-1,4-dithiol was used to bridge a mechanically controllable break junction of around 8 Å.[3] However, for “nonmetallic” molecular wires, the very low current density expected for the interelectrode gaps currently available by nanolithography remains a very crucial problem. For example, for an electrode-to-electrode distance of 8 nm with a bias voltage of 0.1 V, calculation[1a] shows that the expected current intensity would be at maximum ca. $10^{-14}-10^{-15}$ A, at least for the best molecular wires synthesized to date. On the other hand, with current nanolithography technology, nanoelectrodes with an interelectrode gap of less than 5 nm remain difficult to make in a reproducible manner.[4] In order to overcome this low-current problem associated with the difficulty of positioning a molecule between two nanoelectrodes, studies are underway in this laboratory concerning a slightly different experimental set-up (tip−molecule−surface), as shown in Figure 1.

Figure 1. Schematic view of an “STM tip−molecule−electrode” experiment



The experiments are performed under ultra high vacuum conditions, using a clean metallic surface on which the molecules are initially deposited by sublimation. These molecules have a rigid main board (the molecular wire), which is maintained at least 6 Å above the surface by several spacers (legs) R in order to prevent a direct electron flow between the tip and the surface through (and perpendicularly to) the board plane. This main board has an aromatic platform that projects beyond the last spacer for chemisorption (and good electrical contact) with a diatomic terrace on the metal surface. Measurements of current density versus length are made by moving the tip along the molecular board. The similarities between these molecular ladders and landing craft such as the Mars lander has led to the proposal of the name “molecular landers”. The spacers need to be chosen carefully; they must show little electronic coupling with the main board and with the surface in order to minimize tip-to-surface electron leaks, and they must also allow some movement of the molecule on the surface. Although the parameters controlling this mobility are not fully understood,[5] there seems to be a compromise between rigidity, which favors mobility, and softness (slackness), which allows an adaptation of the molecular conformation to suit the surface roughness, as well as physisorp-

1434−193X/98/1212−2797 $ 17.50+.50/0

tion and chemisorption. One further factor is that the spacers must also maintain some solubility of the molecule, at least for purification and spectroscopic studies.

Results and Discussion

For the experiments outlined in the introduction, several types of 17.7 to 30 Å long “molecular landers” have been synthesized, as shown in Figure 2.

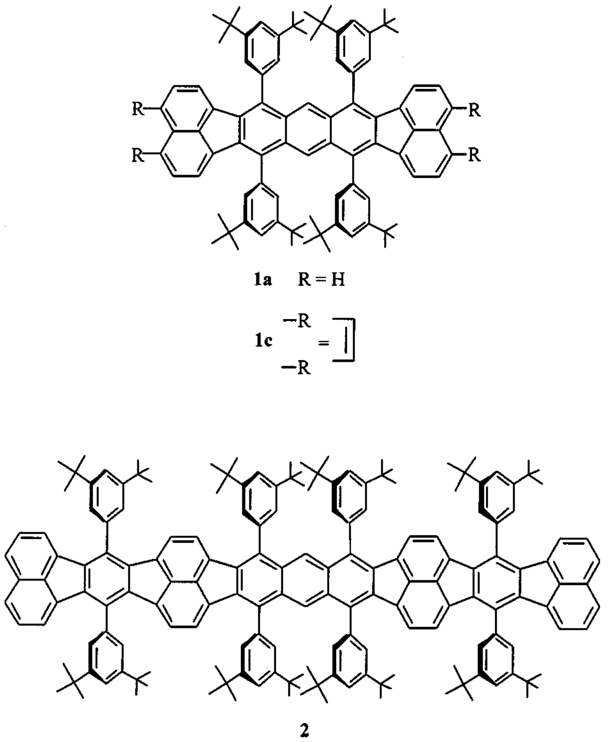


Figure 2. “Molecular ladders”

They comprise a polyaromatic molecular board with a terminal fluoranthene group for chemisorption (and electrical contact) on a metallic diatomic terrace, and 4 to 8 3,5-di-*tert*-butylphenyl spacers. As a result of steric crowding, these spacers are held in such a conformation that the phenyl rings are nearly perpendicular to the main board plane. Figure 3 shows one of the possible conformations of **1c** obtained by semiempirical AM1[6] calculations, which have been shown to give excellent agreement with the X-ray structures of polycyclic aromatic hydrocarbons (PAHs). Steric repulsion between the di-*tert*-butylphenyl and the fluoranthene ends is, however, not sufficient to force substantial distortion of the main board core, as observed in some sterically congested PAHs.[7] These bulky *tert*-butyl groups increase the board−surface distance to ca. 6.8 Å, allow some rotation of the “legs” without significantly reducing this distance, reduce the phenyl−surface electronic coupling, allow easy displacement of the molecule on the surface, and improve its solubility.

The syntheses of molecules **1a** and **1c** are outlined in Scheme 1.

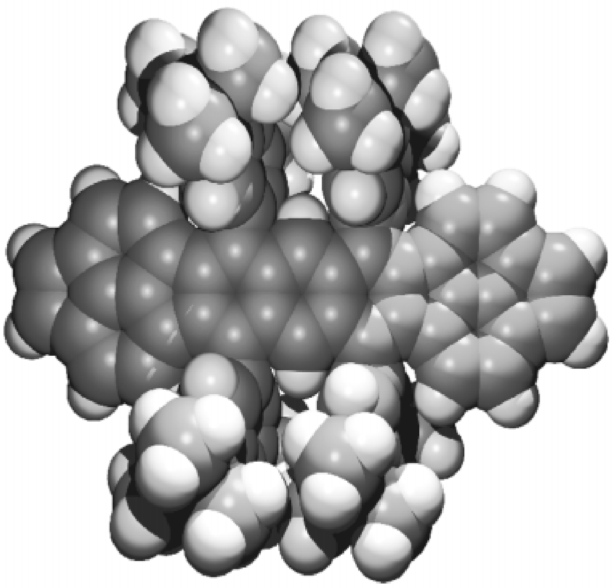
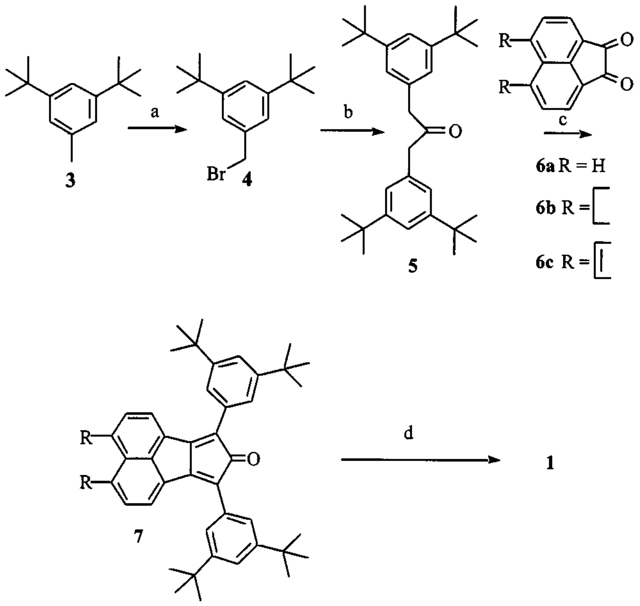


Figure 3. CPK model showing the minimum energy conformation of **1c**

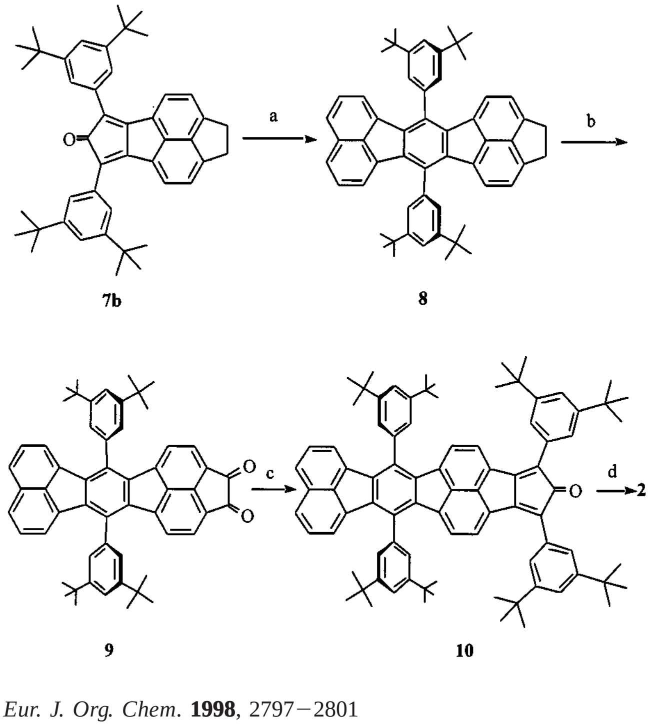
Scheme 1. Reagents: (a) NBS, benzoyl peroxide. − (b) $N(CH_3)_2(C_{18}H_{37})_2Br$, $Fe(CO)_5$, NaOH, H_2O, CH_2Cl_2. − (c) **6**, NaOH, MeOH. − (d) DABT, LTA, THF.



The key reaction is a double Diels−Alder cycloaddition of two molecules of cyclopentadienone **7** with benzadiyne, which provides, after CO extrusion, the anthracene cores of **1**. The benzadiyne intermediate was prepared in situ by oxidation of 1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*′]bis(triazole) by lead tetraacetate, as first described by Hart et al.[8] This route has also been recently used by Schlüter et al.[9] for the preparation of very similar (but much more soluble) molecular boards bearing different substituents. 1-Bromomethyl-3,5-di-*tert*-butylbenzene **4** was obtained by bromination[10] of 3,5-di-*tert*-butyltoluene[11] **3** using NBS in CCl_4. Subsequent carbonylative coupling of **4** with iron pentacarbonyl and a base under phase-transfer conditions[12] gave the 1,3-diaryl ketone **5** in moderate yield (40%). Double Knoevenagel condensation with the naphthenequinone **6a**, the diketopyracene **6b**, or the pyracycloquinone **6c** in dry methanol gave the respective cyclopentadienones **7a**, **7b**, **7c** in good yields.[13] Finally, reactions of two molecules of these dienes **7a** and **7c** with benzadiyne yielded the target products **1a** and **1c**, respectively.

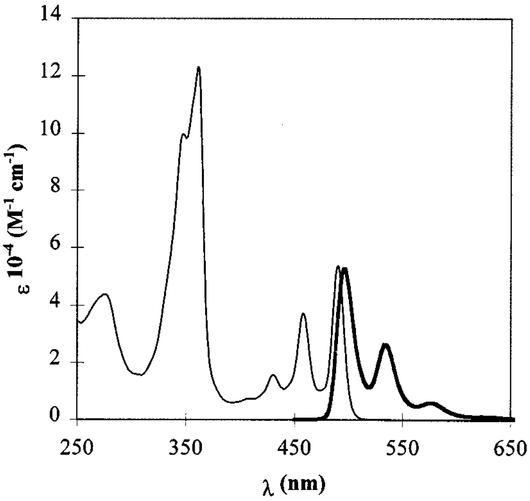
In contrast to similar molecules recently described by Schlüter et al.,[14] **2** cannot be obtained by extension of the dienophile **1c** by Diels−Alder reaction with the acecyclone **7a**. Attempts to perform this reaction invariably led to complex mixtures of by-products and only low yields of the target molecule **2**. This contrasting behaviour can be mainly attributed to the much lower solubility of **1c** and **2** and to the more electron-rich character of the diene **7a** (due to the two 3,5-di-*tert*-butylphenyl substituents) compared with α,ω-dodecanyl or carboxylate groups, which precludes an efficient retro Diels−Alder reaction. The synthesis of **2** is outlined in Scheme 2. It involves the preparation of the soluble cyclopentadienone **10**, which is then reacted with benzadiyne in the final step of the synthetic procedure. The key feature of the preparation of **10** was the oxidation of ethane-bridged **8** by seleninic anhydride[15] according to a procedure described by Rabideau et al. for the synthesis of 1,2,5,6-tetraketopyracene. Intermediate **8** was obtained by Diels−Alder cycloaddition of the diene **7b** to acenaphthylene with concomitant decarbonylation and aromatization. Once again, owing to the electron-rich character of **7b**, this reaction proceeds slowly, requiring 7 days in refluxing toluene, compared with only 2 h in the case of analogous electron-poor carboxylate derivatives.[14] Base-catalysed reaction of the diketone **9** with **5** in a mixture of methanol and dichloromethane gave the cyclopentadienone **10** in 85% yield.

Scheme 2. Reagents: (a) Acenaphthylene, toluene. − (b) $(C_6H_5SeO)_2O$, chlorobenzene. − (c) **5**, NaOH, MeOH, CH_2Cl_2. − (d) DABT, LTA, THF.



These landers with an anthracene core are moderately (**1a**) to very poorly (**2**) soluble, giving yellow (**1a**) or pink-red (**2**), highly luminescent solutions. Figure 4 shows the absorption and emission spectra of **1a** in chloroform. The low-energy absorption bands have a typical vibronic pattern. The emission spectrum displays 4 maxima at 496, 534, 577, and 630 nm, and mirrors (in energy) the absorption spectrum at 490, 458, 430, and 408 nm, with a small Stoke shift (6 nm) as expected for a very rigid molecule. These molecules can be sublimed without decomposition under ultra-high vacuum conditions on warm, clean, copper or silver surfaces, and have allowed the measurement of spatially-resolved electrical conductance along a single molecular wire decay length.[17]

Figure 4. Absorption and emission spectra (bold line) of **1a** in $CHCl_3$. The emission spectra has arbitrary units



Conclusion and Perspectives

In summary, a simple route to PAHs designed for the study of electron transport in an STM single molecule−surface experiment has been devised. Work in progress is directed towards further functionalization of these landers, and their use as real molecular devices such as molecular switches.

I would especially like to thank *C. Joachim* and *H. Tang* for their collaboration in the conception of molecular landers, for calculations and simulations of STM experiments, and their help in the choice of the target molecules described here. Thanks are also due to *V. J. Langlais*, *R. R. Schlittler*, and *J. K. Gimzewski* (IBM Zurich) for performing STM experiments. *Pierre Lavedan* and *Christine Viala* are gratefully acknowledged for experimental assistance. This work was supported by the *CNRS* and the *EEC Esprit-Melari project* 23238 “Nanowires”.

Experimental Section

General: IR (KBr): Perkin-Elmer FT-IR 1725. − UV/vis: Shimadzu UV-3100. − NMR: Bruker WF-250, Bruker AM 300; ^{1}Hand ^{13}C-NMR spectra were recorded in $CDCl_3$ solution at 20°C (except for **2**, which was examined in $C_2D_2Cl_4$ at 130°C) and referenced to the residual solvent signals as internal standards ($CHCl_3$ at δ_H: 7.25, δ_C: 77.0; C_2DHCl_4 at δ_H: 5.95). − DCI- and FAB-MS: Nermag R10-R10. − Elemental analysis: Service d'Analyse du LCC (Toulouse) and ICSN (Paris). − TLC: Merck aluminium sheets, silica gel 60 F_{254}. − Column chromatography: Merck silica gel, grade 60, 230−400 mesh. − Emission spectroscopy: spectrofluorimeter: Photon Technology International M 2011-MS III; xenon lamp: 75 W; slits 4 nm; photomultiplication: 1000 V; solvent: degassed $CHCl_3$.

Starting Materials: 3,5-Di-*tert*-butyltoluene,[11] 1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*′]bis(triazole),[8] 1,2-diketopyracene, and pyracycloquinone[16] were prepared according to published procedures. Commercial acenaphthylene (Aldrich) containing ca. 20% acenaphthene was chromatographed on a short column of silica gel using petroleum ether as eluent to remove a brown impurity. Lead tetraacetate was recrystallized from hot glacial acetic acid and stored over KOH and P_2O_5 before use. THF was distilled from Na/benzophenone. CH_2Cl_2 was distilled over CaH_2 prior to use.

1-Bromomethyl-3,5-di-tert-butylbenzene (**4**): A mixture of 3,5-di-*tert*-butyltoluene (5.0 g, 24.5 mmol), *N*-bromosuccinimide (4.5 g, 25.2 mmol), and dibenzoyl peroxide (0.2 g, 0.8 mmol) in carbon tetrachloride (50 ml) was refluxed for 1 h. After cooling to room temperature, the suspension was filtered and the collected solid was washed with CCl_4 (2 × 50 ml). After evaporation of the solvent from the combined filtrate and washings, the crude product was purified by passage through a short plug of silica gel using petroleum ether as eluent (5.0 g, yield 73%). The product was found to contain up to 8% of the starting material, but was used without further purification for the next step. − $C_{15}H_{23}Br$ (283.25): calcd. C 63.6, H 8.2; found C 64.1, H 8.0. − ^{1}H NMR: δ = 1.32 (s, 18 H), 4.52 (s, 2 H), 7.23 (d, J = 1.8 Hz, 2 H), 7.36 (t, J = 1.8 Hz, 1 H). − ^{13}C NMR: δ = 151.1, 136.9, 123.2, 122.4, 34.8, 34.5, 31.4.

1,3-Bis(3,5-di-tert-butylphenyl)-2-propanone (**5**): To a thoroughly degassed mixture of **4** (4.0 g, 14.1 mmol), dimethyldioctadecylammonium bromide (400 mg, 0.6 mmol), 40 ml of 30% aqueous NaOH, and 40 ml of CH_2Cl_2 under argon, 0.92 ml (7.0 mmol) of iron pentacarbonyl was added. The biphasic system was stirred rapidly (1200 rpm) under argon for 3 h, and then poured into a beaker containing 200 ml of dichloromethane and 100 ml of water. After aerial oxidation of iron carbonyl residues overnight and filtration, the aqueous phase was extracted with dichloromethane (2 × 50 ml). The dichloromethane phases were dried ($MgSO_4$) and the product was purified by chromatography (eluent: petroleum ether/dichloromethane, 2:1). Yield 2.45 g, 40%; pale-yellow oil which solidified on standing. − $C_{31}H_{46}O$ (434.7): calcd. C 85.7, H 10.7; found C 85.5, H 10.8. − ^{1}H NMR: δ = 1.32 (s, 36 H), 3.73 (s, 4 H), 7.0 (d, J = 1.9 Hz, 4 H), 7.31 (t, J = 1.9 Hz, 2 H). − ^{13}C NMR: δ = 206.5, 151.1, 133.3, 123.7, 120.9, 49.5, 34.8, 31.5.

Cyclopentadienone **7a**: To a suspension of acenaphthenequinone **6a** (70 mg, 0.38 mmol) and **5** (179 mg, 0.41 mmol) in dry methanol (10 ml) under argon was added 0.2 ml (0.2 mmol) of a 1 M solution of potassium hydroxide in dry methanol. After stirring for 5 h under argon, the suspension was filtered and the precipitate was extensively washed with cold methanol. If necessary, the crude product was purified by chromatography (SiO_2, CH_2Cl_2/petroleum ether, 1:2) giving 190 mg (0.33 mmol, yield 85%) of green **7a** (blue solutions). − $C_{43}H_{48}O$ (580.8): calcd. C 88.9, H 8.3; found C 88.9, H 8.5. − ^{1}H NMR δ = 1.40 (s, 36 H), 7.46 (d, J = 1.8 Hz, 2 H), 7.58 (dd, J = 7.1 Hz, 8.2 Hz, 2 H), 7.66 (d, J = 1.8 Hz, 4 H), 7.84 (d, J = 8.2 Hz, 2 H), 8.07 (d, J = 7.1 Hz, 2 H). − ^{13}C NMR: δ = 202.5, 153.6, 150.8, 144.8, 13.2, 132.0, 130.7, 128.3, 127.3, 123.6, 122.6, 120.8, 35.1, 31.6. − MS-DCI (NH_3): m/z = 581 [MH^+], 598 [$MNH_4{}^+$].

Cyclopentadienone **7b**: To a solution of diketopyracene **6b** (50 mg, 0.24 mmol) and **5** (110 mg, 0.25 mmol) in dry methanol (5 ml) under argon was added 0.2 ml of a 1 M solution of potassium hydroxide in dry methanol. After stirring overnight under argon, the suspension was filtered and the precipitate was extensively washed with cold methanol and dried in vacuo to afford 140 mg (0.23 mmol, 96%) of **7b** as green crystals (blue solutions). − $C_{45}H_{50}O$ (606.9): calcd. C 89.1, H 8.3; found C 89.0, H 8.5. − ^{1}H NMR: δ = 1.40 (s, 36 H), 3.52 (s, 4 H), 7.34 (d, J = 7.1 Hz, 2 H), 7.44 (t, J = 1.8 Hz, 2 H), 7.69 (d, J = 1.8 Hz, 4 H), 7.93 (d, J = 7.1 Hz, 2 H). − ^{13}C NMR: δ = 202.6, 155.4, 150.7, 146.7, 143.9, 131.0, 128.1, 123.3, 122.4, 122.3, 121.5, 35.1, 32.2, 31.6. − MS-DCI (NH_3): m/z = 607 [MH^+].

Cyclopentadienone **7c**: To a solution of pyracycloquinone **6c** (50 mg, 0.24 mmol) and **5** (150 mg, 0.34 mmol) in dry methanol (10 ml) under argon was added 1 ml of a 1 M solution of potassium hydroxide in dry methanol. After stirring overnight under argon, the suspension was filtered and the precipitate was extensively washed with cold methanol and dried in vacuo to afford 140 mg (0.23 mmol, 96%) of **7c** as a brown powder (red solutions). − $C_{45}H_{48}O$ (604.9): calcd. C 89.4, H 8.0; found C 89.1, H 8.2. − ^{1}H NMR: δ = 1.44 (s, 36 H), 7.45 (s, 2 H), 7.53 (t, J = 1.8 Hz, 2 H), 7.87 (d, J = 1.8 Hz, 4 H), 8.06 (d, J = 7.3 Hz, 2 H), 7.32 (d, J = 7.3 Hz, 2 H). − ^{13}C NMR: δ = 201.3, 150.9, 138.4, 131.0, 130.9, 127.3, 125.4, 123.4, 123.0, 121.9, 35.2, 31.6. − MS-DCI (NH_3): m/z = 605 [MH^+].

Lander **1a**: To a solution of **7a** (300 mg, 0.52 mmol) in THF (20 ml) under argon, 1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*′]bis(triazole) (80 mg, 0.42 mmol) and lead tetraacetate (390 mg, 0.88 mmol) were added alternately in small portions (0.5 h). The suspension was then concentrated in vacuo and, under argon, the residue was thoroughly extracted with 50 ml portions of $CHCl_3$. After decantation, the combined extracts were filtered through Celite. Concentration of the filtrate and recrystallization of the residue from CH_2Cl_2/methanol gave 115 mg (0.097 mmol, 37%) of yellow-orange **1a** (highly fluorescent yellow-green air-sensitive solutions). − $C_{90}H_{98}$ (1179.8): calcd. C 91.6, H 8.4; found C 91.2, H 8.8. − ^{1}H NMR: δ = 0.87−1.25 (br m, 72 H), 6.31 (d, J = 7.3 Hz, 4 H), 7.21 (dd, J = 7.3, 8.0 Hz, 4 H), 7.30 (d, J = 2.0 Hz, 8 H), 7.51 (t, J = 2.0 Hz, H), 7.61 (d, J = 8.0 Hz, 4 H), 8.54 (s, 2 H). − UV/vis ($CHCl_3$): λ_{max} (nm) (ε 10^{-4} mol dm^{-3} cm^{-1}): 490 (5.37), 458 (3.73), 430 (1.58), 408 (0.74), 361 (12.4), 347 (9.99), 274 (4.38) − Emission: $CHCl_3$, (λ_{exc}: 361 nm): 496, 534, 577, 630 nm. − MS-FAB (MNBA): m/z = 1179 [M^+].

Lander **1c**: To a solution of **7c** (70 mg, 0.115 mmol) in THF (20 ml) under argon, 1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d*′]bis(triazole) (20 mg, 0.105 mmol) and lead tetraacetate (120 mg, 0.36 mmol) were added alternately in small portions (0.5 h). The suspension was then concentrated to a volume of 10 ml and filtered. The resulting reddish precipitate was extracted with THF (5 × 20 ml), giving 32 mg (0.026 mmol, 45%) of red **1c**. − $C_{94}H_{98}$ (1227.8): calcd. C 92.0, H 8.0; found C 91.7, H 7.9. − ^{1}H NMR: δ = 1.25 (br m, 72 H), 5.94 (d, J = 7.0 Hz, 4 H), 6.61 (s, 4 H), 7.01 (d, J = 7.0 Hz, 4 H), 7.21 (d, J = 1.8 Hz, 8 H), 7.43 (t, J = 1.8 Hz, 4 H), 8.09 (s, 2 H). − MS-DCI (CH_4): m/z = 1227 [MH^+], 1243 [$MCH_5{}^+$], 1259 [$MC_2H_9{}^+$].

2,5-Bis(3,5-di-tert-butylphenyl)-3,4-(1,8-naphthylene)-1,6-(5,6-acenaphthylene)benzene (**8**): A solution of **7b** (200 mg, 0.33 mmol) and acenaphthylene (125 mg at 80%, 0.66 mmol of acenaphthylene) in toluene (20 ml) was refluxed for 7 d. After evaporation of the toluene in vacuo, the residue was dissolved in dichloromethane and preadsorbed onto silica gel. Purification by silica gel chromatography using first petroleum ether to remove the excess acenaphthene/acenaphthylene and then petroleum ether/dichloromethane gradients led to the isolation of 175 mg (0.24 mmol, 73%) of yellow-orange **8**. − $C_{56}H_{56}$ (729.1): calcd. C 92.3, H 7.7; found C 92.0, H 7.4. − ^{1}H NMR: δ = 1.41 (s, 36 H), 3.43 (s, 4 H), 6.82 (d, *J* = 7.1 Hz, 2 H), 6.87 (d, *J* = 7.1 Hz, 2 H), 7.17 (d, *J* = 7.1 Hz, 2 H), 7.32 (dd, *J* = 7.1, 8.2 Hz, 2 H), 7.58 (d, *J* = 1.8 Hz, 4 H), 7.67 (t, *J* = 1.8 Hz, 2 H), 7.70 (d, *J* = 8.2 Hz, 2 H). − ^{13}C NMR: δ = 151.7, 145.5, 138.3, 136.9, 132.4, 129.6, 127.6, 126.0, 125.0, 123.7, 123.0, 121.0, 120.7, 76.5, 35.2, 32.2, 31.6. − MS-DCI (CH_4): *m/z* = 729 [MH^+].

Quinone **9**: A solution of **8** (75 mg, 0.103 mmol) and benzeneseleninic acid anhydride (74 mg, 0.103 mmol) in chlorobenzene (10 ml) was refluxed for 24 h. The orange solution was then rotary evaporated. Silica gel chromatography of the residue (eluent CH_2Cl_2/petroleum ether) furnished 54 mg (0.071 mmol, 69%) of orange **9**. − $C_{56}H_{52}O_2$ (757.0): calcd. C 88.8, H 6.9; found C 88.5, H 6.8. − ^{1}H NMR: δ = 1.43 (s, 36 H), 6.95 (d, *J* = 6.8 Hz, 2 H), 7.03 (d, *J* = 7.3 Hz, 2 H), 7.39 (dd, *J* = 6.8, 8.2 Hz, 2 H), 7.57 (d, *J* = 1.8 Hz, 4 H), 7.75 (t, *J* = 1.8 Hz, 2 H), 7.81 (d, *J* = 8.2 Hz, 2 H), 7.95 (d, *J* = 7.3 Hz, 2 H). − ^{13}C NMR: δ = 187.6, 152.4, 141.9, 138.8, 137.0, 135.8, 127.9, 127.3, 124.7, 124.2, 124.0, 123.2, 121.8, 35.3, 31.5. − MS-DCI (CH_4): *m/z* = 757 [MH^+], 785 [$MC_2H_5^+$], 797 [$MC_3H_5^+$].

Cyclopentadienone **10**: To a solution of **9** (40 mg, 0.053 mmol) and **5** (35 mg, 0.081 mmol) in a mixture of dry methanol (10 ml) and dry dichloromethane (10 ml) under argon was added 0.25 ml (0.05 mmol) of a 0.2 M solution of potassium hydroxide in dry methanol. After stirring overnight under argon, the suspension was concentrated, filtered, and the precipitate was extensively washed with cold methanol. The crude product was purified by chromatography (SiO_2, CH_2Cl_2/petroleum ether, 1:4) giving 52 mg (0.045 mmol, 85%) of red-orange **10**. − $C_{87}H_{94}O$ (1155.7): calcd. C 90.4, H 8.2; found C 90.1, H 8.0. − ^{1}H NMR: δ = 1.20−1.50 (m, 72 H), 6.97 (d, *J* = 7.0 Hz, 2 H), 7.07 (d, *J* = 7.0 Hz, 2 H), 7.39 (dd, *J* = 7.5 Hz, 2 H), 7.47 (t, *J* = 1.5 Hz, 2 H), 7.63 (d, *J* = 1.5 Hz, 4 H), 7.72−7.79 (m, 8 H), 8.01 (d, *J* = 7.5 Hz, 2 H). − ^{13}C NMR: δ = 201.7, 152.0, 150.8, 140.9, 138.4, 137.6, 137.5, 136.5, 131.1, 130.2, 129.7, 127.8, 126.7, 125.5 124.1, 123.6, 123.4, 123.1, 122.7, 122.1, 121.5, 35.3, 35.1, 31.6. − MS-DCI (CH_4): *m/z* = 1155 [MH^+].

Lander **2**: To a solution of **10** (25 mg, 21.6 μmol) in dry THF (3 ml) under argon, 1,5-diamino-1,5-dihydrobenzo[1,2-*d*:4,5-*d′*]bis(triazole) (10 mg, 52.6 μmol) and 40 mg (90.2 μmol) of lead tetraacetate were added alternately in small portions (1 h). The suspension was then filtered through a short plug of silica gel, which was subsequently washed with THF and dichloromethane until the washings were colourless. Repeated extractions with boiling chlorobenzene (5 × 10 ml) gave highly fluorescent pink solutions, from which **2** precipitated at room temperature. Yield 30%, 7.5 mg, 3.2 μmol. − $C_{178}H_{190}$ (2329.5): calcd. C 91.8, H 8.2; found C 91.6, H 8.0. − ^{1}H NMR ($C_2D_2Cl_4$, 130°C): δ = 1.25−1.40 (br m, 144 H), 5.80 (d, *J* = 7 Hz, 4 H), 6.13 (d, *J* = 7 Hz, 4 H), 6.90 (d, *J* = 7 Hz, 4 H), 7.24 (d, *J* = 1.5 Hz, 8 H), 7.26−7.31 (br m, 4 H), 7.47 (br s, 8 H), 7.65 (br s, 8 H), 7.66 (d, *J* = 7 Hz, 4 H), 8.19 (s, 2 H). − UV/vis (C_6H_5Cl): λ_{max} (nm) = 588, 543, 504, 440, 419, 397, 320. − Emission: $CHCl_2CHCl_2$, (λ_{exc}: 361 nm): 605, 658, 720 nm.

---

[1] [1a] M. Magoga, C. Joachim, *Phys. Rev. B.* **1997**, *56*, 4722−4729. − [1b] M. Magoga, C. Joachim, *Phys. Rev. B.* **1998**, *57*, 1820−1823.

[2] S. J. Tans, M. H. Devoret, H. Dai, A. Thess, R. E. Smalley, L. J. Geerligs, C. Dekker, *Nature* **1997**, *386*, 474−477.

[3] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, J. M. Tour, *Science* **1997**, *278*, 252−254.

[4] V. Rousset, C. Joachim, S. Itoua, B. Rousset, N. Fabre, *J. Phys. III* **1995**, 1983−1989.

[5] T. A. Jung, R. R. Schlittler, J. K. Gimzewski, H. Tang, C. Joachim, *Science* **1996**, *271*, 181−184.

[6] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

[7] See for example: [7a] X. Qiao, D. M. Ho, R. A. Pascal Jr., *Angew. Chem.* **1997**, *109*, 1588−1589; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1531−1532. − [7b] X. Qiao, M. A. Padula, D. M. Ho, N. J. Vogelaar, C. E. Schutt, R. A. Pascal Jr., *J. Am. Chem. Soc.* **1996**, *118*, 741−745.

[8] A. Hart, D. Ok, *J. Org. Chem.* **1986**, *51*, 979−986.

[9] [9a] M. Loffler, A.-D. Schlüter, *Synlett* **1994**, 75−77. − [9b] B. Schlicke, A.-D. Schlüter, P. Hauser, J. Heinze, *Angew. Chem.* **1997**, *109*, 2091−2093; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1996−1998.

[10] S. Chardon-Noblat, J.-P. Sauvage, *Tetrahedron* **1991**, *47*, 5123−5132.

[11] J. Geuze, C. Ruinard, J. Soeterbroek, P. E. Verkade, B. M. Wepster, *Recl Trav. Chim. Pays*-Bas **1956**, *75*, 301−310.

[12] [12a] H. des Abbayes, J.-C. Clément, P. Laurent, G. Tanguy, N. Thilmont, *Organometallics* **1988**, *7*, 2293−2299. − [12b] Y. Kimura, Y. Tomita, Y. Otsuji, *Chem. Lett.* **1979**, 321−324. − [12c] G. Tanguy, B. Weiberger, H. des Abbayes, *Tetrahedron Lett.* **1984**, *25*, 5529−5532. − [12d] G. Tanguy, B. Weiberger, H. des Abbayes, *Tetrahedron Lett.* **1983**, *24*, 4005−4008.

[13] M. A. Ogliaruso, M. G. Tomanelli, E. I. Becker, *Chem. Rev.* **1965**, *65*, 261−367.

[14] B. Schlicke, A.-D. Schlüter, *Synlett.* **1996**, 425−426.

[15] [15a] M. D. Clayton, Z. Marcinov, P. W. Marcineau, *J. Org. Chem.* **1996**, *61*, 6052−6054. − [15b] D. R. H. Barton, R. A. H. F. Hull, D. J. Lester, S. V. Ley, *Tetrahedron Lett.* **1979**, *35*, 3331−3334.

[16] See analogous reactions in : J. K. Stille, G. K. Noren, L. Green, *J. Polym. Sci.* **1970**, *A8*, 2245−2254.

[17] V. J. Langlais, R. R. Schlittler, J. K. Gimzewski, H. Tang, A. Gourdon, C. Joachim, in preparation.

[O98301]