Synthesis of Perfluoroalkylated Bulky Triarylamines

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Abstract: The synthesis of two new triarylamine compounds bearing perfluoroalkylated side chains is described. Good thermal stabilities combined with a blue emission make these compounds promising candidates for materials applications.

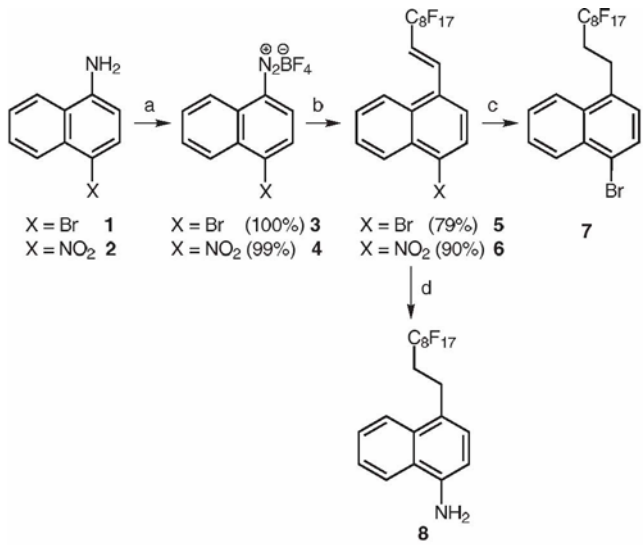
Key words: triarylamines, perfluoroalkylation, cross-coupling, blue emission, amorphous materials

Triarylamines have found wide application in devices that require properties like the generation, the transport, and the recombination of cationic or anionic charges such as organic light emitting diodes (OLED),[1,2] photorefractive systems (PR),[3] and solar cells,[4] besides their use in electrophotographic devices like photocopiers and laser printe r ~These widespread applications are due to the low oxidation potential of the nitrogen atom which, upon hole injection, generates a stable triarylamine radical cation necessary for the hoping mechanism.[6] The difficulty, however, resides in the deposition of a monocrystalline thin film to avoid the formation of defects and grain boundaries that act as traps for the charge carriers. As an alternative approach, the deposition of an amorphous thin film is used. Moreover, the major limitation of arylarnines in these applications is their short lifetime because of the significant degradation caused by impurities and fatigue due to morphological changes during the device operation. Therefore, a high thermal stability, and the ability to form an amorphous phase are the two main properties necessary for the employment of a triarylamine product for such devices?

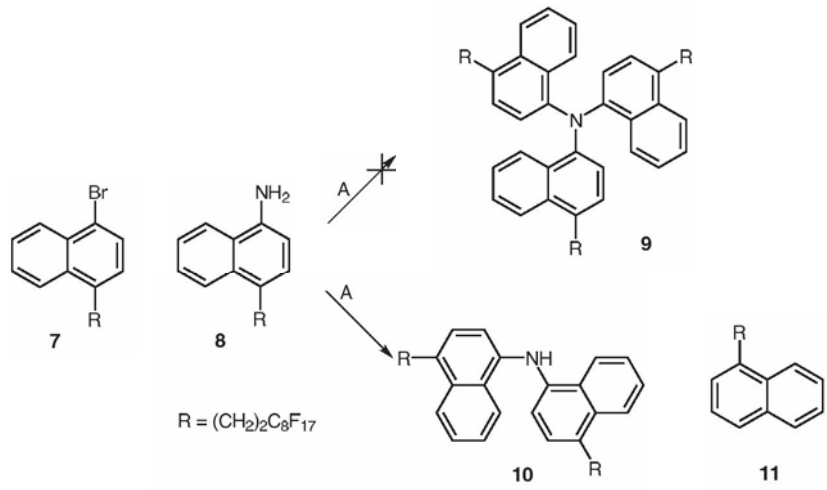
N,*N*′-Diphenyl-*N*,*N*′-(*m*-tolyl)benzidine (TPD) has been first reported[S] as an efficient hole transporting material for electroluminescent (EL) devices, due to its ability to form an amorphous phase. Since then, various papers have been published on the synthesis of new nitrogen-containing aryl products ranging from low molecular weight molecules? to starbust assemblies,[10,11] oligomers,[12] dendrimers[13] as well as polymers.[14] We wish to report herein a new strategy to achieve amorphous phases, simply by the addition of peripheral perfluorinated chains to relatively small N-containing aryl products. The perfluorinated chains are generally known to weaken the van der Waals interactions leading to reduction of the lateral intermolecular aggregation and, consequently, to a macroscopic amorphism.[15] Additionally, the inert behavior of the perfluorinated chains in terms of chemical reactivity bestows the molecule with a better thermal stability.

The perfluoroalkylated starting materials 7 and **8** were synthesized by applying the most convenient Heck cross-coupling reaction conditions:[16] the naphthylamine derivatives **1** and 2 were first transformed into their respective arenediazoniurn salts[1'] in quantitative yield. These stable and isolable tetrafluoroborate salts were reacted in a subsequent step with an appropriate commercially available perfluoroalkene, in the presence of a catalytical amount of palladium(II) acetate under ligandless conditions, affording the fluorinated alkene compounds 5 and **6** in 79 and 90% yields, respectively, after short reaction times. The hydrogenation of the brominated naphthalene derivative 5 was achieved by Rh/C catalyst, under 50 bar pressure of hydrogen, affording the perfluoroalkylated naphthalene 7 in 91% yield. On the other hand, the nitronaphthylated alkene **6** was hydrogenated in presence of a Pd/C catalyst reducing both the nitro and the olefin groups, yielding the desired product **8** in 94% yield (Scheme 1).

The reaction between the naphthylamine moiety **8** with two-fold excess of the brominated naphthalene 7 employing the palladium-catalyzed amination reaction under the



Scheme 1 Synthesis of the perfluoroalkylated naphthalene building blocks 7 and **8.** ***Reagents*** *and* conditions: a) $BF_3{\cdot}OEt_2$, *t*-$BuNO_2$, DME; b) 1*H*,1*H*,2*H*-perfluorodecene, $Pd(OAc)_2$, MeOH, 40 °C c) Rh/C, 50 bar H_2, CH_2Cl_2, r.t., 1 d, 91%; d) Pd/C, 3 bar H_2, MeOH–THF, r.t., 1 d, 94%.



Scheme 2 Attempted synthesis of the perfluoroalkylated trinaphthylamine **9** via the one pot Pd-catalyzed amination reaction. *Reagents and conditions:* $Pd(OAc)_2$, *t*-Bu_3P, *t*-BuONa, toluene, reflux.

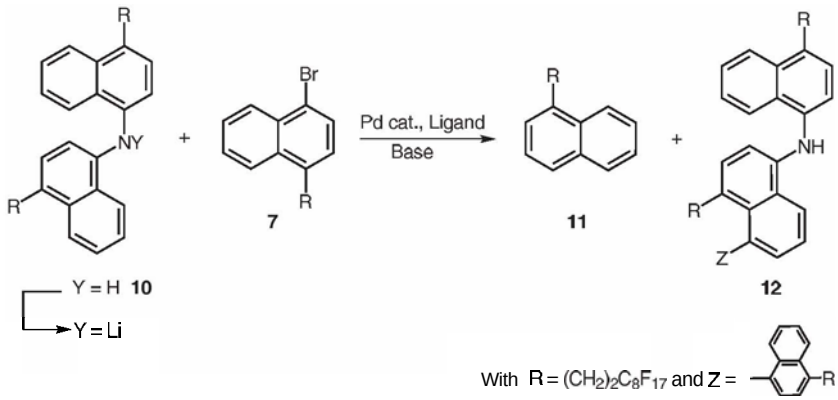
mild Buchwald–Hartwig conditions[18] (Scheme 2) only yields the perfluoroalkylated binaphthylarnine **10.** Increasing the reaction time resulted in the formation of trace amount of the debrominated species **11** along with the binaphthylamine derivative **10.** No trace of the perfluoroalkylated trinaphthylamine derivative **9** was found despite corresponding claims in the patent literature.[19,20]

Thus, the cross-coupling reaction between an equimolar mixture of 7 and **8** yields the building block **10** in 71% yield. The palladium-catalyzed amination reaction between **10** and the perfluoroalkylated bromonaphthalene 7 using several bases like, sodium *tert*-butoxide, cesium carbonate, and sodium hydroxide does not lead to the formation of any product at room temperature, while it affords a mixture of the debrominated naphthalene **11** and the naphthalene–naphthalene homocoupling product **12** when the reaction mixture was heated at reflux (Scheme **3).** When performing the more reactive lithiated derivative of **10** by exchange of the acidic proton by reaction with *n*-BuLi, the subsequent reaction with 7 under suitable conditions[13,21,22] yields exclusively the debrominated perfluoroalkylated naphthalene **11.**

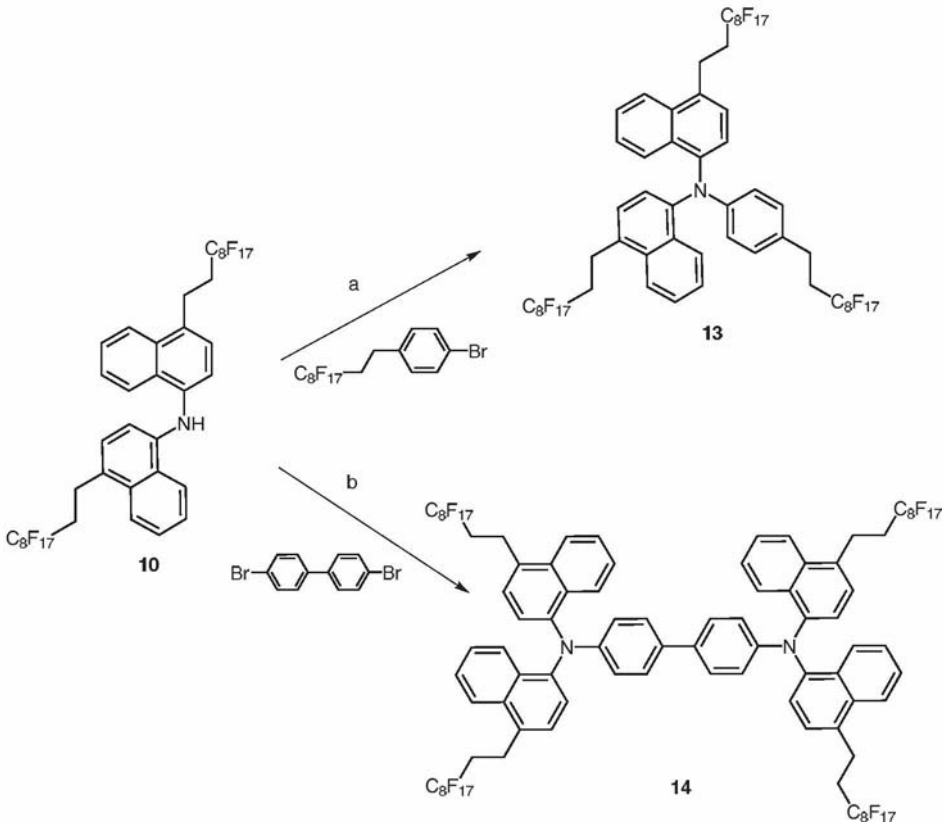
We believe that steric hindrance caused by the two bulky naphthalene groups prevents the third perfluoroalkylated naphthyl species to bind to the nitrogen atom and, hence, leads to attack at the non-activated carbon-5 position. Only few patents describe the synthesis of the parent trinaphthylamine **9** (R = H)[19,20] characterized by elemental analysis and mass spectrometry, methods which do not allow for distinction between **9** and **12.**

Applying the Buchwald–Hartwig conditions, the binaphthylarnine derivative **10** and either the perfluoroalkylated bromobenzene or 4,4′-dibromobiphenyl, affords the desired triarylamine derivatives **13** and **14** in 64 and 57% yield, respectively (Scheme 4).

Both products are isolated as colorless solids showing relatively good solubility in common organic solvents. The W-vis spectra of 10^{-3} M solutions of **13** and **14** in THF reveal the presence of two absorption bands for each compound: The former at 267 and 349 nm whereas the latter has the maxima at 301 and 367 nm. Measuring the fluorescence of both compounds at the same concentration (10^{-3} M in THF) reveals their blue emission nature: the excitation of **13** at 349 nm yields an emission peak at 430



Scheme 3 Attempted synthesis of the perfluoroalkylated trinaphthylamine **9** using the binaphthylamine (or amide) as a starting material.



Scheme 4 Synthesis of the perfluoroalkylated arylamine derivatives **13** and **14.** Reagents and conditions: $Pd(OAc)_2$, *t*-Bu_3P, *t*-BuONa, toluene, reflux: a) 3.5 d, 64%; b) 7 *d,* 57%.

nm, whereas the fluorescence spectrum of **14** shows an emission peak at 455 nm upon irradiating the solution at 367 nm (Figure 1).

Interestingly, the perfluoroalkylated triarylamine **13,** isolated from synthesis as a transparent, amorphous waxy solid, was found to produce fibers even at room temperature. The investigation of such a fiber drawn at room temperature, under a polarized optical microscope, reveals a long homogeneous structure showing aligned features (Figure 2), a behavior which is normally observed for polymer melts. We therefore conclude that **13** aggregates in one dimension to a supramolecule, thereby mimicking a much larger species.

The preliminary differential scanning calorimetry (DSC) investigation of the thermal properties of **13** and **14** reveal very puzzling properties: product **13** remains glassy down to –20 °C and does not melt even at high temperature (–450 °C), while the triarylamine derivative, **14** exhibits a melting point at a relatively high temperature (242 °C).

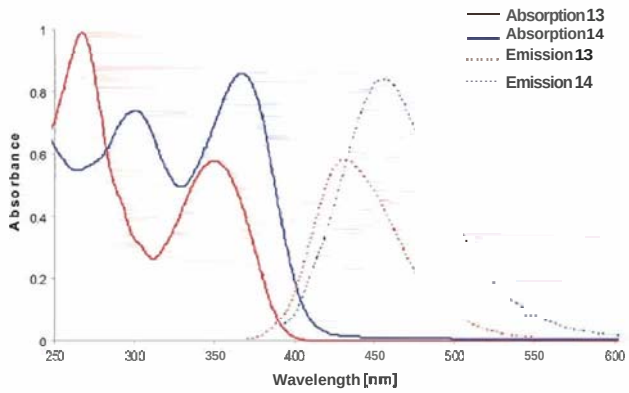


Figure 1 UV-vis spectra of **13** (red) and **14** (blue). Normalized emission spectra of **13** (dotted red) and **14** (dotted blue) in THF.

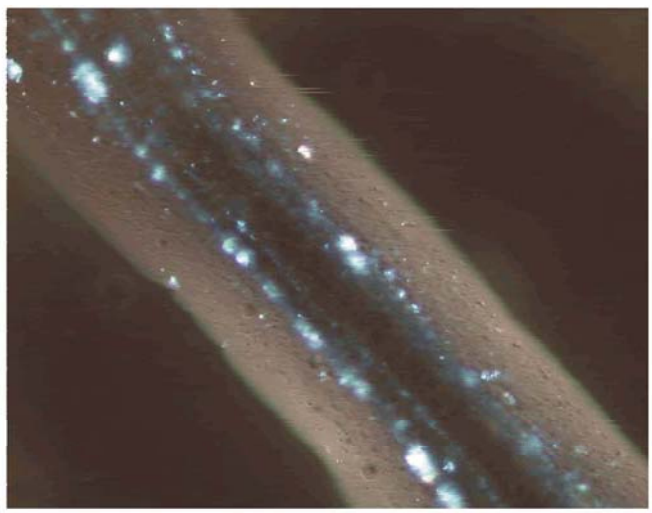


Figure 2 POM micrograph (x 100) of a fiber of **13** drawn at room temperature.

Finally, significant thermal stability was also observed since both products were heated several times up to 450 °C without causing any degradation.

In conclusion, new triarylamine compounds bearing perfluoroalkylated side chains were synthesized in good yields. The amorphous nature of the products was introduced, by design, by the addition of peripheral perfluoroalkylated chains well known for their weak van der Waals interaction. These materials excel by their excellent thermal stability over a wide temperature range allowing them to be used for applications as blue-emissive materials.

NMR spectra were recorded with Bruker Avance DRX 500 and Bruker Avance DPX 360 spectrometers. Chemical shifts are referred to TMS as an internal standard. TLC analyses were done using aluminum sheets coated with silica gel 60 F_{254}. Column chromatography was carried out using Merck silica gel 60 (0.04–0.063, 230–400 mesh). Electron impact (EI) and electrospray ionization (ESI) mass spectra (MS) were recorded on a Vacuum Generators Micromass VG 70/70E spectrometer and on a FT/ICR mass spectrometer Bruker 4.7T BioApex II. Differential scanning calorimetry traces were recorded using a Mettler Toledo DSC822e, calibrated with indium (mp 156.6 °C, $\Delta H_f = 28.45$ KJ mol^{-1}) before each series of measurements. Polarization optical microscopy (POM) was carried out using an Axioscope Zeiss microscope; the photographs were taken with a Fujix Digital camera HC-300Z.

1-Bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)benzene was prepared according to literature[16] starting from 4-bromophenylamine. All the other chemical reagents were purchased from commercial sources. Solvents were dried by passing them under argon through a special purification system similar to the one proposed by Grubbs.[23] The solvents were saturated with argon for 15–30 min prior to use.

Diazotization; 4-Bromonaphthalene-1-diazoniumTetrafluoroborate (3); Typical Procedure

$BF_3{\cdot}OEt_2$ (2.5 mL, 19.5 mmol) was placed in a three-necked round-bottomed flask equipped with an addition funnel, a septum, and a reflux condenser. The temperature was lowered to –15 °C and a solution of 4-bromonaphthylamine **(1;** 3 g, 13 mmol) in DME (15 mL) was added dropwise first, followed by the addition of a solution of *t*-$BuNO_2$ (2.1 mL, 15.6 mmol) in DME (25 mL) at the same temperature during 15 min. After stirring the mixture at –15 °C for 20 min, the temperature was raised to 5 °C over aperiod of 20 min. Pentane (50 mL) was then added and the suspended compound was collected by suction filtration, washed with Et_2O (50 mL at 0 °C, and 50 mL at r.t.) yielding a green-bmwn solid (4.16 g, –100%).

4-Nitronaphthalene-1-diazoniumTetrafluoroborate (4)

Prepared following the diazotization reaction described above: 4-nitronaphthylamine (2; 2.52 g, 13 mmol), $BF_3{\cdot}OEt_2$ (2.5 mL, 19.5 mmol), *t*-$BuNO_2$ (2.1 mL, 15.6 mmol), and DME (65 mL); bright yellow solid (3.82 g, 99%).

Heck Cross-Coupling Reaction; 1-Bromo-4-[(1*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodec-1-enyl]naphthalene (5); Typical Procedure

To a stirred suspension of the diazonium salt **3** (0.32 g, 1 mmol) and $Pd(OAc)_2$ (11.2 mg, 50 ymol) in MeOH (3 mL), was added dropwise 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodec-1-ene (0.28 mL, 1 mmol) during 10–15 min. The mixture was then warmed to 40 °C and allowed to react for additional 90 min. After removal of the solvent, the resulting grey product was passed through a silica gel chromatographic column using a 4:1 mixture of CH_2Cl_2–pentane as eluent to afford 5 (0.52 g, 79%) as a white solid; $R_f = 0.73$ (hexane).

^{1}H NMR (360 MHz, CDCl,): 6 = 8.34–8.31 (br d, 1 H_{arom}), 8.04–8.02 (br d, 1 H_{arom}), 7.9–7.95 (br d, 1 H, C*H*=CHC$_8$F$_{17}$), 7.80–7.82 (d, 1 H_{arom}), 7.62–7.68 (m, 2 H_{arom}), 7.47–7.49 (d, 1 H_{arom}), 6.22–6.33 (q, 1 H, CH=C*H*C$_8$F$_{17}$).

1-[(1*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodec-1-enyl]-4-nitronaphthalene (6)

Prepared following the diazotization reaction described above: **4** (1.7 g, 5.9 mmol), $Pd(OAc)_2$ (66.5 mg, 0.3 mmol), 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodec-1-ene (1.56 mL, 5.9 mmol), and MeOH (20 mL); time: 3 h; yellow solid (3.27 g, 90%); $R_f = 0.61$ (4:1 pentane–CH_2Cl_2).

^{1}H NMR (360 MHz, CDCl,): 6 = 8.58–8.55 (d, J = 8.17 Hz, 1 H_{arom}), 8.18–8.2 (d, *J* = 8.17 Hz, 1 H_{arom}), 8.1–8.13 (d, *J* = 8.17 Hz, 1 H_{arom}), 7.95–7.99 (br d, 1 H, C*H*=CHC$_8$F$_{17}$), 7.72–7.81 (m, 2 H_{arom}), 7.67–7.69 (d, 1 H_{arom}) 6.3–6.41 (q, *J* = 8.17 Hz, 1 H, CH=C*H*C$_8$F$_{17}$).

1-Bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)naphthalene (7)

A solution of **5** (4.43 g, 6.7 mmol) and Rh/C (0.28 g, 0.13 mmol) in degassed CH_2Cl_2 (35 mL) was placed under 50 bar H_2 and the mixture was stirred at r.t. for 24 h. The solvent was evaporated and the residual black solid was then purified by chromatographicfiltration over a silica gel column using CH_2Cl_2 as eluent to afford **7** (4 g, 91%); $R_f = 0.62$ (pentane).

^{1}H NMR (360 MHz, CDCl,): 6 = 8.31–8.34 (m, 1 H_{arom}), 7.94–7.98 (m, 1 H_{arom}), 7.72–7.74 (d, *J* = 7.27 Hz, 1 H_{arom}), 7.61–7.66 (m, 2 H_{arom}) 7.22–7.24 (d, *J* = 7.70 Hz, 1 H_{arom}), 3.34–3.38 (m, 2 H, C*H*$_2$CH$_2$C$_8$F$_{17}$), 2.4–2.55 (m, 2 H, CH$_2$C*H*$_2$C$_8$F$_{17}$).

^{13}C NMR (90.55 MHz, CDCl,): 6 = 135.2 (arom), 132.62 (arom), 132.35 (arom), 129.71 (arom), 128.4 (arom), 127.38 (arom), 127.3 (arom), 126.75 (arom), 123.33 (arom), 122.26 (arom), 31.87–32.36 (m, CH$_2$*C*H$_2$C$_8$F$_{17}$), 23.5–23.6 (m, *C*H$_2$CH$_2$C$_8$F$_{17}$).

4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl)-1-naphthylamine (8)

A solution of **6** (0.93 g, 1.5 mmol) and Pd/C (0.08 g, 75 ymol, 10% Pd) in degassed THF–MeOH (I:I, 15 mL) was placed under 3 bar of H_2 and the mixture was stirred at r.t. for 24 h. The solvent was evaporated and the residual black solid was then purified by chromatographic filtration over a silica gel column with pentane–CH_2Cl_2 (2:1) as eluent (0.83 g, 94%); $R_f = 0.21$ (2:1 pentane–CH_2Cl_2).

^{1}H NMR (360 MHz, C_6D_6): 6 = 7.74–7.76 (d, *J* = 8.17 Hz, 1 H_{arom}), 7.49–7.51 (d, *J* = 8.17 Hz, 1 H_{arom}), 7.2–7.35 (m, 2 H_{arom}), 6.81–6.83 (d, *J* = 7.74 Hz, 1 H_{arom}), 6.29–6.31 (d, *J* = 7.74 Hz, 1 H_{arom}), 3.3 (br s, 2 H, NH), 3.06–3.1 (m, 2 H, C*H*$_2$CH$_2$C$_8$F$_{17}$), 2.12–2.24 (m, 2 H, CH$_2$C*H*$_2$C$_8$F$_{17}$).

Palladium-Catalyzed Amination Reaction; *N*,*N*-Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-1-naphthyl]amine (10); Typical Procedure

A Schlenk flask was charged with **7** (5.54 g, 8.48 mmol), **8** (5 g, 8.48 mmol), $Pd(OAc)_2$ (190 mg, 0.82 mmol), *t*-Bu_3P (0.7 g, 3.5 mmol), *t*-BuONa (1.23 g, 12.8 mmol), and toluene (150 mL). The reaction was refluxed for 2 d under argon. The dark brown solution was diluted with aq sat. NH_4Cl (30 mL) and extracted with Et_2O (3 × 25 mL). The combined organic layers were washed with H_2O (3 × 25 mL), dried (K_2CO_3), and filtered. Removal of the solvent yielded a brown product which was chromatographed using a mixture of pentane–CH_2Cl_2 (9:1) to afford 9 (7 g, 71%) as a faint yellow product; $R_f = 0.41$ (9:1 pentane–CH_2Cl_2).

^{1}H NMR (360 MHz, C_6D_6): δ = 7.94–7.96 (d, J = 9.05 Hz, 2 H_{arom}), 7.81–7.83 (d, J = 8.35 Hz, 2 H_{arom}), 7.23–7.34 (m, 4 H_{arom}), 6.80–6.82 (d, J = 7.70 Hz, 2 H_{arom}), 6.75–6.77 (d, J = 7.70 Hz, 2 H_{arom}), 5.8 (br s, 1 H, NH), 3.09–3.13 (m, 4 H, $CH_2CH_2C_8F_{17}$), 2.19–2.24 (m, 4 H, $CH_2CH_2C_8F_{17}$).

^{13}C NMR (90.55 MHz, C_6D_6): δ = 140.3 (arom), 132.73 (arom), 131.91 (arom), 128.15 (arom), 126.82 (arom), 126.8 (arom), 125.66 (arom), 123.71 (arom), 123.31 (arom), 115.73 (arom), 31.4 (m, $CH_2CH_2C_8F_{17}$), 23.34 (m, $CH_2CH_2C_8F_{17}$).

ESI-MS (HCO_2H–THF): m/z (%) = 1206 ([M + CO_2] +35), 1162 ([M + H]$^+$, 100), 288 (22).

1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluorodecyl)naphthalene (11)
R_f = 0.66 (9:1 hexane).

^{1}H NMR (500 MHz, C_6D_6): δ = 7.72–7.74 (m, 1 H_{arom}), 7.64–7.66 (m, 1 H_{arom}), 7.54–7.56 (br d, 1 H_{arom}), 7.24–7.28 (m, 2 H_{arom}), 7.14–7.17 (br d, 1 H_{arom}), 6.87–6.89 (br d, 1 H_{arom}), 3.06–3.1 (m, 2 H, $CH_2CH_2C_8F_{17}$), 2.09–2.2 (m, 2 H, $CH_2CH_2C_8F_{17}$).

^{13}C NMR (125.77 MHz, C_6D_6): δ = 135.09 (arom), 134.46 (arom), 131.85 (arom), 129.33 (arom), 128.29 (arom), 126.64 (arom), 126.44 (arom), 125.98 (arom), 125.75 (arom), 123.04 (arom), 111.06–120.80 (m, CF_2), 31.9–31.3 (m, $CH_2CH_2C_8F_{17}$), 23.58.

***N*-[4′,8-Bis(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-1,1′-binaphthalen-4-yl]-*N*-[4-(3,3,4,4,5,5, 6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-1-naphthyl]amine** (12)
The reaction was carried out following the Pd-catalyzed amination reaction: 10 (116 mg, 0.1 mmol), 7 (66 mg, 0.1 mmol), $Pd(OAc)_2$ (1.12 mg, 5 μmol), t-Bu_3P (4 mg, 20 μmol), Cs_2CO_3 (100 mg, 0.3 mmol), and degassed xylene (10 mL); yield: 27 mg (16%).

^{1}H NMR (500 MHz, C_6D_6): δ = 8.23–8.25 (m, 1 H_{arom}), 7.92–7.94 (d, 1 H_{arom}), 7.88–7.9 (m, 1 H_{arom}), 7.72 (br s, 1 H_{arom}), 7.62–7.63 (d, 1 H_{arom}), 7.52 (br s, 1 H_{arom}), 7.31–7.36 (overlapped peaks, 3 H_{arom}), 7.2–7.25 (m, 4 H_{arom}), 6.98–7.01 (br t, 1 H_{arom}), 6.63 (br s, 2 H_{arom}), 6.48–6.49 (d, 1 H_{arom}), 5.96 (s, 1 H, NH), 3.19–3.3 (m, 2 H, $CH_2CH_2C_8F_{17}$), 2.89–3.02 (m, 4 H, $CH_2CH_2C_8F_{17}$), 2.31–2.39 (m, 2 H, $CH_2CH_2C_8F_{17}$), 1.94–2.07 (m, 4 H, $CH_2CH_2C_8F_{17}$).

EI-MS: m/z (%) = 1733 (M +70), 1714 ([M – F]$^{+\cdot}$, 8), 1300 ([M – $CH_2(R_f)_8$]$^{+\cdot}$, 100), 156 (60).

***N*,*N*-Bis[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-1-naphthyl]-*N*-[4-(3,3,4,4,5,5,6,6,7,7,8,8, 9,9,10,10-heptadecafluorodecyl)phenyl]amine** (13)
Prepared following the amination reaction described as above: 9 (116 mg, 0.1 mmol), 1-bromo-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)benzene (60 mg, 0.1 mmol), $Pd(OAc)_2$ (1.12 mg, 5 μmol), t-Bu_3P (4 mg, 20 μmol), t-BuONa (15 mg, 0.15 mmol), and toluene (5 mL); time: 3.5 d; glassy colorless solid; yield: 108 mg (64%); mp >450 °C; R_f = 0.65 (9:1 pentane–CH_2Cl_2).

^{1}H NMR (360 MHz, THF-d_8): δ = 8.26–8.28 (d, J = 8.17 Hz, 2 H_{arom}), 8.17–8.19 (d, J = 8.64 Hz, 2 H_{arom}), 7.63–7.68 (t, J = 7.7 Hz, 2 H_{arom}), 7.45–7.48 (m, 4 H_{arom} and C_6H_4), 7.25–7.27 (d, J = 7.7 Hz, 2 H, C_6H_5), 7.13–7.15 (d, J = 8.64 Hz, 2 H_{arom}), 6.73–6.76 (d, J = 8.17 Hz, 2 H_{arom}), 3.50–3.54 (br t, 4 H, $CH_2CH_2C_8F_{17}$), 2.92–2.96 (br t, 2 H, $CH_2CH_2C_8F_{17}$), 2.67–2.78 (m, 4 H, $CH_2CH_2C_8F_{17}$), 2.53–2.62 (m, 2 H, $CH_2CH_2C_8F_{17}$).

^{1}H NMR (360 MHz, C_6D_6): δ = 8.45–8.48 (d, J = 8.64 Hz, 2 H_{arom}), 7.73–7.76 (d, J = 8.17 Hz, 2 H_{arom}), 7.21–7.23 (d, 2 H_{arom}), 7.09–7.17 (m, 4 H_{arom}, and C_6H_5), 6.8–6.84 (t, 4 H_{arom}), 6.62–6.64 (d, J = 8.17 Hz, 2 H_{arom}), 3.05–3.09 (br t, 4 H, $CH_2CH_2C_8F_{17}$), 2.49–2.53 (br t, 2 H, $CH_2CH_2C_8F_{17}$), 2.08–2.23 (m, 4 H, $CH_2CH_2C_8F_{17}$), 1.83–1.98 (m, 2 H, $CH_2CH_2C_8F_{17}$).

^{13}C NMR (90.55 MHz, C_6D_6): δ = 133.92 (arom), 133.35 (arom), 131.45 (arom), 129.8 (arom), 127.28 (arom), 127.3 (arom), 127.13 (arom), 126.08 (arom), 125.27 (arom), 124.38 (arom), 33.3 (br s, $CH_2CH_2C_8F_{17}$), 32.51 (br s, $CH_2CH_2C_8F_{17}$), 23.95 (br s, $CH_2CH_2C_8F_{17}$).

ESI-MS (HCO_2H–THF): m/z (%) = 1732 ([M + HCO_2]$^+$, 55), 1683 (M$^{+\cdot}$, 100).

EI-MS: m/z (%) = 1683 (M$^{+\cdot}$, 100), 1664 ([M – F]$^{+\cdot}$, 40), 1250 ([M – $CH_2C_8F_{17}$]$^{+\cdot}$, 45), 789 (10).

***N*,*N*,*N*′,*N*′-Tetrakis[4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl)-1-naphthyl]-1,1′-biphenyl-4,4′-diamine** (14)
Prepared following the amination reaction described above; 9 (3.5 g, 3 mmol), 4,4′-dibromobiphenyl (0.46 g, 1.47 mmol), $Pd(OAc)_2$ (64 mg, 0.29 mmol), t-Bu_3P (71 mg, 0.35 mmol), t-BuONa (0.38 g, 3.95 mmol), and toluene (100 mL); time: 7 d. After washing the mixture with aq sat. NH_4Cl (25 mL) and aq 5% solution of KCN (10 mL), the organic phase was filtered and the faint brown precipitate was suspended in CH_2Cl_2, sonicated for 15–20 min and collected by suction filtration. The precipitate was purified by successive washings with CH_2Cl_2 and Et_2O affording **11** (2.07 g, 57%) as an off-white solid; mp 242 °C.

^{1}H NMR (360 MHz, THF-d_8): δ = 8.16–8.18 (d, J = 8.64 Hz, 4 H_{arom}), 8.05–8.07 (d, J = 8.6 Hz, 4 H_{arom}), 7.51–7.55 (t, J = 7.27 Hz, 4 H_{arom}), 7.34–7.37 (m, 8 H_{arom}), 7.29–7.31 (d, J = 8.17 Hz, 4 H, C_6H_4), 6.65–6.67 (d, J = 8.17 Hz, 4 H, C_6H_4), 2.56–2.68 (m, 8 H, $CH_2CH_2C_8F_{17}$).

ESI-MS (HCO_2H–THF): m/z (%) = 2473 (M$^{+\cdot}$, 100), 1957 (58), 686 (48).

EI-MS: m/z = 2473 (M +, 100%).

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