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Molecular machines: synthesis and characterization of two prototypes of molecular wheelbarrows

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In memoriam Guy Ourisson (1926–2006)

Abstract—Technomimetic molecules are molecules designed to imitate macroscopic objects at the molecular level, also transposing the motions that these objects are able to undergo. This article focuses on the synthesis of two polyaromatic hydrocarbons designed by analogy with macroscopic wheelbarrows. The molecular wheelbarrows are synthesized following a modular strategy based on sequential double Knoevenagel and Diels–Alder reactions. Our strategy allowed to easily vary the chemical nature of the handles, which is crucial for subsequent manipulation with an STM tip.

1. Introduction

The main current challenge in nanosciences is the miniaturization of objects via a top–down approach.[1] A second approach starts from atoms and molecules and follows a monumentalization strategy consisting in the incorporation of different functions within only one molecule.[2] In this context, a rotor or a wheel, one of the most simple mechanical working units, is an interesting system to study and control at the atomic scale. The continuous rotation of a molecular wheel on a surface was observed with a scanning–tunneling microscope (STM) for the first time in 1998.[3] In this experiment, the wheel, a decacyclene-based molecule, rotates around its symmetry axis (which is perpendicular to the surface) within a supramolecular bearing of neighboring molecules. In this case the wheel is flat on the surface and therefore cannot move upon rotation. In order to improve the mechanical abilities of a molecular nanomachine, new molecules should be designed with wheels able to rotate, thereby allowing a lateral 'rolling' motion of the entire functionalized molecule. Recently, Tour's group prepared a family of nanovehicles[4] consisting of a molecular scale chassis, axles, and wheels, that can roll across solid surfaces. They have gathered some convincing indirect proofs that the motion of the nanovehicles takes place via a rotation of the wheels, but could not illustrate this undoubtedly by measuring a variation of the tunneling current, due to the experimental temperature. In contrast, we very recently succeeded to prove the rotation of a triptycene wheel linked to an axle by working at low temperature.[5] This result opens the way to more complex molecules designed to be capable to undergo simultaneously translation and rotation motions. With this aim in view, we designed a molecular wheelbarrow as a further step toward the development of nanomachines displaying complex functionalities at the atomic scale.[6] In the case of a macroscopic wheelbarrow, pushing the wheelbarrow results in the rotation of the wheel. We present here the synthesis of two prototypes of molecular wheelbarrows, undertaken following a modular strategy which allows to vary the key parts of the molecule, in particular the region which will be in contact with the tip of the STM during the manipulation of the molecule.

The molecules belonging to the 'lander' family are known for their interesting electronic properties leading to molecular wires, switches, and rectifiers[7] but they only incorporate a polyaromatic platform with four or more legs to isolate the board from the surface. The wheelbarrow is derived from the lander, substituting two legs by two wheels. This difference in the design is the source of synthetic difficulties since the number of steps increases with a lower symmetry. The triptycene fragment was again selected as wheel motif for the reasons described above. Moreover, due to the three wings of the triptycene skeleton, any rotation of the wheel will induce a change in the distance between the front part of the board and the surface, as shown in Figure 1. This will enhance the signature of the wheel's rotation in the tunneling current signal measured by the tip apex. This design imposes the use of a triple bond connector per wheel to ensure both

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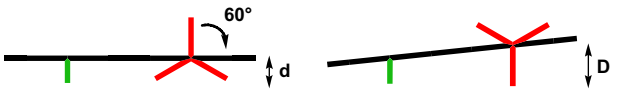


Figure 1. Change in the altitude of the aromatic board during the rotation of the wheel. The minimum altitude is *d* and after a rotation of 60°, the altitude is maximal (*D*).

the structural stability of the front axle and a very low rotation barrier. Figure 2 clearly shows the two three-cogged wheels, which can freely rotate around their axle due to the acetylenic spacers.

As shown in Figure 2, the wheelbarrow consists in a polyaromatic central platform (in black) based on a Polycyclic Aromatic Hydrocarbon (PAH)[8] skeleton, which has been chosen for its rigidity and resistance to the deposition techniques.[9] On this platform are covalently attached different fragments: two wheels (9-triptycenyl groups, in red) which are connected through ethynyl spacers allowing free rotation, and two legs (3,5-di-*tert*-butylphenyl groups, in green).[10] It must be noted that we opted for two wheels instead of one for obvious synthetic reasons.

It has been shown that the 3,5-di-*tert*-butylphenyl groups are held in a conformation in which the phenyl groups are nearly perpendicular to the main aromatic board. Furthermore, in the imaging process the left part of the molecule will be extremely important since it contains the R groups, which will interact with the STM tip (in blue). They will be modulated in order to have different kinds of 'handles'. The two handles are 4-*tert*-butylphenyl groups in wheelbarrow **13a** and an acenaphthylene fragment in wheelbarrow **13b**. The most important feature of the molecule are the wheels, which are able to rotate around the σ-bond (i.e., their axis) so that they should enable a lateral motion of the entire molecule on the surface upon rotation, by analogy with a macroscopic wheelbarrow. Figure 3 shows a three-dimensional view of one of the possible conformations of a molecular wheelbarrow in the gas phase obtained by semiempirical calculation[11] and the two three-cogged wheels which can freely rotate around their axle due to the acetylenic spacers. It also shows the function of the *tert*-butylphenyl groups which should maintain the polyaromatic board away from the surface by

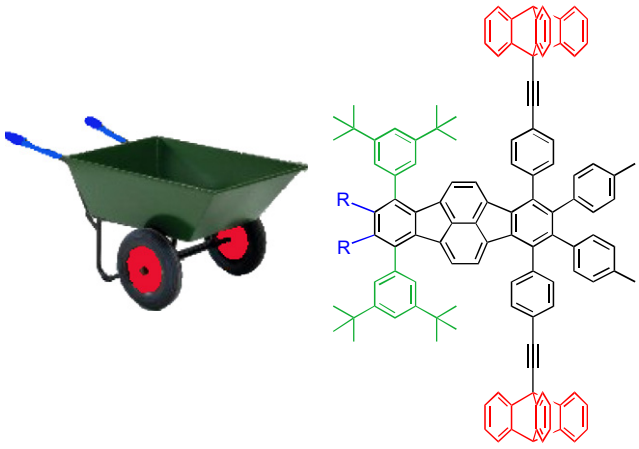


Figure 2. Macroscopic analog and chemical structure of a molecular wheelbarrow. R groups allow to vary the 'handles' in order to optimize the interaction of the molecule with the STM tip.

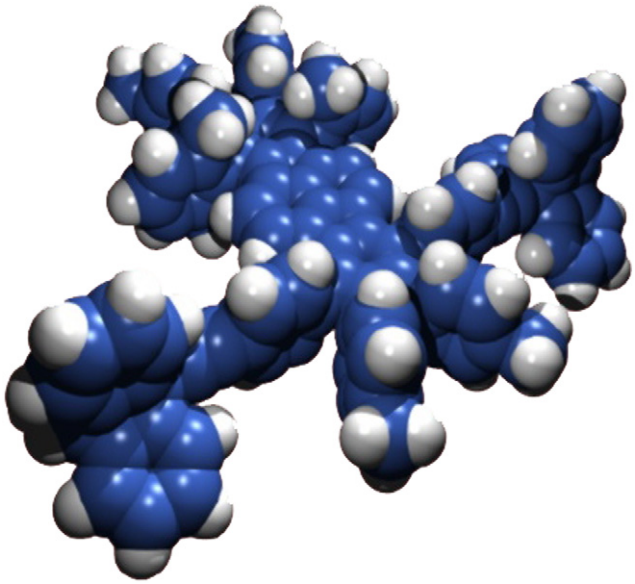


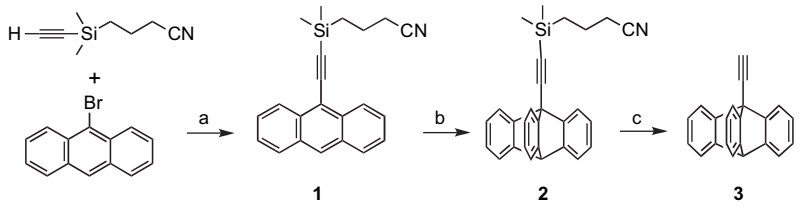
Figure 3. CPK model showing the minimum energy conformation of the molecular analog.

staying perpendicular to the polyaromatic platform. Moreover, *tert*-butyl groups connected to PAHs are also used to increase organic solubility and are easily observed by STM techniques, inducing a good contrast in the image.

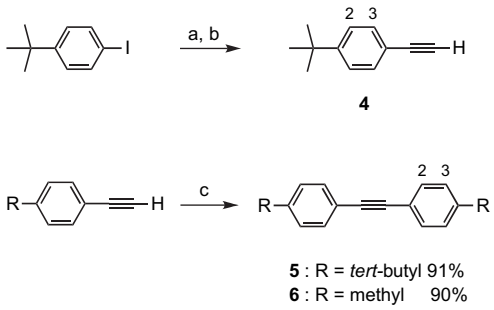
2. Results and discussion

The 9-ethynyltriptycene synthon (**3**) was obtained in three steps from commercial 9-bromoanthracene by a modified published procedure[12] as shown in Scheme 1. The procedure involves the coupling of 9-bromoanthracene with a monoprotected alkyne followed by a [4+2] addition of benzyne (prepared in situ by reaction of anthranilic acid with isopentyl nitrite) and deprotection of the silyl group. The use of a (3-cyanopropyl)dimethylsilyl protecting group, a polar analog of trimethylsilyl,[13] allowed the easy separation of triptycene **2** from unreacted anthracene **1** obtained after reaction with benzyne. Triptycene **2** was isolated in 61% yield, corresponding to an improvement in yield of 50% compared to the published procedure. Contrary to the analogous reaction using TMS-acetylene, the chromatographic separation of these compounds is easy because of their significantly different R_f values (0.40 for **2** vs 0.20 for **1** in cyclohexane/dichloromethane 1:1). With the TMS protecting group, the R_f value was 0.73 in the same conditions for both the anthracene and the triptycene derivatives. After the desilylation of **2** with potassium carbonate in a mixture of THF and MeOH (1:1), the terminal acetylene **3** was obtained in a reasonable isolated yield. The diphenylacetylene compounds **5** and **6** necessary for the Diels–Alder reactions have been synthesized in two steps according to Scheme 2.

The synthesis of the molecular wheelbarrow **13a** is outlined in Scheme 3. Our strategy is based on the repetition of a double Knoevenagel–Diels–Alder reaction sequence on an α-diketo fragment. The first sequence allows the connection of the two 3,5-di-*tert*-butylphenyl legs, while the second sequence provides the precursor for wheels' connection. For



Scheme 1. Reagents and conditions: (a) $Pd(PPh_3)_4$ 10%, CuI 20%, piperidine/THF (1:1), Ar, 84%; (b) anthranilic acid, isopentyl nitrite, DME, 61%; (c) K_2CO_3, THF/MeOH (1:1), 75%.



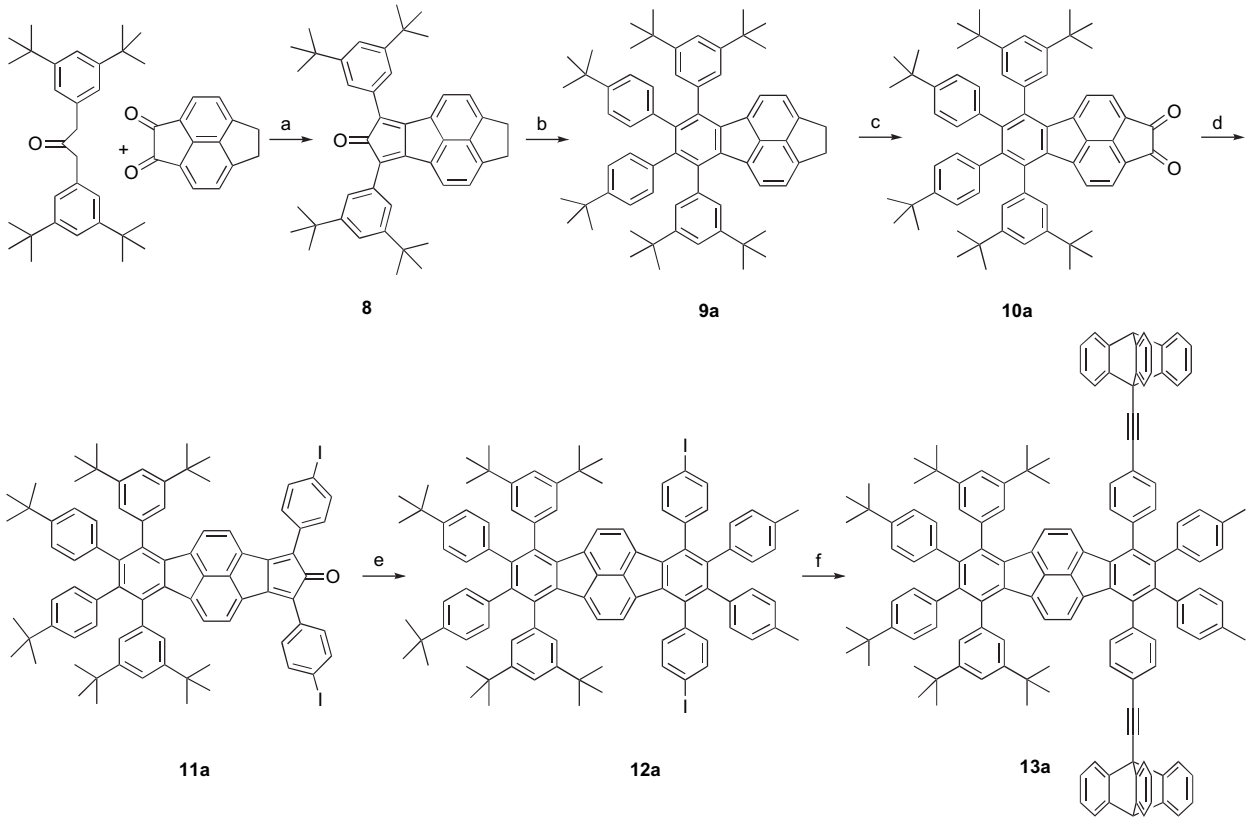
Scheme 2. Reagents and conditions: (a) TIPS-acetylene, $Pd(PPh_3)_4$ 5%, CuI 10%, piperidine, Ar, 20 °C, 21 h, 100%; (b) KF, DMF, 80 °C, 3 h, 85%; (c) 4-*tert*-butyl-1-iodobenzene (for the synthesis of **5**) or 4-bromotoluene (for the synthesis of **6**), $Pd(PPh_3)_4$ 5%, CuI 10%, piperidine, Ar, 80 °C, 6 h.

that purpose we selected 1,3-di(4-iodophenyl)propan-2-one (**7**) to introduce iodine centers via a double Knoevenagel condensation. Finally, a double Sonogashira coupling yields the molecular wheelbarrow.

The synthesis of **7** was accomplished in two steps.[14] The generation of the ketone using TOSMIC with NaH in DMSO was not reproducible in terms of yield, which varies from 10 to 40%. When freshly opened DMSO is used yields tend to be higher, whereas when using older DMSO yields decrease. In order to find more suitable conditions for this reaction, we tried THF as solvent. The reaction gave the product **7** in a 45% yield with a good reproducibility and an easier work-up.

The starting cyclopentadienone **8** was obtained via a first double Knoevenagel reaction of 1,3-bis(3,5-di-*tert*-butylphenyl)propan-2-one with diketopyracene[15] following a described procedure.[7]

The Diels–Alder reaction of **8** with di(4-*tert*-butylphenyl)ethyne (**5**) provided, after CO extrusion and aromatization, ethane-bridged **9a** with a 97% yield. The ^1H NMR spectrum of **9a** clearly showed the 2:1 ratio between the different types of *tert*-butyl groups. For all the Diels–Alder reactions in this



Scheme 3. Reagents and conditions: (a) EtOH, 20 h, Ar, 20 °C, 90%; (b) 1,2-di(4-*tert*-butylphenyl)ethyne (**5**), diphenylether, 16 h, Ar, reflux, 97%; (c) $(C_6H_5SeO)_2O$, chlorobenzene, 62 h, Ar, reflux, 60%; (d) 1,3-di(4-iodophenyl)propan-2-one (**7**), KOH, EtOH, Ar, reflux, 100%; (e) 1,2-di(4-tolyl)ethyne (**6**), diphenylether, 16 h, Ar, reflux, 30%; (f) 9-ethynyltriptycene (**3**), $Pd(PPh_3)_4$ 10 mol %, CuI 20 mol %, piperidine/THF (1:1), 24 h, Ar, 20 °C, 55%.

paper, the solvent, diphenylether, was distilled using a Kugelrohr distillation apparatus prior to the purification by column chromatography on silica. Oxidation of the ethane bridge of the pyracene in **9a** with benzeneseleninic anhydride yielded the α-diketo fragment **10a** necessary for the connection of the second axle.[16] This is the key step of our strategy.

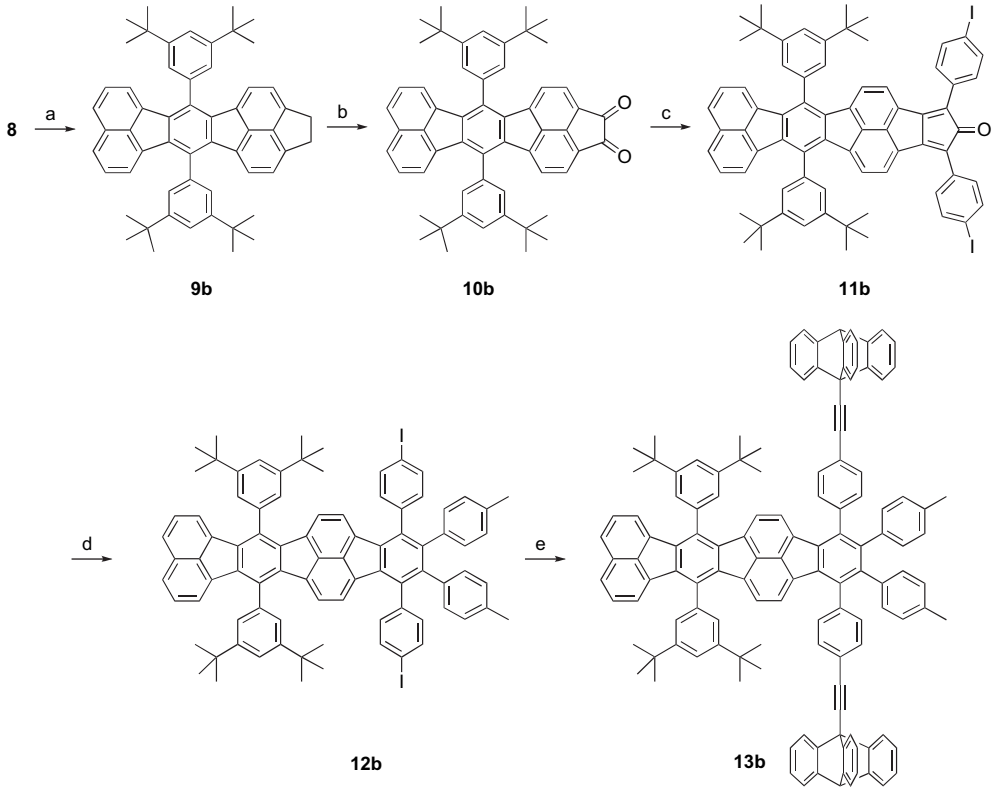
Halogens are introduced at this stage for subsequent coupling in order to connect the triptycene wheels. The double Knoevenagel condensation of **10a** with 1,3-di(4-iodophenyl)propan-2-one (**7**) gave the diiodo derivative of cyclopentadienone **11a** with a quantitative yield, due to the strong acidic character of the protons involved in the reaction. For the synthesis of products **8**, **11a**, and **11b** by a double Knoevenagel condensation we had to optimize the number of base equivalents. After several tries we could establish that for the synthesis of cyclopentadienone **8**, 1 equiv of KOH was the best proportion of base. Increasing to 2 equiv diminished the yield considerably. On the contrary, for the synthesis of compounds **11a** and **11b**, 2 equiv gave the best yields.

The Diels–Alder reaction of **11a** with di(4-tolyl)ethyne provided, after CO extrusion and aromatization, the precursor **12a** with 30% yield. This low yield may be due to steric hindrance between the overcrowded alkyne and the *tert*-butyl groups of the substrate but the methyl groups are necessary to improve the solubility of this family of molecules in organic solvents.

The two wheels were then simultaneously covalently attached to the axle by a double coupling of 9-ethynyltriptycene (**3**) with **12a** under classical Sonogashira conditions (step f).[17] The double coupling afforded **13a** in 55% yield after column chromatography (SiO_2, cyclohexane/CH_2Cl_2 0–20% , R_f=0.31) as an orange solid.

The synthesis of the wheelbarrow **13a** has thus been achieved in six steps from diketopyracene with an overall yield of 9%.

The second prototype (**13b**) was prepared via the same strategy based on the repetition of a double Knoevenagel–Diels–Alder reaction sequence on an α-diketo fragment (Scheme 4). The Diels–Alder reaction of **8** with acenaphthylene is the key step of the synthesis of this second prototype, when the handles are introduced. After CO extrusion and aromatization, the ethane-bridged **9b** was obtained with an 83% yield. The ^{1}H NMR spectrum of **9b** clearly showed the 2:1 ratio between the different types of *tert*-butyl groups. Oxidation of the ethane bridge with benzeneseleninic anhydride yielded the α-diketo fragment **10b** necessary for the connection of the second axle.[16] The introduction of the halogens for subsequent coupling in order to connect the triptycene wheels was performed via the double Knoevenagel condensation of **10b** with 1,3-di(4-iodophenyl)propan-2-one (**7**) and 2 equiv of base (KOH). The diiodo derivative of cyclopentadienone **11b** was obtained with a best yield of 64%, which was rather disappointing compared to the quantitative yield obtained for **11a**. The difference in yield



Scheme 4. Reagents and conditions: (a) acenaphthylene, diphenylether, 16 h, Ar, reflux, 83%; (b) $(C_6H_5SeO)_2O$, chlorobenzene, 62 h, Ar, reflux, 67%; (c) 1,3-di(4-iodophenyl)propan-2-one (**7**), KOH, EtOH, Ar, reflux, 64%; (d) 1,2-di(4-tolyl)ethyne (**6**), diphenylether, 16 h, Ar, reflux, 49%; (e) 9-ethynyltriptycene (**3**), $Pd(PPh_3)_4$ 10 mol %, CuI 20 mol %, piperidine/THF (1:1), 24 h, Ar, 20 °C, 70%.

could be due to the higher dilution of the reaction mixture, required by the lower solubility of the compounds.

The Diels–Alder reaction of **11b** with di(4-tolyl)ethyne provided, after CO extrusion and aromatization, the precursor **12b** with 49% yield. This yield is much higher compared to the poor 30% obtained for the analogous compound **12a**. The two wheels were then simultaneously covalently attached to the axle by a double coupling of 9-ethynyltriptycene (**3**) with **12b** as described before for **12a**. The double coupling afforded **13b** in a high 70% yield after column chromatography (SiO_2, cyclohexane/CH_2Cl_2 0–20%) as an orange solid. The synthesis of wheelbarrow **13b** has therefore been achieved in six steps from diketopyracene with an overall yield of 11%.

3. Conclusion

In summary, we have presented the design and the synthesis of polyaromatic hydrocarbons designed by analogy with macroscopic wheelbarrows. Our modular strategy provided us with the possibility to assemble different handles. Studies are currently in progress to image and manipulate the molecular wheelbarrows with an STM tip, in particular to bring to the fore the rotation of the wheels on a metallic surface. We are hoping to reproduce the mechanical behavior of a wheelbarrow at the molecular level, i.e., to convert the translation movement of the tip into the rotation of the wheels, similarly to what has been done on a submodule of the wheelbarrow: a molecule with an axle terminated by two triptycene wheels.[5]

In terms of synthesis, the next step is now to build more complex architectures such as a nanocar with four wheels or a family of nanotrucks with six to twelve wheels. Since polyaromatic hydrocarbon molecules allow to transport atoms on a small distance of a few nanometers,[18] we hope that a molecule equipped with wheels will be capable to move atoms or small molecules around over large distances across surfaces, with potential applications in molecular electronics.

4. Experimental

4.1. General

All commercially available chemicals were of reagent grade and were used without further purification. Acenaphthylene, 4-*tert*-butyl-1-iodobenzene, 4-bromotoluene, and 4-iodobenzylbromide were purchased from Aldrich. Diketopyracene,[15] 1,3-di(3,5-di-*tert*-butylphenyl)propan-2-one,[9] and [(3-cyanopropyl)dimethylsilyl]acetylene[13] were prepared according to literature procedures. Toluene was dried and distilled over CaH_2, THF over sodium with benzophenone, and diethylamine over KOH. All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Flash column chromatography was carried out on silica gel 230–400 mesh from SDS. NMR spectra were recorded on Bruker AM 250 spectrometer at 250 MHz, except when it is mentioned in the experimental part, and full assignments were made using COSY, ROESY, HMBC, and HMQC methods when necessary. Chemical shifts are defined with respect to TMS=0 ppm for ^1H and ^{13}C NMR spectra and were measured relative to residual solvent peaks. The following abbreviations have been used to describe the signals: s for singlet; d for doublet; t for triplet; dt for doublet of triplets; q for quadruplet; m for multiplet. The numbering scheme is given in Schemes 1 and 2 (vide supra). UV–visible spectra were recorded on a Shimadzu UV-3100 spectrometer. FAB and DCI mass spectrometry was performed using a Nermag R10-10.

4.1.1. 1-(9-Anthracenyl)-2-(cyanopropyldimethylsilyl)-ethyne (1). $Pd(PPh_3)_4$ (1.15 g, 1 mmol), CuI (380 mg, 2 mmol), and 9-bromoanthracene (2.57 g, 10 mmol) were suspended under argon in 25 mL of freshly distilled tetrahydrofuran (THF) and 25 mL of degassed piperidine was added with a syringe under argon. [(3-Cyanopropyl)dimethylsilyl]acetylene (1.51 g, 10 mmol) was added and the mixture maintained for 6 h at 70 °C and left overnight at room temperature. The dark brown solution was then treated with 100 mL of saturated NH_4Cl solution and the organic phase extracted three times with 150 mL portions of CH_2Cl_2. The combined organic layers were thereafter washed with 200 mL of 1 M HCl. After the separation of the blue aqueous phase, the organic phase was dried on anhydrous $MgSO_4$. The filtrate was evaporated and the oil was chromatographed (SiO_2, hexane). Compound **1** was obtained as a luminescent oil in 84% yield (1.8 g). ^1H NMR ($CDCl_3$) δ (ppm) 8.53 (d, 2H, ^3J=8.7 Hz), 8.43 (s, 1H, H_{10}), 7.99 (d, 2H, ^3J=8.3 Hz), 7.62 (dt, 2H, ^3J=6.5 Hz, ^4J=1.2 Hz), 7.51 (dt, 2H, ^3J=6.5 Hz, ^4J=1.2 Hz), 2.46 (t, 2H, ^3J=7 Hz, CH_2CN), 1.95 (m, 2H, CH_2), 1.05 (m, 2H, CH_2Si), 0.44 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm) 0.38, 15.9, 20.7, 20.9, 53.2, 53.6, 98.4, 100.1, 122.5, 123.4, 125.6, 125.8, 144.3, 144.5. Elemental analysis: calcd for $C_{22}H_{21}NSi$: C 80.68, H 6.46, found C 80.54, H 6.35; MS (DCI/NH_3, CH_2Cl_2) *m/z* 327.0 (M^+, 100%, calcd 327.1).

4.1.2. 1-(9-Triptycenyl)-2-(cyanopropyldimethylsilyl)-ethyne (2). To a solution of **1** (1.2 g, 3.66 mmol) in 20 mL of 1,2-dimethoxyethane (DME) were slowly added (3 h) at the same speed with a syringe pump a solution of 5.48 g (60 mmol) of anthranilic acid in 20 mL DME and a solution of 7.02 g (40 mmol) of isopentyl nitrite in 20 mL of DME. The reaction mixture was further kept at reflux for 2 h. After evaporation of the solvent, the residue was purified by chromatography (SiO_2, hexane/dichloromethane 20%). Compound **2** was obtained in 61% yield as a pale yellow oil (900 mg). ^1H NMR ($CDCl_3$) δ (ppm) 7.70 (dd, 3H, ^3J= 6.5 Hz, ^4J=2.0 Hz), 7.40 (dd, 3H,=6.5 Hz, ^4J=2.0 Hz), 6.98–7.10 (m, 6H), 5.44 (s, 1H, H_{10}), 2.49 (t, 2H, ^3J=7 Hz, CH_2CN), 1.99 (m, 2H, CH_2), 1.07 (m, 2H, CH_2Si), 0.50 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm) 0.42, 15.9, 20.7, 20.9, 97.7, 101.6, 106.3, 117.1, 119.7, 125.7, 126.7, 126.9, 128.0, 128.7, 131.2, 133.1. Elemental analysis: calcd for $C_{28}H_{25}NSi$: C 83.33, H 6.24, found C 83.14, H 6.37; MS (DCI/NH_3, CH_2Cl_2) *m/z* 403.2 (M^+, 100%, calcd 403.2).

4.1.3. 9-Ethynyltriptycene (3). Compound **2** (900 mg, 2.23 mmol, 1 equiv) was dissolved in 15 mL of THF and diluted with 15 mL of MeOH. Potassium carbonate (850 mg, 6.15 mmol) was added and the solution was stirred at room temperature overnight. The reaction mixture was

poured into water (50 mL) and extracted with ether (3×50 mL). The organic phase was washed with brine (50 mL), dried on $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane) to afford **3** as a colorless solid (460 mg, 75%). ^{1}H NMR ($CDCl_3$) δ (ppm) 7.75 (m, 3H), 7.39 (m, 3H), 6.98–7.10 (m, 6H), 5.43 (s, 1H, H_{10}), 3.28 (s, 1H, alkyne); ^{13}C NMR ($CDCl_3$) δ (ppm) 52.9, 53.2, 78.4, 80.5, 122.3, 123.4, 125.2, 125.7, 143.9, 144.3. Elemental analysis: calcd for $C_{22}H_{14}$: C 94.93, H 5.07, found C 94.82, H 4.97; mp 239 °C; MS (DCI/NH_3, CH_2Cl_2) *m/z* 278.1 (M^+, 46%, calcd 278.1).

4.1.4. 1-*tert*-Butyl-4-ethynylbenzene (4). $Pd(PPh_3)_4$ (0.26 g, 0.225 mmol), CuI (86 mg, 0.45 mmol), and 4-*tert*-butyl-1-iodobenzene (1.3 g, 0.9 mL, 5 mmol) were suspended under argon in 40 mL of degassed piperidine. Triisopropylsilylacetylene (1.003 g, 1.3 mL, 5.5 mmol) was added dropwise and the mixture maintained for 21 h at room temperature. The dark brown solution was then treated with 100 mL of a saturated solution of NH_4Cl and the organic phase extracted three times with 150 mL portions of CH_2Cl_2. The combined organic layers were thereafter washed with 200 mL of 1 M HCl. After the separation of the blue aqueous phase, the organic phase was dried on anhydrous $MgSO_4$. The filtrate was evaporated and the oil was chromatographed (SiO_2, petroleum ether) to afford 1.7 g (100%) of the product as a clear oil. The product was then deprotected by reaction with a solution of potassium fluoride (0.627 g, 10.8 mmol) in water (5 mL), which was added to a solution of TIPS-protected **4** (1.7 g, 5.4 mmol) in DMF (50 mL). After heating to 80 °C for 3 h, the reaction mixture was poured into water (100 mL) and extracted with toluene (3×100 mL). The organic phase was washed with water (100 mL), dried on $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, petroleum ether) to afford **4** as a clear oil (0.727 mg, 85%). ^{1}H NMR ($CDCl_3$) δ (ppm) 7.41 (dt, 2H, $^3J_{2-3}$=8.7 Hz, ^4J=2.0 Hz, H_3), 7.12 (dt, 2H, $^3J_{2-3}$=8.7 Hz, ^4J=2.0 Hz, H_2), 3.07 (s, 1H, alkyne), 1.30 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm) 151.7, 132.2, 125.8, 119.2, 82.4, 81.2, 34.8, 33.9. Elemental analysis: calcd for $C_{12}H_{14}$: C 91.08, H 8.92, found C 90.97, H 8.89; MS (DCI/NH_3, CH_2Cl_2) *m/z* 158.1 (M^+, 18%, calcd 158.1).

4.1.5. 1,2-Di(4-*tert*-butylphenyl)ethyne (5). $Pd(PPh_3)_4$ (0.238 g, 0.20 mmol), CuI (78 mg, 0.20 mmol), and 4-*tert*-butyl-1-iodobenzene (1.3 g, 0.9 mL, 5 mmol) were suspended under argon in 40 mL of degassed piperidine. 1-*tert*-Butyl-4-ethynylbenzene **4** (0.727 g, 4.59 mmol) was added dropwise and the mixture maintained for 6 h at 80 °C. The reaction mixture was poured into a saturated solution of NH_4Cl (100 mL) and extracted with dichloromethane (100 mL+50 mL). The organic layer was washed with a saturated solution of NH_4Cl (100 mL) and water (100 mL+50 mL) and then dried with $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography (SiO_2, cyclohexane) to afford 1.221 g (91%) of the product as a white solid. ^{1}H NMR ($CDCl_3$) δ (ppm) 7.44 (dt, 4H, $^3J_{2-3}$=8.7 Hz, ^4J=1.9 Hz, H_2), 7.35 (dt, 4H, $^3J_{2-3}$=8.7 Hz, ^4J=2 Hz, H_3), 1.30 (s, 18H, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm) 151.5, 132.6, 125.6, 119.2, 88.4, 34.7, 33.8. Elemental analysis: calcd for $C_{22}H_{26}$: C 90.98, H 9.02, found C 90.91, H 8.87; MS (DCI/NH_3, CH_2Cl_2) *m/z* 290.2 (M^+, 14%, calcd 290.2).

4.1.6. 1,2-Di(4-tolyl)ethyne (6). $Pd(PPh_3)_4$ (0.289 g, 0.25 mmol), CuI (0.095 g, 0.5 mmol), and 4-bromotoluene (0.855 g, 5 mmol) were suspended under argon in 35 mL of degassed piperidine. 4-Ethynyltoluene (0.580 g, 0.634 mL, 5 mmol) was added dropwise and the mixture maintained for 6 h at 80 °C. The reaction mixture was poured into a saturated solution of NH_4Cl (100 mL) and extracted with dichloromethane (100 mL+50 mL). The organic layer was washed with a saturated solution of NH_4Cl (100 mL) and water (100 mL+50 mL) and then dried with $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography (SiO_2, cyclohexane) to afford 0.937 g (90%) of the product as a clear oil. ^{1}H NMR ($CDCl_3$) δ (ppm) 7.46 (d, 4H, $^3J_{2-3}$=8.0 Hz, H_2), 7.15 (d, 4H, $^3J_{2-3}$=8.0 Hz, H_3), 2.36 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm) 137.4, 132.5, 125.8, 119.3, 88.7, 21.8. Elemental analysis: calcd for $C_{16}H_{14}$: C 93.16, H 6.84, found C 92.89, H 6.69; MS (DCI/NH_3, CH_2Cl_2) *m/z* 206.1 (M^+, 18%, calcd 206.1).

4.1.7. 1,3-Di(4-iodophenyl)propan-2-one (7). To a solution of 4-iodobenzylbromide (1 g, 3.36 mmol) in THF (40 mL) was added portionwise NaH 60% in oil (0.202 g, 5.05 mmol) under argon. The mixture was then stirred for 0.5 h followed by the dropwise addition of a solution of (*p*-tolylsulfonyl)methyl isocyanide (0.328 g, 1.68 mmol) in dry THF (40 mL). The mixture was stirred for an extra 16 h at room temperature and the solvent was evaporated to dryness. Water (100 mL) was added and extracted with dichloromethane (3×60 mL), the organic layer was washed with brine (2×50 mL), dried over $MgSO_4$, and evaporated. The residue was then dissolved in dichloromethane (20 mL) and hydrolyzed by addition of 3 mL of 35% HCl. After stirring overnight at room temperature, the solution was washed with water (50 mL) and with a saturated solution of $NaHCO_3$ (2×50 mL). After drying the organic phase over $MgSO_4$, evaporation of the solvent gave a crude material, which was purified by column chromatography (SiO_2, cyclohexane/dichloromethane 4:1). Compound **7** was obtained as a white solid in 45% yield (0.353 g). ^{1}H NMR ($CDCl_3$) δ (ppm) 7.61 (d, 4H, ^3J=9 Hz), 6.83 (d, 4H, ^3J=9 Hz), 3.62 (s, 4H, CH_2); ^{13}C NMR ($CDCl_3$) δ (ppm) 204.8, 137.5, 133.4, 130.9, 93.2, 49.7. Elemental analysis: calcd for $C_{15}H_{12}I_2O$: C 38.99, H 2.62, found C 38.70, H 2.57; MS (DCI/NH_3, CH_2Cl_2) *m/z* 461.9 (M^+, 100%, calcd 461.9).

4.1.8. Cyclopentadienone 8. To a solution of α-diketopyracene[15] (0.172 mg, 0.83 mmol) and of 1,3-bis(3,5-di-*tert*-butylphenyl)propan-2-one[9] (0.360 mg, 0.83 mmol) in dry methanol under argon was added 0.83 mL of a 1 M solution of KOH in dry methanol. After stirring for 4 h at reflux and overnight at room temperature under argon, the suspension was filtered and the precipitate was extensively washed with 15 mL of cold methanol and dried in vacuo to afford 0.452 g (90%) of a dark green solid. R_f (20% dichloromethane/cyclohexane)=0.4. The solid sometimes needs to be purified by flash column chromatography (SiO_2, cyclohexane/dichloromethane 2–5%). The product is clearly visible in the column as a blue band. ^{1}H NMR ($CDCl_3$) δ (ppm)

7.94 (d, 2H, ^3J=7.0 Hz, H_1), 7.70 (d, 4H, ^4J=1.8 Hz, H_p), 7.45 (t, 2H, ^4J=1.8 Hz, H_o), 7.35 (d, 2H, ^3J=7.0 Hz, H_2), 3.52 (s, 4H, ethane bridge), 1.40 (s, 36H, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm) 202.6, 155.4, 150.7, 146.7, 143.9, 131.0, 128.1, 123.3, 122.4, 122.3, 121.4, 35.1, 32.2, 31.6. Elemental analysis: calcd for $C_{45}H_{49}O$: C 89.06, H 8.30, found C 89.00, H 8.50; MS (DCI/NH_3, CH_2Cl_2) *m/z* 607.2 (MH^+, 100%, calcd 607.4).

4.1.9. Compound 9a. A mixture of 1,2-bis(4-*tert*-butylphenyl)ethyne (**5**) (0.048 g, 0.165 mmol) and **8** (0.100 g, 0.165 mmol) was dissolved in diphenylether (3 mL) and heated at reflux (260 °C) overnight under argon. After cooling, the solvent was evaporated using the Kugelrohr distillation apparatus and the red solid was purified by column chromatography (SiO_2, hexane/dichloromethane 0–10%). Compound **9a** was obtained as a yellow oil with a 97% yield. ^{1}H NMR ($CDCl_3$) δ (ppm) 7.22 (t, 2H, ^4J=1.7 Hz), 7.19 (d, 4H, ^4J=1.7 Hz), 7.14 (d, 2H, ^3J=7.1 Hz), 7.01 (d, 2H, ^3J=7.1 Hz), 6.80 (d, 4H, ^3J=8.1 Hz), 6.69 (d, 4H, ^3J=8.1 Hz), 3.43 (s, 4H, ethane bridge), 1.21 (s, 36H, *tert*-butyl), 1.11 (s, 18H, *tert*-butyl). Elemental analysis: calcd: C 91.19, H 8.81, found C 91.02, H 8.72; MS (DCI/NH_3, CH_2Cl_2) *m/z* 886 (M^++NH_4^+, 100%, calcd for $C_{66}H_{80}N$: 886.6), 868 (M^+, 5%, calcd for $C_{66}H_{76}$: 868.6).

4.1.10. Diketone 10a. Compound **9a** (80 mg, 0.092 mmol) and benzeneseleninic anhydride (33 mg, 0.092 mmol) were placed under argon in a 50 mL flask and chlorobenzene was added. The solution was heated at reflux for 62 h. The solvent was evaporated and the residue was adsorbed on silica and purified by column chromatography (SiO_2, hexane/dichloromethane 0–40%). Compound **10a** was obtained as an orange solid (50 mg, 60%). ^{1}H NMR ($CDCl_3$) δ (ppm) 7.96 (d, 2H, ^4J=7.3 Hz), 7.33 (t, 2H, ^4J=1.8 Hz), 7.29 (s, 2H), 7.14 (d, 4H, ^3J=1.8 Hz), 6.88 (d, 4H, ^3J=8.5 Hz), 6.71 (d, 4H, ^3J=8.5 Hz), 1.23 (s, 36H, *tert*-butyl), 1.13 (s, 18H, *tert*-butyl). ^{13}C NMR ($CDCl_3$) δ (ppm) 192.4, 155.8, 152.4, 150.3, 148.7, 146.2, 143.8, 131.0, 128.1, 127.4, 126.9, 123.3, 122.4, 122.3, 121.4, 34.7 (4 Cq-*tert*), 34.0 (2 Cq-*tert*), 31.1 (12 CMe_3), 30.8 (6 CMe_3). Elemental analysis: calcd for $C_{66}H_{72}O_2$: C 88.35, H 8.09, found C 87.98, H 7.90; MS (DCI/NH_3, CH_2Cl_2) *m/z* 897 (MH^+, 8%, calcd 896.6), 914 (M+NH_4^+, 82%, calcd 913.6), 931 (M+2NH_4^+, 82%, calcd 930.6).

4.1.11. Cyclopentadienone 11a. To a solution of compound **10a** (50 mg, 0.0557 mmol) and 1,3-di(4-iodophenyl)propan-2-one **7** (25 mg, 0.05573 mmol) in dry ethanol under argon was added 0.055 mL of a 2 M solution of KOH in dry ethanol. The reaction mixture was heated to reflux for 24 h under argon. The solvent was then evaporated and the crude reaction residue was adsorbed on silica and purified by column chromatography (SiO_2, hexane/dichloromethane 0–10%). Compound **11a** was obtained as a dark brown solid (73 mg, 100%). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.66 (d, 4H, ^3J=7.2 Hz), 7.50 (d, 4H, ^3J=8 Hz), 7.32 (t, 2H, ^4J=1.7 Hz), 7.22 (d, 4H, ^4J=1.7 Hz), 7.12 (d, 4H, ^3J=8 Hz), 7.04 (d, 2H, ^3J=7.2 Hz), 6.84 (d, 4H, ^3J=8 Hz), 6.75 (d, 4H, ^3J=8 Hz), 1.26 (s, 36H, *tert*-butyl), 1.11 (s, 18H, *tert*-butyl); ^{13}C NMR ($CDCl_3$) δ (ppm) 200.1, 165.1, 150.4, 150.1, 137.7, 136.9, 135.6, 135.4, 134.9, 134.6, 131.5, 131.3, 131.1, 130.7, 127.4, 127.1, 125.5, 124.4, 123.3, 122.4, 122.3, 121.4, 98.4, 35.1, 34.7, 32.2, 31.6. Elemental analysis: calcd for $C_{81}H_{80}I_2O$: C 73.52, H 6.09, found C 73.22, H 5.98; MS (DCI/NH_3, CH_2Cl_2) *m/z* 1340 (M^++NH_4^+, 7%, calcd for $C_{81}H_{84}I_2NO$: 1340.5), 1323 (M+H^+, 100%, calcd for $C_{81}H_{81}I_2O$: 1323.4).

4.1.12. Diiodo compound 12a. A mixture of **11a** (0.073 g, 0.055 mmol) and 1,2-di(4-tolyl)ethyne **6** (0.011 g, 0.055 mmol) was dissolved in diphenylether (3 mL) and heated at reflux (260 °C) overnight under argon. After cooling, the solvent was evaporated using the Kugelrohr distillation apparatus. The dark brown solid was adsorbed on silica and purified by column chromatography (SiO_2, hexane/dichloromethane 0–10%) to afford **12a** as a dark brown solid (23 mg, 30%). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.53 (d, 4H, ^3J=8.4 Hz), 7.15 (t, 2H, ^4J=1.8 Hz), 7.04 (d, 4H, ^4J=1.8 Hz), 6.94 (d, 4H, ^3J=8.4 Hz), 6.76 (d, 4H, ^3J=8.4 Hz), 6.65 (d, 4H, ^3J=3.1 Hz), 6.57 (d, 4H, ^3J=8.4 Hz), 6.43 (d, 2H, ^3J=7.2 Hz), 6.00 (d, 2H, ^3J=7.2 Hz), 2.10 (s, 6H, Me), 1.14 (s, 36H, *tert*-butyl), 1.05 (s, 18H, *tert*-butyl); ^{13}C NMR ($CDCl_3$) δ (ppm) 150.4, 150.1, 137.8, 136.9, 135.4, 135.5, 134.8, 134.6, 131.5, 131.3, 131.1, 130.9, 129.4, 129.1, 128.7, 128.5, 127.4, 127.1, 125.5, 124.6, 123.3, 122.4, 122.3, 121.5, 98.2, 35.1, 34.7, 32.2, 31.6, 23.1; MS (DCI/NH_3) *m/z* 1519 (M^++NH_4^+, 100%, calcd for $C_{96}H_{98}I_2N$: 1518.6), 1501 (M+H^+, 7%, calcd for $C_{96}H_{95}I_2$: 1501.5).

4.1.13. Wheelbarrow 13a. Compound **12a** (15 mg, 0.01 mmol) and 9-ethynyltriptycene (**3**) (12.23 mg, 0.043 mmol) were placed under argon in a 10 mL round bottomed flask. A mixture of a degassed solution of piperidine/THF (1:1, 2 mL) was added. In a different flask a 1:2 mixture of $Pd(PPh_3)_4$ (5.77 mg, 0.005 mmol) and copper iodide (1.9 mg, 0.01 mmol) in degassed THF (2 mL) was prepared under argon. The second solution was added into the first one via cannula and the reaction was allowed to stir at room temperature for 24 h. The yellow solution was then treated with 10 mL of a saturated solution of NH_4Cl and the organic phase extracted three times with 15 mL portions of CH_2Cl_2. The combined organic layers were thereafter washed with 15 mL of 1 M HCl. After the separation of the blue aqueous phase, the organic phase was dried over anhydrous $MgSO_4$. The filtrate was evaporated and the oil was chromatographed (SiO_2, cyclohexane/dichloromethane 0–20%). Compound **13a** was obtained as an orange solid (10 mg, 55%). λ_{max} (ε) (CD_2Cl_2)/nm 450 (9450), 425 (8040), 319 (22,150), 276 (sh, 17,600), 246 (sh, 39,250), 230 (55,400); ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) 7.84 (m, 6H, Tript), 7.70 (d, 4H, ^3J=8 Hz), 7.49 (m, 6H, Tript), 7.42 (d, 4H, ^3J=8 Hz), 7.19 (m, 4H), 7.14 (m, 12H, Tript), 7.08 (m, 4H), 6.89 (d, 4H, ^3J=8 Hz), 6.80 (m, 6H, H9), 6.71 (d, 4H, ^3J=9 Hz), 6.40 (d, 2H, ^3J=8 Hz), 6.18 (d, 2H, ^3J=7 Hz), 5.50 (s, 2H, Tript), 2.2 (s, 6H, Me), 1.8 (s, 36H, *tert*-butyl), 1.1 (s, 18H, *tert*-butyl); ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 150.1, 148.3, 148.0, 145.5, 144.7, 144.5, 140.8, 139.3, 138.2, 137.9, 137.3, 136.8, 136.7, 132.0, 131.2, 131.0, 130.4, 127.8, 126.2, 126.0, 125.6, 125.4, 125.2, 125.1, 124.9, 124.5, 123.8, 123.7, 123.5, 122.6, 122.5, 121.5, 120.0, 93.0 (alkynes), 34.8 (4 Cq-*tert*), 34.1 (2 Cq-*tert*), 31.2 (12 CMe_3), 31.0 (6 CMe_3), 21.0 (2 CH_3); MS (MNBA FAB) *m/z* 1802 (M+H^+, 100%), HRMS (FAB) *m/z* 1801.9500 (M^+, calcd for $C_{140}H_{120}$: 1801.9468).

4.1.14. Compound 9b. A mixture of acenaphthylene (0.025 g, 0.165 mmol) and cyclopentadienone **8** (0.1 g, 0.165 mmol) was dissolved in xylene (5 mL) and heated at reflux (145 °C) overnight under argon. The solvent was evaporated and the dark solid adsorbed on silica. Column chromatography (SiO_2, cyclohexane/dichloromethane 0–10%) afforded the product as a yellow solid (100 mg, 83%). ^{1}H NMR ($CDCl_3$) δ (ppm) 7.70 (d, 2H, ^3J=8.2 Hz), 7.68 (t, 4H, ^4J=1.7 Hz), 7.58 (d, 2H, ^4J=1.7 Hz), 7.33 (dd, 2H, ^3J=7.1 Hz, ^3J=8.2 Hz), 7.17 (d, 4H, ^3J=7.1 Hz), 6.87 (d, 2H, ^3J=7.1 Hz), 6.83 (d, 2H, ^3J=7.1 Hz), 3.43 (s, 4H, CH_2), 1.41 (s, 36H, *tert*-butyl); ^{13}C NMR ($CDCl_3$) δ (ppm) 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. Elemental analysis: calcd for $C_{56}H_{56}$: C 92.3, H 7.7, found C 92.1, H 7.5; MS (DCI/NH_3, CH_2Cl_2) *m/z* 729 ($M+H^+$, 5%, calcd 729), 746 (M^++NH_4^+, 100%), 764 ($M+N_2H_7^+$, 50%).

4.1.15. Diketone 10b. Compound **9b** (25 mg, 0.034 mmol) and benzeneseleninic anhydride (14 mg, 0.041 mmol) were placed under argon in a 50 mL flask and chlorobenzene (10 mL) was added. The solution was heated at reflux for 62 h. The solvent was evaporated and the residue was adsorbed on silica and purified by column chromatography (SiO_2, cyclohexane/dichloromethane 0–50%). Compound **10b** was obtained as an orange solid (42 mg, 67%). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.95 (d, 2H, ^3J=7.3 Hz), 7.82 (d, 2H, ^3J=8.1 Hz), 7.75 (t, 2H, ^4J=1.8 Hz), 7.57 (d, 4H, ^4J=1.8 Hz), 7.39 (dd, 2H, ^3J=6.7 Hz, ^3J=8.1 Hz), 7.03 (d, 2H, ^3J=7.3 Hz), 6.95 (d, 2H, ^3J=6.7 Hz), 1.42 (s, 36H, *tert*-butyl); ^{13}C NMR ($CDCl_3$) δ (ppm) 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. Elemental analysis: calcd for $C_{56}H_{56}O_2$: C 88.8, H 6.9, found C 88.5, H 6.8; MS (DCI/NH_3, CH_2Cl_2) *m/z* 774 (M^++NH_4^+, 80%, calcd 774), 757 ($M+H^+$, 100%, calcd 757).

4.1.16. Cyclopentadienone 11b. To a solution of **10b** (25 mg, 0.033 mmol) and 1,3-di(4-iodophenyl)propan-2-one **7** (15 mg, 0.033 mmol) in dry ethanol under argon was added 0.033 mL of a 2 M solution of KOH in dry ethanol. The reaction mixture was heated at reflux for 24 h under argon. The solvent was then evaporated and the crude reaction residue was adsorbed on silica and purified by column chromatography (SiO_2, cyclohexane/dichloromethane 0–10%). Compound **11b** was obtained as a dark brown solid (25 mg, 64%). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.87 (d, 2H, ^3J=7.3 Hz), 7.82 (d, 2H, ^3J=8.1 Hz), 7.75 (t, 2H, ^4J=1.8 Hz), 7.57 (d, 4H, ^4J=1.9 Hz), 7.41 (d, 2H, ^3J=7.3 Hz), 7.37 (dd, 2H, ^3J=7.2 Hz, ^3J=8.0 Hz), 6.98 (d, 2H, ^3J=7.3 Hz), 6.89 (d, 2H, ^3J=7 Hz), 1.42 (s, 36H *tert*-butyl); ^{13}C NMR ($CDCl_3$) δ (ppm) 200.6, 152.4, 150.9, 140.8, 138.4, 137.8, 137.2, 135.5, 131.0, 130.2, 129.5, 127.5, 126.6, 125.2, 124.9, 124.6, 124.3, 123.0, 122.7, 122.1, 121.9, 93.7, 35.3, 31.5. Elemental analysis: calcd for $C_{71}H_{60}I_2O$: C 72.1, H 5.1, found C 71.9, H 5.0; MS (DCI/NH_3, CH_2Cl_2) *m/z* 1183 ($M+H^+$, 100%, calcd 1183).

4.1.17. Diiodo compound 12b. A mixture of compound **11b** (0.025 g, 0.021 mmol) and 1,2-di(4-tolyl)ethyne **6** (0.004 g, 0.021 mmol) was dissolved in diphenylether (3 mL) and heated at reflux (260 °C) overnight under argon. After cooling, the solvent was evaporated using a Kugelrohr distillation apparatus. The dark brown solid was adsorbed on silica and purified by column chromatography (SiO_2, hexane/dichloromethane 0–10%) to afford **12b** as a dark brown solid (14 mg, 49%). ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) 7.53 (d, 4H, ^3J=8 Hz), 7.15 (t, 2H, ^4J=1.8 Hz), 7.03 (d, 4H, ^4J=1.8 Hz), 6.94 (d, 4H, ^3J=8 Hz), 6.76 (d, 4H, ^3J=8 Hz), 6.65 (d, 4H, ^3J=8 Hz), 6.57 (d, 4H, ^3J=8 Hz), 6.43 (d, 2H, ^3J=7.2 Hz), 6.00 (d, 2H, ^3J=7.2 Hz), 2.10 (s, 6H, Me), 1.13 (s, 36H, *tert*-butyl), 1.05 (s, 18H, *tert*-butyl); MS (DCI/NH_3) *m/z* 1378 (M^++NH_4^+, 100%, calcd for $C_{86}H_{78}I_2N$: 1378.4), 1362 ($M+H^+$, 40%, calcd for $C_{86}H_{75}I_2$: 1361.4).

4.1.18. Wheelbarrow 13b. Compound **12b** (14 mg, 0.01 mmol) and 9-ethynyltriptycene **3** (6.3 mg, 0.0226 mmol) were placed under argon in a 10 mL round bottomed flask. A mixture of a degassed solution of piperidine/THF (1:1, 2 mL) was added. In a different flask a 1:2 mixture of $Pd(PPh_3)_4$ (5.9 mg, 0.0051 mmol) and copper iodide (1.95 mg, 0.01 mmol) in degassed THF (2 mL) was prepared under argon. The second solution was added into the first one via cannula and the reaction was allowed to stir at room temperature for 24 h. The yellow solution was then treated with 10 mL of a saturated solution of NH_4Cl and the organic phase extracted three times with 15 mL portions of CH_2Cl_2. The combined organic layers were thereafter washed with 15 mL of 1 M HCl. After the separation of the blue aqueous phase, the organic phase was dried over anhydrous $MgSO_4$. The filtrate was evaporated and the oil was chromatographed (SiO_2, cyclohexane/dichloromethane 0–20%). Compound **13a** was obtained as an orange solid (12.7 mg, 70%). λ_{max} (ε) (CD_2Cl_2)/nm 450 (9450), 425 (8040), 319 (22,150), 276 (sh, 17,600), 246 (sh, 39,250), 230 (55,400); ^{1}H NMR (400 MHz, CD_2Cl_2) δ (ppm) 7.91 (dd, 2H, ^3J=7.5 Hz, ^4J=1.1 Hz), 7.84–7.81 (m, 6H, Tript), 7.76 (d, 4H, ^3J=7.8 Hz), 7.72–7.67 (m, 4H), 7.61 (t, 2H, ^3J=1.8 Hz), 7.49–7.44 (m, 12H, Tript), 7.40 (d, 4H, ^3J=8.2 Hz), 7.29 (t, 2H, ^3J=7.4 Hz), 7.19–7.15 (m, 4H), 7.16–7.12 (m, 6H), 6.87 (t, 4H, ^3J=8.4 Hz), 6.83 (d, 4H, ^3J=7.8 Hz), 6.70 (d, 2H, ^3J=7.1 Hz), 6.36 (d, 2H, ^3J=7.4 Hz), 6.21 (d, 2H, ^3J=7.3 Hz), 5.59 (s, 2H, Tript), 2.21 (s, 6H, 2Me), 1.41 (s, 36H, 4 *tert*-butyl); ^{13}C NMR (100 MHz, CD_2Cl_2) δ (ppm) 152.2, 144.9, 144.8, 144.7, 144.3, 141.6, 140.9, 140.0, 139.4, 138.7, 138.3, 138.1, 137.9, 137.8, 137.0, 136.6, 136.5, 135.7, 132.2, 131.4, 130.7, 128.2, 128.0, 126.9, 126.4, 126.2, 125.8, 125.7, 124.9, 124.0, 123.9, 123.7, 122.8, 122.7, 121.9, 121.7, 93.3 (alkyne), 84.1 (alkyne), 54.2 (Cq-Tript), 54.3 (Cq-Tript), 31.6 (12 CMe_3), 30.1 (4 Cq-*tert*), 21.2 (2 CH_3); MS (MNBA FAB) *m/z* 1661 ($M+H^+$, 100%), HRMS (FAB) *m/z* 1661.7863 (M^+, calcd for $C_{140}H_{120}$: 1661.7903).

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References and notes

1. Anderson, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 2451–2453 and references cited therein.
2. (a) Joachim, C.; Gimzewski, J. K.; Tang, H. *Phys. Rev. B* **1998**, *58*, 16407–16417; (b) Rapenne, G.; Launay, J. P.; Joachim, C. *J. Phys.: Condens. Matter* **2006**, *18*, S1797–S1808.
3. Gimzewski, J. K.; Joachim, C.; Schlitter, R. R.; Langlais, V.; Tang, H.; Johannsen, I. *Science* **1998**, *281*, 531–533.
4. (a) Shirai, Y.; Zhao, Y.; Chen, L.; Tour, J. M. *Org. Lett.* **2004**, *6*, 2129–2132; (b) Shirai, Y.; Osgood, A. J.; Zhao, Y.; Kelly, K. F.; Tour, J. M. *Nano Lett.* **2005**, *5*, 2330–2333; (c) Shirai, Y.; Osgood, A. J.; Zhao, Y.; Yao, Y.; Saudan, L.; Yang, H.; Yu-Hung, C.; Alemany, L. B.; Sasaki, T.; Morin, J. F.; Guerrero, J. M.; Kelly, K. F.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 4854–4864; (d) Morin, J. F.; Shirai, Y.; Tour, J. *Org. Lett.* **2006**, *8*, 1713–1716; (e) Shirai, Y.; Morin, J. F.; Sasaki, T.; Guerrero, J. M.; Tour, J. M. *Chem. Soc. Rev.* **2006**, *35*, 1043–1055.
5. Grill, L.; Rieder, K. H.; Moresco, F.; Rapenne, G.; Stojkovic, S.; Bouju, X.; Joachim, C. *Nat. Nanotechnol.* **2007**, *2*, 95–98.
6. (a) Joachim, C.; Tang, H.; Moresco, F.; Rapenne, G.; Meyer, G. *Nanotechnology* **2002**, *13*, 330–335; (b) Jimenez-Bueno, G.; Rapenne, G. *Tetrahedron Lett.* **2003**, *44*, 6261–6263.
7. Gourdon, A. *Eur. J. Org. Chem.* **1998**, 2797–2801.
8. Berresheim, A. J.; Müller, M.; Müllen, K. *Chem. Rev.* **1999**, *99*, 1747–1786.
9. (a) Moresco, F.; Meyer, G.; Rieder, K. H.; Tang, H.; Gourdon, A.; Joachim, C. *Phys. Rev. Lett.* **2001**, *86*, 672–675; (b) Moresco, F. *Phys. Rep.* **2004**, *399*, 175–225 and references therein.
10. Rapenne, G. *Biomol. Chem.* **2005**, *3*, 1165–1169.
11. Accelrys. *Cerius2 4.6*; San Diego, 2001.
12. Toyota, S.; Yamamori, T.; Asakura, M.; Oki, M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 205–213.
13. Höger, S.; Bonrad, K. *J. Org. Chem.* **2000**, *65*, 2243–2245.
14. (a) Possel, O.; van Leusen, A. M. *Tetrahedron Lett.* **1977**, *48*, 4229–4232; (b) Tichý, M.; Holanová, J.; Závada, J. *Tetrahedron: Asymmetry* **1998**, *9*, 3497–3504.
15. Richter, H. J.; Stocker, F. B. *J. Org. Chem.* **1959**, *24*, 366–367.
16. Clayton, M. D.; Marcinow, Z.; Rabideau, P. W. *J. Org. Chem.* **1996**, *61*, 6052–6054.
17. Sonogashira, K. *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1997; pp 203–229.
18. (a) Gross, L.; Rieder, K. H.; Moresco, F.; Stojkovic, S.; Gourdon, A.; Joachim, C. *Nat. Mater.* **2005**, *4*, 892–895; (b) Rosei, F.; Schunack, M.; Jiang, P.; Gourdon, A.; Lægsgaard, E.; Stensgaard, I.; Joachim, C.; Besenbacher, F. *Science* **2002**, *296*, 328–331.