Synthesis of Polyaromatic Hydrocarbons with a Central Rotor

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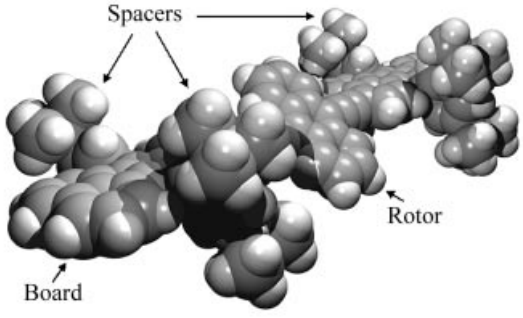
A series of molecular landers comprising a central mobile part has been synthesised. The two rigid main boards consist of acenaphtho[1,2-*k*]fluoranthene groups, each substituted in positions 7 and 14 by 3,5-di-*tert*-butylphenyl groups. The boards are linked by a diethynylanthracene, a phenyl, or a biphenyl rotor.

Introduction

The development of nanoelectronic devices using single molecules calls for a better understanding of the electrical and mechanical properties of isolated molecules.[1,2] Since the early 1990s, the development of Scanning Tunneling Microscopy has allowed not only imaging of molecules but also exploration of molecular electrical,[3] mechanical,[4,5] and chemical[6,7] properties on an individual non-statistical basis.

We have recently designed specific molecules, which are named landers by analogy with landing craft, such as the Mars lander, for the study of electron transport along a single molecular wire in a UHV-STM tip-molecule-metallic surface experiment.[8] These molecules comprise a rigid polyaromatic board, which can be maintained several Å above a surface by appropriate spacers (legs), in order to prevent direct electron flow between the tip and the surface through, and perpendicular to, the board plane. In order to minimize electron leaks, the spacers must show little electronic coupling with the board and with the metal. This device has allowed us to measure for the first time the spatially resolved conductance of a single molecular wire.[9] Molecular landers can also be used as templates to accommodate metal atoms at the step edges of a metal substrate, and for moulding metallic nanowires.[10] This work is being extended to the study of single molecular switches, i.e. molecules for which the conductance can be controlled by an external action (Scheme 1).

We have recently been able to fully control the conformational changes of a single molecule by STM,[11] by using the tip to reversibly induce the rotation of an external part of the molecule, thus modifying its electronic properties and thereby realizing a conformational molecular switch. We are currently extending this study to systems in which the mobile part is incorporated within the core of the molecule so that the electrons tunnel through the rotor.



Scheme 1. General scheme of a lander with rotor

Any modification of the angle between the planes of the main boards and the rotor plane will have a large impact on the longitudinal conductance of the molecule, as it alters the electronic coupling between these components. Therefore, manipulation of the rotor conformation by the STM tip could lead to a switching effect. We have also envisaged using this type of device to study the influence of the inelastic part of the tunnelling current on the movement of the central rotor. As the tunnel current passes through the molecule, the internal temperature increases by inelastic absorption, thus populating higher energy rotational modes. Fine analysis of the tunnel noise should show this variation of internal motion.

Results and Discussion

We have carried out the syntheses of several landers designed according to the above architecture and shown in Scheme 2.

From previous studies,[12] it was found that the 7,14-bis(3,5-di-*tert*-butylphenyl)acenaphtho[1,2-*k*]fluoranthene

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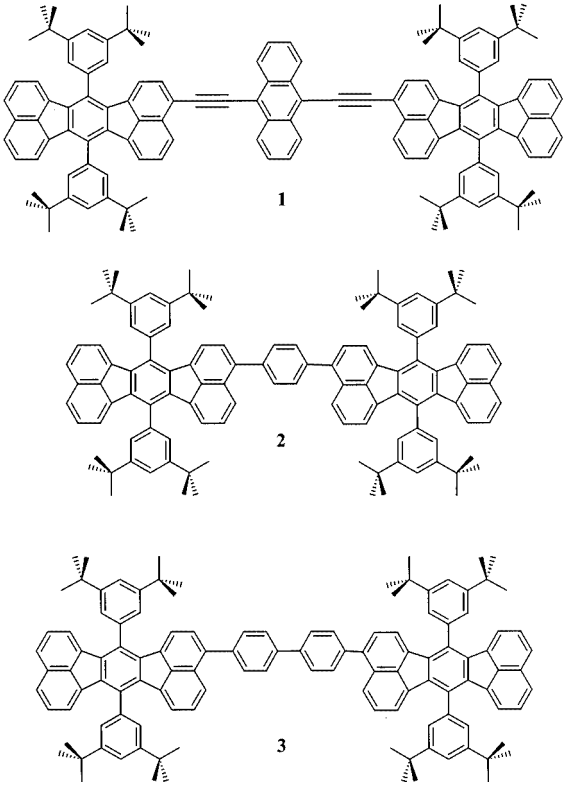


Scheme 2. Landers with a rotor

board is suitable for the terminal parts of the device. Despite important distortions of the spacers on metallic surfaces, the central core is rigid and maintained above the surface at distances which are large enough that there is little electronic coupling with the metal, owing to the steric crowding and insulating properties of the di-*tert*-butylphenyl substituents (Figure 1).

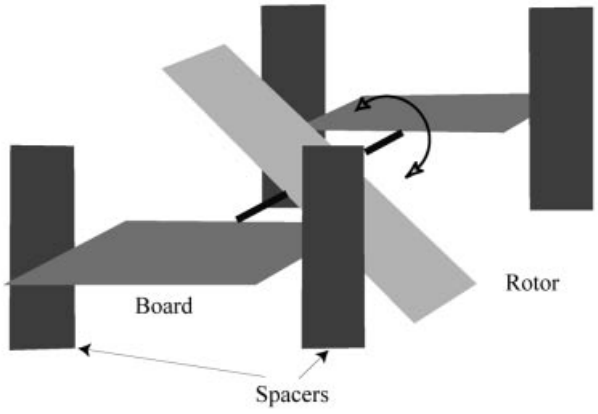
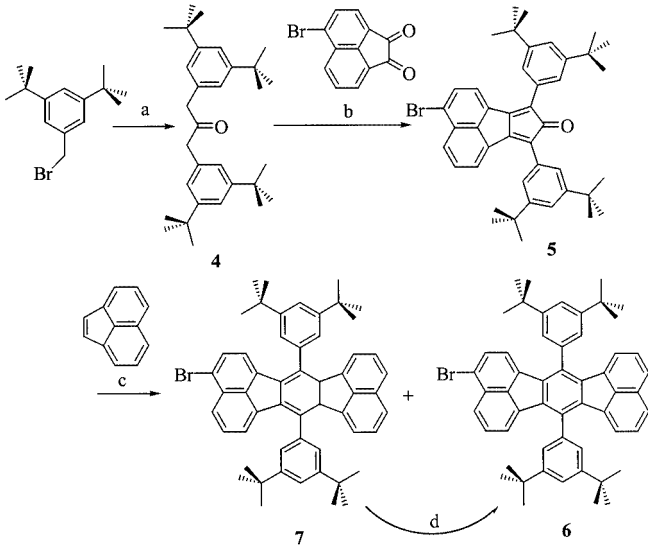


Figure 1. Perspective view of a CPK model of **1** showing the minimum energy conformation under vacuum; the di-*tert*-butylphenyl spacers' planes are maintained nearly perpendicular to the main board plane by steric crowding

Similar molecules show a rather low diffusion barrier with some mobility at low temperatures, allowing a single molecule manipulation and stabilisation of the molecule on step edges at lower temperatures.

For these studies, three compounds with different types of rotors were synthesized: one with a low energy rotation barrier comprising diethynylanthracene, one with a phenyl and one with a biphenyl moiety. Attempts to transfer **1** to the substrate by sublimation in an STM chamber showed that this molecule could often not withstand the process under UHV conditions, due to thermal decomposition during sublimation and/or reaction with the bare metallic surface. This led us to prepare molecules such as **2** and **3**, which have higher rotation barriers than **1** but which have more robust rotors and better thermal stability on bare metallic surfaces.

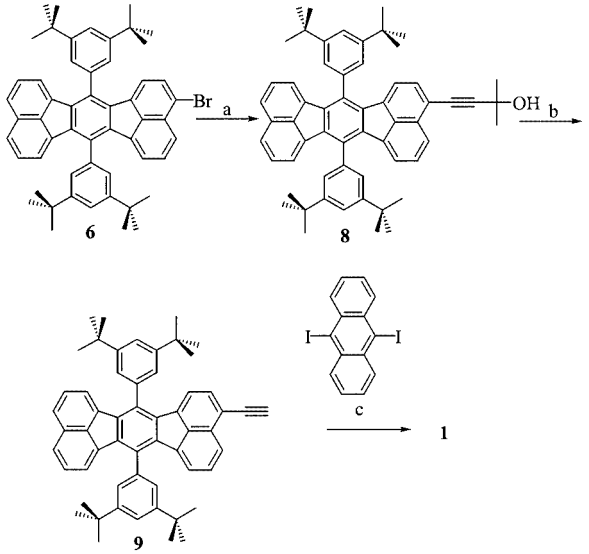
The synthesis of the main-board molecule is shown in Scheme 3. The first step is the preparation of 1,3-bis(3,5-di-*tert*-butylphenyl)propan-2-one (**4**) by reaction of 1-(bromomethyl)-3,5-di-*tert*-butylbenzene with tosylmethyl isocyanide followed by hydrolysis.[13] The best yields (45%) were obtained using dry DMF as solvent and NaH as base at room temperature. This route is more practical than carbonylation[8] with toxic $Fe(CO)_5$ or $Fe_2(CO)_9$ which also requires a difficult separation of iron hydroxide from the aqueous suspension.



Scheme 3. Synthesis of the main board: (a) TosMIC, NaH, DMF; HCl, CH_2Cl_2, 45%; (b) KOH, MeOH, 92%; (c) *o*-xylene or toluene; (d) DDQ, CH_2Cl_2

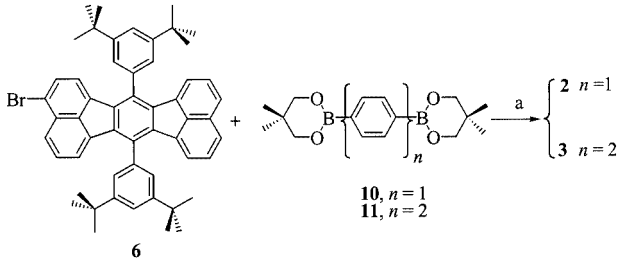
Subsequently, a double Knoevenagel condensation with bromoacetophenone[14] in methanol/KOH gave the cyclopentadienone **5** in good yield (92%). Reaction with acenaphthylene, decarbonylation, and rearomatization gave, depending on the reaction conditions, **6** and/or **7**. In refluxing toluene, the reaction was slow (3 d) and yielded first **7** and, by in situ air oxidation, **6**. In *o*-xylene, the reaction was faster (1 d) and yielded exclusively **6**. Alternatively, **7** could be oxidized by DDQ/dichloromethane in quantitative yields.

The synthesis of **1** was then carried out as shown in Scheme 4. The alkynyl precursor **8** was obtained in 91% yield by palladium coupling of **6** and 2-methyl-3-butyn-2-ol using Crisp's procedure.[15] Retro Favorsky elimination of acetone from **8** by *t*BuOK in refluxing THF gave the alkyne **9** in good yield (92%). Sonogashira coupling with 9,10-diiodoanthracene under Linstrumelle conditions[16] then provided the lander **1** as a bright orange powder in 61% yield.



Scheme 4. Synthesis of compound **1**: (a) 2-methyl-3-butyn-2-ol, $Pd(PPh_3)_4$, PPh_3, CuI, LiBr, piperidine, 91%; (b) *t*BuOK, THF, 92%; (c) $Pd(PPh_3)_2Cl_2$, CuI, piperidine, THF, 61%

The synthetic route to **2** and **3** is given in Scheme 5. It involves Suzuki coupling of phenyl- and biphenyldiboronic acid bis(neopentylglycol) cyclic esters **10** and **11** with the substituted bromoacenaphthofluoranthene **6**. The electron-rich character of **6** hinders the oxidative insertion of Pd^0 into the C−Br bond and prevents efficient catalysis with, for instance, $Pd(PPh_3)_4$. Extensive study of the coupling conditions led to satisfactory yields (41−46%) of this double coupling using 0.47 equiv. of diboronic bis(neopentylglycol) cyclic esters, 1.5 mol % of $Pd_2(dba)_3$, 3.5 mol % of tBu_3P and CsF (2 equiv.) in refluxing THF.[17−19] These conditions minimise formation of the monocoupled derivative (less than 15%) and of reduced species, the main by-product under other reaction conditions.



Scheme 5. Synthesis of **2** and **3**: $Pd_2(dba)_3$, tBu_3P, CsF, THF, 41% (**2**), 46% (**3**)

The electronic spectra of compounds **2** and **3** recorded in CH_2Cl_2 showed similar absorption bands at relatively low energy, due to the extended polyaromatic character of the acenaphtho[1,2-*k*]fluoranthene groups. For **1**, the red shift of the maximum absorption is attributed to a smaller HOMO−LUMO gap by extended conjugation between the two main boards and the diethynylanthracene group.

All of the compounds **1**−**3** are fluorescent in dichloromethane solutions with small (22 nm for **1**) to moderate (42 nm for **2** and **3**) Stokes shifts, as expected for relatively rigid molecules.

Conclusion

The synthesis of polyaromatic hydrocarbons designed for the study of intramolecular movements in STM single molecule surface experiments has been carried out. These molecular devices comprise two acenaphtho[1,2-*k*]fluoranthene main boards, each substituted by two 3,5-di-*tert*-butylphenyl spacers to maintain the central part above the metallic surface. These two parts are connected by a central mobile unit. Work in progress is directed toward UHV-STM studies of the mechanical and switching properties of these devices.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded with a Bruker WF-250 in $CDCl_3$ or CD_2Cl_2 solutions at 20 °C and internal standard ($CDCl_3$: δ_H = 7.25 ppm, δ_C = 77.0 ppm; CD_2Cl_2: δ_H = 5.30 ppm, δ_C = 53.8 ppm). Mass spectrometry was performed with a Nermag R10-R10 (DCI). Elemental analyses were carried out by

Table 1. Spectroscopic properties of **1**−**3** in dichloromethane

Compound	Absorption: λ_{max} [nm] ($\varepsilon \times 10^4$ [M^{-1} cm^{-1}])	Emission: λ_{max} [nm] ($\lambda_{exc.}$ [nm])[a]
1	542 (5.5), 514 (6.12), 319 (8.6)	564, 604 (540)
2	447 (7.1), 425 (sh.),[b] 317 (12.3)	489, 514 (445)
3	445 (5.4), 423 (sh.),[b] 319 (9.7)	487, 512 (445)

[a] Concentration 10^{-6} M. [b] sh = shoulder.

the Service d'Analyse de l'ICSN (Paris). 1-(Bromomethyl)-3,5-di-*tert*-butyltoluene,[8] bromoacetophenone,[14] and 9,10-diiodoanthracene[20] were prepared according to published procedures. THF was distilled from Na/benzophenone. Other solvents and reagents were used as obtained in the best quality available.

1,3-Bis(3,5-di-*tert*-butylphenyl)propan-2-one (4): NaH (0.53 g, 22.1 mmol) was added to a solution of 1-(bromomethyl)-3,5-di-*tert*-butylbenzene (5.0 g, 17.7 mmol) and tosylmethyl isocyanide (TosMIC; 1.7 g, 9 mmol) in dry DMF (25 mL). The resulting heterogeneous mixture was stirred overnight at room temperature, then the solvent was removed under vacuum. The residue was diluted with CH_2Cl_2 (25 mL) and water (50 mL). The separated organic phase was then treated with a concentrated HCl solution (37%, 10 mL) for 30 min with vigorous stirring. The organic layer was then separated, washed neutral with water, dried ($MgSO_4$) and the solvents were completely evaporated. Purification of the residue by flash chromatography [light petroleum ether/dichloromethane (2:1)] provided 1,3-bis(3,5-di-*tert*-butylphenyl)propan-2-one (**4**) (1.72 g, 45%) as a white solid. $C_{31}H_{46}O$ (434.7): calcd. C 85.7, H 10.7; found C 85.4, H 10.9. ^{1}H NMR (CD_2Cl_2): δ = 7.31 (t, *J* = 1.9 Hz, 2 H), 7.0 (d, *J* = 1.9 Hz, 4 H), 3.73 (s, 4 H), 1.32 (s, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 206.5, 151.1, 133.3, 123.7, 120.9, 49.5, 34.8, 31.5 ppm. MS (DCI, NH_3): *m*/*z* = 435 [MH^+].

3-Bromo-7,9-bis(3,5-di-*tert*-butylphenyl)-8*H*-cyclopenta[*a*]-acenaphthylen-8-one (5): A 1 M solution of KOH in methanol (1 mL) was added dropwise to a suspension of 1,3-bis(3,5-di-*tert*-butylphenyl)propan-2-one (**4**; 500 mg, 1.15 mmol) and 5-bromoacenaphthylene-1,2-dione (300 mg, 1.15 mmol) in methanol (10 mL). After stirring for 4 h at room temperature, the resulting dark green heterogeneous mixture was filtered and the precipitate was washed twice with small portions of methanol. Further drying under vacuum provided 0.7 g (92%) of compound **5** as a dark-green solid. $C_{43}H_{47}BrO$ (659.74): calcd. C 78.3, H 7.2; found C 78.9, H 7.4. ^{1}H NMR ($CDCl_3$): δ = 8.11 (d, *J* = 7.1 Hz, 1 H), 8.04 (d, *J* = 8 Hz, 1 H), 7.91 (d, *J* = 7.7 Hz, 1 H), 7.82 (d, *J* = 7.7 Hz, 1 H), 7.71−7.64 (m, 5 H), 7.48 (t, *J* = 1.5 Hz, 2 H), 1.41 (s, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 202.0, 152.7, 152.2, 150.8, 145.0, 132.1, 131.6, 131.6, 130.3, 129.4, 126.5, 123.3, 123.2, 123.0, 122.7, 122.3, 121.3, 120.8, 35.0, 31.4 ppm. MS (DCI, NH_3): *m*/*z* = 660 [MH^+].

3-Bromo-7,14-bis(3,5-di-*tert*-butylphenyl)acenaphtho[1,2-*k*]-fluoranthene (6): A solution of the cyclopentadienone derivative **5** (0.5 g, 0.76 mmol) and acenaphthylene (80%, 0.14 g, 0.76 mmol) in *o*-xylene (10 mL) was refluxed for 24 h, then the solvent was completely removed under vacuum. Purification of the resulting sticky residue by flash chromatography [light petroleum ether/dichloromethane (9:1)] afforded compound **6** (0.48 g, 80%) as a yellow solid. $C_{54}H_{53}Br$ (781.90): calcd. C 82.95, H 6.8; found C 82.6; H 7.1. ^{1}H NMR ($CDCl_3$): δ = 7.87 (d, *J* = 8.4 Hz, 1 H), 7.74−7.67 (m, 4 H), 7.53−7.50 (m, 5 H), 7.38−7.34 (m, 3 H), 6.81−6.75 (m, 3 H), 6.53 (d, *J* = 7.6 Hz, 2 H), 1.41 (m, 36 H). ^{13}C NMR (CD_2Cl_2): δ = 152.5, 137.8, 137.3, 136.9, 136.7, 135.5, 134.7, 133.4, 131.3, 129.9, 129.6, 129.2, 128.0, 126.7, 125.6, 124.2, 124.0, 123.7, 123.5, 121.9, 35.4, 31.6 ppm. MS (DCI, NH_3): *m*/*z* = 781 [MH^+]. Alternatively, after removal of the solvent under reduced pressure, the desired compound **6** can be recovered by triturating the residue with hot absolute ethanol. This procedure yielded only 0.35 g (60%) of pure compound but no further purification was required.

Compound 7: With toluene as solvent, the intermediate **7** was isolated by precipitation with light petroleum ether in 46% yield. $C_{54}H_{55}Br$ (783.92): calcd. C 82.74; H 7.07; found C 82.81, H 7.09. ^{1}H NMR ($CDCl_3$): δ = 7.67 (d, *J* = 8.2 Hz, 1 H), 7.58−7.52 (m, 4 Hz), 7.44 (s, 2 H), 7.36 (d, *J* = 7.8 Hz, 2 H), 7.27−7.14 (m, 5 H), 6.73 (d, *J* = 7.2 Hz, 1 H), 6.49 (d, *J* = 8.0 Hz, 1 H), 6.22 (d, *J* = 7.0 Hz, 2 H), 5.29 (br. s, 2 H), 1.42 and 1.33 (2 br. s, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.5, 150.3, 145.2, 145.1, 140.1, 139.1, 137.1, 136.8, 136.5, 134.8, 131.4, 130.6, 130.4, 130.2, 129.9, 128.5, 127.2, 126.0, 123.0, 121.4, 121.2, 120.9, 119.4, 119.2, 118.5, 50.3, 35.1, 31.6 ppm. MS (DCI, NH_3): *m*/*z* = 784 [MH^+].

Compound 8: A solution of **6** (400 mg, 0.51 mmol), 2-methyl-3-butyn-2-ol (0.25 mL, mmol), PPh_3 (4 mg, 15.2 μmol), and $Pd(Ph_3)_4$ (10 mg, 8.6 μmol) in degassed piperidine (20 mL) was treated with copper iodide (4 mg, 21.0 μmol) and lithium bromide (15 mg, 0.17 mmol) in dry and degassed THF (5 mL). After refluxing for 5 h under argon, the solvents were evaporated from the reaction mixture. The residue was extracted with dichloromethane (200 mL) and then washed with 5% HCl (2 × 50 mL) and water (2 × 50 mL). After drying ($MgSO_4$), the solution was concentrated and the product was purified by column chromatography using dichloromethane as eluent. This yielded the protected alkyne as a yellow powder (361 mg, 91%). $C_{59}H_{60}O$ (785.11): calcd. C 90.26, H 7.70; found C 89.60, H 7.39. ^{1}H NMR ($CDCl_3$): δ = 7.94 (d, *J* = 8.5 Hz, 1 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 7.67 (br. s, 2 H), 7.53 (br. s, 4 H), 7.42 (d, *J* = 7.25 Hz, 1 H), 7.35−7.25 (m, 3 H), 6.87−6.75 (m, 3 H), 6.63 (d, *J* = 7.25 Hz, 1 H), 2.16 (s, 1 H), 1.68 (s, 6 H), 1.40 (s, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.0, 137.7, 137.4, 137.2, 136.9, 136.5, 135.3, 133.2, 133.0, 132.0, 129.5, 128.2, 127.6, 126.3, 124.6, 123.6, 123.4, 122.5, 121.1, 119.2, 99.0, 65.9, 35.1, 31.5 ppm. MS (DCI, NH_3): *m*/*z* = 728 [MH^+].

Compound 9: A solution of the alcohol **8** (100 mg, 0.13 mmol) in dry and degassed THF (100 mL) was treated with *t*BuOK (30 mg, 0.267 mmol), then refluxed under argon for 0.5 h. After evaporation of the solvents under vacuum, the residue was extracted with dichloromethane (100 mL), washed with water (2 × 25 mL), and passed though a short plug of silica gel. Yield 87 mg (92%). The product is stable when stored in the dark at −30 °C. $C_{56}H_{54}$ (727.03): calcd. C 92.5, H 7.5; found C 91.1, H 7.8. ^{1}H NMR (CD_2Cl_2): δ = 8.01 (d, *J* = 7.8 Hz, 1 H), 7.77−7.73 (m, 4 H), 7.54−7.50 (m, 5 H), 7.42−7.32 (m, 3 H), 6.85−7.78 (m, 3 H), 6.70 (d, *J* = 7.25 Hz, 1 H), 1.50 (br. s, 36 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.01, 137.70, 137.36, 136.98, 136.51, 135.20, 132.97, 132.75, 128.43, 127.65, 126.37, 124.58, 123.68, 123.36, 122.33, 121.17, 118.54, 82.14, 81.60, 35.15, 31.52 ppm. MS (DCI, NH_3): *m*/*z* = 786 [MH^+].

Compound 1: A solution of **9** (100 mg, 0.137 mmol) in degassed piperidine (10 mL) and THF (2 mL) was treated with 9,10-diiodoanthracene (25 mg, 58.1 μmol), dichlorobis(triphenylphosphane)palladium (5 mg, 7.1 μmol) and copper iodide (5 mg, 15.7 μmol). After refluxing for 1 h under argon, the solvents were evaporated under vacuum and the residue was extracted with dichloromethane (100 mL). The solution was washed with 10% aqueous ammonia, water and 5% aqueous hydrochloric acid, then washed with water to neutrality and dried with magnesium sulfate. Flash chromatography using petroleum ether/dichloromethane (1:8) as eluent gave the product as a bright orange solid. Yield 57 mg (61%). $C_{126}H_{114}$ (1628.25): calcd. C 92.9, H 7.1; found C: 92.4, H 7.7. ^{1}H NMR (CD_2Cl_2): δ = 8.87−8.83 (m, 4 H), 8.37 (d, *J* = 8 Hz, 2 H), 8.87 (d, *J*= 7.5 Hz, 2 H), 7.78−7.72 (m, 12 H), 7.60−7.58 (m, 8 H), 7.53 (dd, *J1* = *J2* = 7 Hz, 2 H), 7.37 (dd, *J1* = *J2* = 7.5 Hz, 4 H), 6.9−6.83 (m, 8 H), 1.52 (br. s, 72 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.0, 137.7, 137.5, 137.2, 137.2, 136.6, 135.4, 135.3, 133.2, 132.5, 132.2, 129.8, 129.5, 128.7, 127.7, 127.3, 127.0, 126.4, 124.8, 123.8, 123.4, 122.7, 121.2, 119.9, 101.2, 91.9, 77.5, 76.9, 76.4, 35.2, 31.9 ppm. MS (DCI, NH_3): *m*/*z* = 1628 [MH^+].

Compound 2: An oven-dried Schlenk flask was filled with argon and charged with **6** (400 mg, 0.51 mmol), 1,4-benzenediboronic acid bis(neopentylglycol) cyclic ester (72 mg, 0.24 mmol), CsF (155 mg, 1.02 mmol), and $Pd_2(dba)_3$ (7 mg, 0.008 mmol). After a few vacuum/argon cycles, THF (25 mL) and a 0.01 M solution of tBu$_3$P in THF (1.8 mL, 0.018 mmol) were added through a rubber septum. After refluxing for 48 h, the mixture was allowed to cool to room temperature, then diluted with THF (25 mL), filtered through a short pad of silica gel, and concentrated under vacuum. The deep yellow residue was purified by flash chromatography [light petroleum ether/dichloromethane (9:1)], to provide lander **2** (145 mg, 41%) as a yellow solid. $C_{114}H_{110}$ (1480.1): calcd. C 92.5, H 7.49; found C 91.9, H 8.1. ^{1}H NMR ($CDCl_3$): δ = 7.92 (d, J = 8.2 Hz, 2 H), 7.71 and 7.69−7.67 (d, m, J = 8.2 Hz, 8 H), 7.64 (s, 4 H), 7.58 and 7.56 (2 d, $J1$ = $J2$ = 1.8 Hz, 8 H), 7.41−7.30 (m, 8 H), 6.86−6.78 (m, 8 H), 1.42 (br. s, 72 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 152.0, 139.3, 138.8, 138.0, 137.1, 136.9, 136.7, 136.2, 135.2, 135.1, 133.6, 133.3, 130.2, 129.6, 128.6, 127.9, 127.7, 126.3, 125.2, 123.5, 123.2, 123.1, 122.1, 35.2, 31.6 ppm. MS (DCI, NH_3): m/z = 1479 [MH^+], 1497 [MNH_4^+].

Compound 3: An oven-dried Schlenk flask was filled with argon and charged with **6** (400 mg, 0.51 mmol), 4,4′-biphenyldiboronic acid bis(neopentylglycol) cyclic ester (90 mg, 0.24 mmol), CsF (155 mg, 1.02 mmol), and $Pd_2(dba)_3$ (7 mg, 0.008 mmol). After a few vacuum/argon cycles, THF (25 mL) and a 0.01 M solution of tBu$_3$P in THF (1.8 mL, 0.018 mmol) were added through a rubber septum. After refluxing for 48 h, the mixture was allowed to cool to room temperature, then diluted with THF (25 mL), filtered through a short pad of silica gel, and concentrated under vacuum. The deep yellow residue was purified by flash chromatography [light petroleum ether/dichloromethane (9:1)], to provide lander **3** (170 mg, 46%) as a yellow solid. $C_{120}H_{114}$ (1556.2): calcd. C 92.6, H 7.4; found C 92.1, H 7.8. ^{1}H NMR ($CDCl_3$): δ = 7.90 (d, J = 8.3 Hz, 2 H), 7.78−7.63 (m, 16 H), 7.58 and 7.57 (2 d, $J1$ = $J2$ = 1.8 Hz, 8 H), 7.40−7.31 (m, 8 H), 6.87−6.79 (m, 8 H), 1.43 (br. s, 72 H) ppm. ^{13}C NMR ($CDCl_3$): δ = 151.9, 139.5, 139.2, 139.0, 138.0, 137.0, 136.7, 135.1, 135.0, 133.6, 133.2, 130.7, 129.6, 128.4, 127.9, 127.6, 126.9, 126.2, 125.1, 123.5, 123.1, 121.1, 116.7, 35.1, 31.6 ppm. MS (DCI, NH_3): m/z = 1556 [MH^+ + 1], 1573 [MNH_4^+].

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