DOI: 10.1002/ejoc.200800954

Synthesis of Two Complementary Molecular Moulds

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Keywords: Arenes / Molecular devices / Molecular electronics / Self-assembly

The synthesis of two complementary molecular moulds is described. These molecules comprise a polyaromatic central part and four lateral bulky *tert*-butylphenyl or di-*tert*-butylphenyl groups so that when they are deposited onto a surface, a cavity prone to metallic moulding is created.

Introduction

One of the big challenges for molecular electronics is to find a way to build integrated circuits through a bottom-up approach from the molecular scale. Along this line, we recently showed that suitable molecules can not only restructure[1] to create holes or trenches *in* a metallic surface[2] but also be used as molecular moulds to fabricate metallic nanowires[3] or clusters[4] *on* a surface. These moulds comprise a polyaromatic central part, which favours the interaction with metallic atoms, and spacers that lift the polyaromatic board above the surface; this creates a cavity under the plane in which metallic atoms can be trapped. This family of molecules has been named "molecular landers".[5] We have performed this moulding with two different experimental setups: (a) Static moulding: the molecular lander is left to diffuse on a copper surface at room temperature and self-assembles by adsorption at surface step edges; mobile metal atoms then gather under the polyaromatic plateau to form a nanowire extending away from the step edge.[3] We also confirmed that the shape of the metallic nanowire is a function of the shape of the molecular mould.[6] (b) Dynamic moulding: in this case, the experiment is done at low temperature[4] so that isolated atoms do not diffuse. The mould, pushed on the surface by using an STM tip, collects and transports these metallic atoms (up to six in the described experiment), which are trapped in the cavity under the mould.

Our next goal is now to fully use the well-know potential of molecular self-assembly[7] to organize, on a surface, ordered networks of such molecular moulds with the objective to fabricate metallic circuitries, in a bottom-up approach, by diffusion and molecular trapping of metallic atoms. Figure 1 illustrates such a concept.

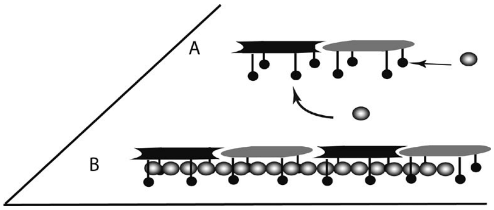

Figure 1. Schematic illustration of the formation of metallic lines on a surface by self-assembly of complementary molecular moulds and diffusion of metal atoms in the line of cavities.

Results and Discussion

In Figure 1A, two complementary molecular moulds have been transferred onto a surface and then diffused and self-assembled; this creates a stable line of cavities in which (step B) metallic atoms can be trapped. Of course the type of metallic circuitry, here a linear chain, is a function of the chemical design and can be varied at will.

For synthetic reasons, we designed two types of moulds to be coadsorbed onto a surface. It was foreseen that a lander comprising both two complementary functions would be fully insoluble, which would have hindered purification and characterization steps and prevented sublimation to the substrate.

Figure 2 shows the final design of the molecules. The central hydrocarbon cores are similar to those used for dynamic (compound **1**) and static (compound **2**) moulding in ref.[4] and ref.,[3] respectively. These central parts are equipped with complementary functions, that is, diaminotriazine and imide groups, respectively. Indeed, we recently showed[8] that the triple hydrogen bonds between these

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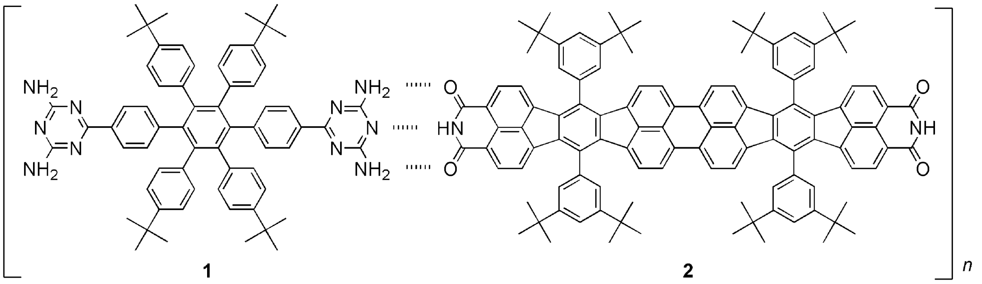


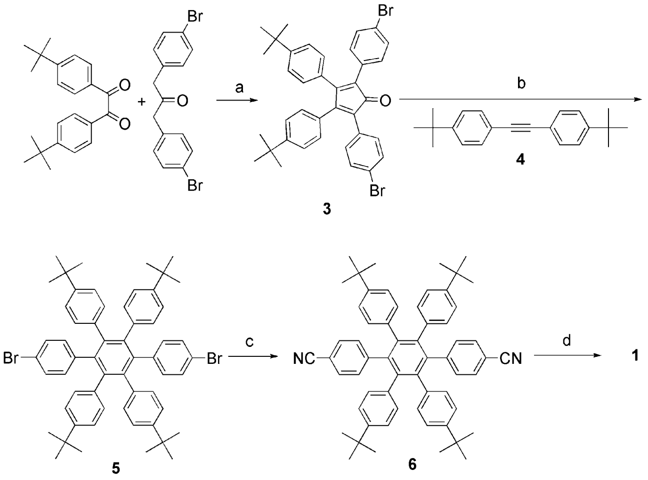
Figure 2. Self-assembly of landers **1** and **2**.

groups provided very stable lines of alternant molecules. Such a good thermal stability is required for room-temperature diffusion of metallic atoms.

The synthesis of substituted hexaphenylbenzene **1** is outlined in Scheme 1. Double Knoevenagel condensation between 1,2-bis(4-*tert*-butylphenyl)ethane-1,2-dione[9] and 1,3-bis(4-bromophenyl)acetone[10] gave cyclopentadienone **3** in 88% yield with a procedure similar to that described by Thomas et al.[11] Then, a reverse-demand Diels–Alder reaction with bis(*tert*-butylphenyl)acetylene (**4**) under microwave irradiation gave hexaarylbenzene **5** in 65% yield. Known tolane **4**[12] was obtained in nearly quantitative yield through a Sonogashira coupling reaction by using controlled microwave heating of ethynyltrimethylsilane (TMSA) and 1-bromo-4-*tert*-butylbenzene,[13] deprotection of the alkyne by NaOH/MeOH/H_2O,[14] and again coupling of obtained 1-*tert*-butyl-4-ethynylbenzene with 1-bromo-4-*tert*-butylbenzene under similar conditions. Then microwave-assisted cyanation[15] of aryl bromide **5** with CuCN in 1-methyl-2-pyrrolidinone (NMP) gave dicyanohexaphenylbenzene **6** in 55% yield. The nitrile group was then converted into a diaminotriazine group by reaction with dicyandiamide and KOH in 2-methoxyethanol under microwave irradiation.[16] In a first attempt, even with the use of an excess amount of dicyandiamide, only the monodiaminotriazine compound was isolated. To complete the reaction, additional amounts of the reagents (dicyandiamide and KOH) had to be added, and the mixture required additional irradiation. As a result of its low solubility in 2-methoxyethanol, bis(diaminotriazine) hexaarylbenzene **1** precipitated and could be easily isolated by filtration. To avoid contamination of the sample with melamine, which can be produced by condensation of dicyandiamide under such basic conditions, the solid was thoroughly washed with boiling water (melamine solubility: 37 $\mathrm{g\,L^{-1}}$) and sonicated in chloroform.

Compound **1** was then obtained as a white solid; it is poorly soluble in DMSO and insoluble in other solvents. The NMR spectroscopic data and mass spectroscopic data are in accordance with the proposed structure.

The synthesis of lander imide **2** is shown in Scheme 2. The key step is the oxidative cyclodehydrogenation of functionalized **11**, which was prepared in two steps from cyclopentadienone **7**.[17]

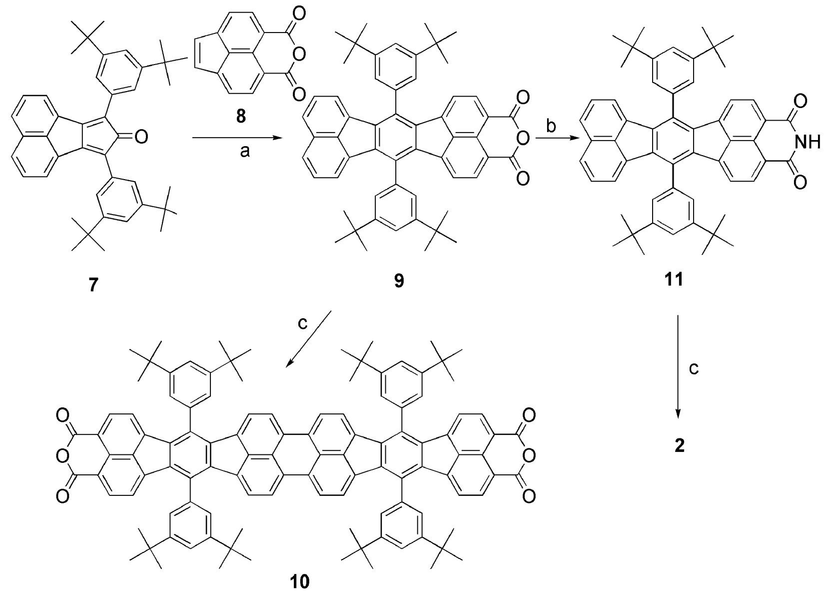


Scheme 1. Reagents and conditions: (a) KOH, EtOH, room temp.; (b) diphenyl ether, microwave, 225 °C; (c) CuCN, NMP, microwave, 220 °C; (d) dicyandiamide, KOH, 2-methoxyethanol, microwave, 225 °C.

Diels–Alder condensation of cyclopentadienone **7** with dione **8** with concomitant decarbonylation and aromatization afforded compound **9**, following the general method described previously.[17] Compound **8** was obtained in five steps from acenaphthene by Friedel–Crafts acylation with dimethylcarbamoyl chloride to give acenaphthene-4,5-dicarboxylic acid-di-*N*,*N*-dimethylamide.[18] The two dimethylamide groups were then hydrolyzed, which after esterification, yielded dimethyl acenaphthene-4,5-dicarboxylate.[19] Monobromination with NBS and dehydrobromination with LiBr/DMF provided dimethylacenaphthylene-4,5-dicarboxylate.[19] This latter was finally hydrolyzed and dehydrated to give **8** as an orange powder (see Supporting Information).[20]

Attempts were made to convert directly dicarboxylic anhydride **8** into its dicarboxylic imide derivative. Methods described in the literature involving the use of concentrated NH_4OH solution[21] or formamide[22] did not allow the formation of the imide, probably as a result of the low solubility of compound **8** under these conditions. In this way, the direct synthesis of half lander **11** from cyclopentadienone **7** could not be achieved.

From compound **9**, two routes are possible for the synthesis of lander imide **2**. The first one consists of the oxidative coupling of precursor **9** to afford lander **10**, followed by the formation of imide **2** from the anhydride. The second



Scheme 2. Reagents and conditions: (a) *o*-xylene, heat; (b) urea, DMF, heat; (c) $FeCl_3$, DCM, room temp.

starts with the prior conversion of the anhydride group into an imide group to afford half lander **11**, upon which oxidative cyclodehydrogenation is performed to obtain lander **2**.

Lander anhydride **10** was easily obtained in quantitative yield from compound **9** by treatment with solid $FeCl_3$ in dichloromethane.[23] Surprisingly, the use of predissolved $FeCl_3$ in nitromethane, reported by Müllen et al. on similar products,[24] led to an undesired mixture of products that could not be easily purified.

Acenaphthofluorantheneimide **11** was obtained from anhydride **9** in quantitative yield by prolonged heating with urea in DMF, by modifying the conditions reported by Kacprzak.[22b] Similar conditions applied to lander anhydride **10** did not allow the formation of lander imide **2**. The conversion seems to be very slow and large amounts of the starting material were recovered.

Lander imide **2** was finally obtained from half lander imide **11** by using the oxidative cyclodehydrogenation method described above. Conversion was not quantitative and difficult purification by column chromatography was necessary to afford pure lander **2** as a blue solid. Compound **2** is only poorly soluble and degrades in chloroform.

Conclusions

In summary, we prepared two complementary molecular moulds for self-assembly on surfaces. Further work is now underway to use these moulds for the bottom-up fabrication of metallic wires on insulators

Experimental Section

General Methods: 1D and 2D ^1H and ^{13}C NMR spectra were recorded with a Bruker Avance-300 in solutions at 20 °C and internal standard {$CDCl_3$ at δ_H = 7.25 ppm, δ_C = 77.0 ppm, CD_2Cl_2 at δ_H = 5.30 ppm, δ_C = 53.8 ppm, [D6]DMSO at δ_H = 2.52 ppm and δ_C = 40.08 ppm}. Mass spectrometry was performed with a Nermag R10-R10 (DCI). Elemental analyses were done by the Service d'Analyse de l'ICSN (Paris). THF and ethyl ether were distilled from Na/benzophenone. Dichloromethane was distilled from calcium hydride. Other solvents and reagents were used as obtained in the best quality available. Microwave heating was carried out in closed vials with a CEM-Discover monomode microwave apparatus under the conditions (power, temperature, time) given here. After completion of the reaction, the vessel was cooled down rapidly to 60 °C.

2,5-Bis(4-bromophenyl)-3,4-bis(4-*tert*-butylphenyl)cyclopenta-2,4-dien-1-one (3): To a boiling solution of 1,2-bis(4-*tert*-butylphenyl)-ethane-1,2-dione (501 mg, 1.55 mmol) and 1,3-bis(4-bromophenyl)-acetone (572 mg, 1.55 mmol) in ethanol (5 mL) was added a solution of KOH (2 M, 0.5 mL) in water. The solution was heated at reflux for 3 h and then cooled to 0 °C. The suspension was filtered, and the precipitate was washed with cold ethanol and dried in vacuo to afford compound **3** (891 mg, 1.36 mmol, 88%) as a black powder. ^1H NMR (300 MHz, CD_2Cl_2): δ = 1.27 (s, 18 H, 6 × CH_3), 6.83 (d, J = 8.6 Hz, 4 H, Ar-H), 7.12 (d, J = 8.7 Hz, 4 H, Ar-H), 7.21 (d, J = 8.6 Hz, 4 H, Ar-H), 7.39 (d, J = 8.7 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 30.9 (CH_3), 34.6 (C), 121.5 (C), 124.0 (C), 124.9 (CH), 128.9 (CH), 129.7 (C), 130.2 (C), 131.1 (CH), 131.7 (CH), 152.3 (C), 155.5 (C), 199.6 (C) ppm. MS (DC/NH_3): m/z (%) = 655 (100) $[M + H]^+$, 672 $[M + NH_4]^+$. $C_{37}H_{34}Br_2O$ (654.47): calcd. C 67.90, H 5.24; found C 67.02, H, 4.89.

1,4-Bis(4-bromophenyl)-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene (5): A mixture of compound **3** (800 mg, 1.22 mmol) and bis(*tert*-butylphenyl)acetylene **4** (354 mg, 1.22 mmol) in diphenyl ether (6 g) was subjected to microwave irradiation (300 W) for 45 min at 250 °C. After cooling, the solution was diluted with CH_2Cl_2 (25 mL) and poured into methanol (100 mL). The suspension was filtered, and the precipitate was washed with methanol and vacuum dried to afford compound **5** (731 mg, 65%) as a white solid. It can be further purified by column chromatography (hexane/CH_2Cl_2, 3:2). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 36 H, 12 × CH_3), 6.63 (d, J = 8.4 Hz, 8 H, Ar-H), 6.70 (d, J = 8.4 Hz, 4 H, Ar-H), 6.84 (d, J = 8.4 Hz, 8 H, Ar-H), 6.96 (d, J = 8.4 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 31.2 (CH$_3$), 34.1 (C), 119.2 (C), 123.4 (CH), 129.6 (CH), 130.9 (CH), 133.1 (CH), 137.2 (C), 139.0 (C), 139.9 (C), 140.5 (C), 147.9 (C) ppm. MS (DC/NH$_3$): *m/z* (%) = 935 (100) [M + NH$_4$]$^+$. $C_{58}H_{60}Br_2$ (916.90): calcd. C 75.98, H 6.60; found C 76.1, H 6.34.

1,4-Bis(4-cyanophenyl)-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene (6): A mixture of compound **5** (450 mg, 0.49 mmol) and CuCN (120 mg, 1.35 mmol) in NMP (6 mL) was subjected to microwave irradiation (300 W) for 15 min at 220 °C. After irradiation, the mixture was cooled to room temperature and poured into ice water. The precipitate was filtered and washed successively with aqueous ammonia and water. The crude product was taken up in chloroform and filtered through Celite. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (cyclohexane/CHCl$_3$, 1:1) to afford compound **6** (220 mg, 55%) as a white solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.11 (s, 36 H, 12 × CH$_3$), 6.61 (d, *J* = 8.45 Hz, 8 H, Ar-H), 6.84 (d, *J* = 8.45 Hz, 8 H, Ar-H), 6.94 (d, *J* = 8.5 Hz, 4 H, Ar-H), 7.15 (d, *J* = 8.5 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 31.1 (CH$_3$), 34.1 (C), 108.8 (C), 119.3 (C), 123.6 (CH), 130.4 (CH), 130.8 (CH), 132.1 (CH), 136.4 (C), 139.1 (C), 140.4 (C), 146.2 (C), 148.6 (C) ppm. MS (DC/NH$_3$): *m/z* (%) = 827 (100) [M + NH$_4$]$^+$. $C_{60}H_{60}N_2$ (809.13): calcd. C 89.06, H 7.47, N 3.46; found C 89.36, H 7.59, N 3.05.

1,4-Bis[4-(3,5-diamino-2,4,6-triazine)phenyl]-2,3,5,6-tetrakis(4-*tert*-butylphenyl)benzene (1): A mixture of compound **8** (84 mg, 0.104 mmol), dicyandiamide (108 mg, 1.28 mmol) and powdered KOH (25 mg, 0.45 mmol) in 2-methoxyethanol (2.5 mL) was subjected to microwave irradiation (300 W) for 15 min at 225 °C. After cooling, dicyandiamide (112 mg, 1.34 mmol) and powdered KOH (23 mg, 0.40 mmol) were added and irradiation was continued for 15 min at 225 °C. The resulting mixture was cooled, diluted with boiling water (30 mL) and filtered. The solid was extracted thoroughly with hot water, washed with chloroform and dried in vacuo to afford compound **1** (63 mg, 62%) as a white solid. It can be further purified by crystallization from acetic acid. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.03 (s, 36 H, 12 × CH$_3$), 6.56 (s, 8 H, NH$_2$), 6.71 (d, *J* = 4.8 Hz, 8 H, Ar-H), 6.81 (d, *J* = 4.8 Hz, 8 H, Ar-H), 6.99 (d, *J* = 5.1 Hz, 4 H, Ar-H), 7.72 (d, *J* = 5.1 Hz, 4 H, Ar-H) ppm. ^{13}C NMR data not recorded for solubility reasons. MS (DC/NH$_3$): *m/z* (%) = 978 (100) [M + H]$^+$. $C_{64}H_{68}N_{10}$ (977.29): calcd. C 78.65, H 7.01, N 14.33; found C 78.45, H 7.11, N 14.53.

Half Lander Dicarboxylic Anhydride (9): A mixture of cyclopentadienone **7** (154 mg, 0.265 mmol) and dicarboxylic anhydride **8** (57 mg, 0.256 mmol) in *o*-xylene (2 mL) was subjected to microwave irradiation (300 W) for 40 min at 210 °C. The resulting mixture was cooled, diluted with dichloromethane (30 mL) and concentrated in vacuo. The residue was purified by column chromatography (dichloromethane/petroleum ether, 7:3) to afford anhydride **9** (103 mg, 52%) as an orange solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.43 (s, 36 H, 12 × CH$_3$), 6.78 (d, *J* = 7.48 Hz, 2 H, Ar-H), 6.89 (d, *J* = 7.1 Hz, 2 H, Ar-H), 7.39 (dd, 2 H, Ar-H), 7.52 (d, *J* = 1.8 Hz, 4 H, Ar-H), 7.74 (t, *J* = 1.8 Hz, 2 H, Ar-H), 7.81 (d, *J* = 8.1 Hz, 2 H, Ar-H), 8.22 (d, *J* = 7.48 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 31.5 (CH$_3$), 35.3 (C), 117.3 (C), 121.9 (CH), 123.0 (CH), 123.5 (CH), 124.3 (CH), 127.0 (C), 127.4 (CH), 127.9 (CH), 129.6 (C), 132.3 (C), 133.2 (C), 134.3 (CH), 135.7 (C), 136.6 (C), 137.2 (2 C), 139.3 (C), 144.2 (C), 152.5 (C), 160.3 (C) ppm. MS (DC/NH$_3$): *m/z* (%) = 791 (100) [M + NH$_4$]$^+$. $C_{56}H_{52}O_3$ (773.01): calcd. C 87.01, H 6.78; found C 87.36, H 7.01.

Lander Dicarboxylic Anhydride (10): To a degassed solution of anhydride **9** (104 mg, 0.134 mmol) in dry dichloromethane (8 mL) was added iron(III) chloride (120 mg, 0.740 mmol). The violet mixture was stirred for 1.5 h at room temperature under a slow flow of argon. Another aliquot of FeCl$_3$ (120 mg, 0.740 mmol) was added. After stirring for 2 h, more FeCl$_3$ (165 mg, 1.020 mmol) was finally added and stirring was continued overnight at room temperature (solution became blue). Methanol (20 mL) was added to quench the reaction. After filtration under vacuum, the blue solid was thoroughly washed with methanol and hot ethanol. The blue solid was then dissolved in chloroform and precipitated in pentane. After filtration, lander **10** (99 mg, 95%) was obtained as a blue solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.42 (s, 72 H, 24 × CH$_3$), 6.76 (d, *J* = 4.7 Hz, 4 H, Ar-H), 6.80 (d, *J* = 4.7 Hz, 4 H, Ar-H), 7.51 (s, 8 H, Ar-H), 7.74 (s, 4 H, Ar-H), 7.93 (d, *J* = 5.1 Hz, 4 H, Ar-H), 8.21 (d, *J* = 4.5 Hz, 4 H, Ar-H) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 31.6, 35.3, 117.0, 122.0, 122.5, 122.9, 122.9, 123.5, 125.1, 127.0, 131.0, 132.3, 134.3, 134.6, 136.3, 137.0, 137.2, 137.5, 139.2, 144.0, 152.5, 160.3 ppm. MS (DC/NH$_3$): *m/z* (%) = 1543 (100) [M + H]$^+$. $C_{112}H_{100}O_6$ (1542.04): calcd. C 87.24, H 6.54; found C 86.81, H 6.34.

Half Lander Dicarboxylic Imide (11): A suspension of compound **9** (200 mg, 0.26 mmol) and urea (326 mg, 5.43 mmol) in dry DMF (4 mL) was heated at reflux under an atmosphere of argon for 20 h. After cooling to room temperature, the mixture was filtered and the resultant orange solid was washed with water and dried in vacuo to afford compound **11** (199 mg, quant.). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.43 (s, 36 H, 12 × CH$_3$), 6.74 (d, *J* = 7.5 Hz, 2 H, Ar-H), 6.88 (d, *J* = 7.1 Hz, 2 H, Ar-H), 7.37 (dd, 2 H, Ar-H), 7.53 (d, *J* = 1.8 Hz, 4 H, Ar-H), 7.73 (t, *J* = 1.8 Hz, 2 H, Ar-H), 7.78 (d, *J* = 8.2 Hz, 2 H, Ar-H), 8.15 (d, *J* = 7.5 Hz, 2 H, Ar-H), 8.25 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 31.5 (CH$_3$), 35.3 (C), 121.1 (C), 121.7 (CH), 123.1 (CH), 123.2 (CH), 124.1 (CH), 126.3 (C), 127.2 (CH), 127.8 (CH), 129.6 (C), 131.8 (CH), 132.7 (C), 133.2 (C), 135.9 (C), 136.8 (C), 136.9 (C), 137.4 (C), 138.9 (C), 143.4 (C), 152.4 (C), 163.8 (C) ppm. MS (DC/NH$_3$): *m/z* (%) = 772 (100) [M + H]$^+$. $C_{56}H_{53}NO_2$ (771.41): calcd. C 87.12, H 6.92, H 1.81; found C 86.52, H 6.39.

Lander Dicarboxylic Imide (2): To a degassed solution of half lander imide **11** (86 mg, 0.111 mmol) in dry dichloromethane (11 mL) was added iron(III) chloride (100 mg, 0.620 mmol). The violet mixture was stirred for 1 h at room temperature under a slow flow of argon. Another aliquot of FeCl$_3$ (120 mg, 0.740 mmol) was added. After stirring for 2 h, more FeCl$_3$ (150 mg, 0.925 mmol) was finally added and stirring was continued overnight at room temperature (solution became blue). Methanol (20 mL) was added to quench the reaction. After filtration under vacuum, the blue solid was thoroughly washed with methanol and hot ethanol. The blue solid was then purified by column chromatography (CHCl$_3$/MeOH, 9.7:0.3); the product was then dissolved in a minimum volume of chloroform and precipitated by the addition of methanol or pentane. Yield: 18%. The product is only poorly soluble in chloroform and degrades in solution. ^{1}H NMR (300 MHz, CDCl$_3$) (low solubility, broad peaks, unstable in CDCl$_3$): δ = 1.43 (s, 72 H, 24 × CH$_3$), 6.76 (d, *J* = 9 Hz, 4 H, Ar-H), 7.52 (s, 8 H, Ar-H), 7.73 (s, 4 H, Ar-H), 7.92 (d, *J* = 7 Hz, 4 H, Ar-H), 8.08–8.16 (m, 8 H, Ar-H) ppm; main impurities at saturation: residual solvent. ^{13}C NMR not recorded for solubility and stability reasons. $C_{112}H_{102}N_2O_4$ (1540.07): calcd. C 87.35, H 6.68, N 1.82; found C 87.01, H 7.34, N 1.67.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra for new compounds **1**–**3**, **5**, **6**, **9**–**11**. Synthesis and characterization data of compound **8**.

Acknowledgments

S. Nagarajan and C. Barthes are gratefully acknowledged for technical help in some parts of the syntheses. Partial support by the European Commission (project PicoInside, contract no. IST-015847) is gratefully acknowledged.

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Received: September 30, 2008
Published Online: January 14, 2009