

Classical Benzotriazole-Mediated α -Aminoalkylations of Alkynes: Synthesis and Characterization of Alk-2-yn-1-amines as Amphiphilic Materials

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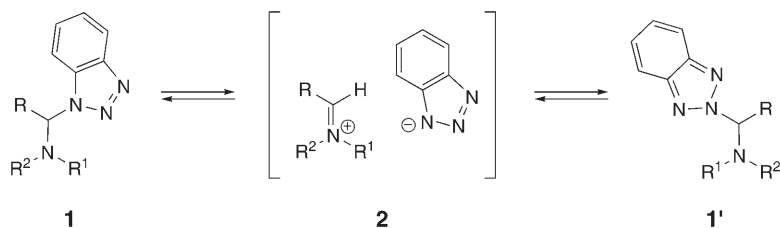
Reactions of readily available and stable benzotriazolemethanamines **1a–l**, obtained from aldehydes and secondary amines (*Scheme 2*), gave the expected alk-2-yn-1-amines **3a–t** (*Scheme 3*). The amphiphilic character of the synthesized products was responsible for physicochemical measurements. Specific aggregation properties of the obtained compounds make them useful as electroactive materials in the *Langmuir–Blodgett* technique.

Introduction. – The formation of C–C bonds is of fundamental importance in organic chemistry. The *Mannich* reaction is a prominent method for forming C–C bonds and provides a key step for the synthesis of numerous N-containing pharmaceuticals, natural products, polymers, dyes, and cross-linking agents [1–5]. However, the classical *Mannich* reaction is confined to aminomethylation and is frequently accompanied by deamination [6]. On the other hand, the use of preformed iminium salts has some basic advantages, *e.g.*, the reactions require milder conditions and allow the aminoalkylation of structurally diverse nucleophiles [7][8]. As the intermediates are frequently thermally unstable and hygroscopic and often undergo deprotonation with basic nucleophiles in preference to normal addition [1], novel advantageous aminoalkylating reagents are still highly desirable.

Benzotriazolemethanamines **1** have a high potential in organic synthesis [9][10]. The methine C-atom in **1** possesses a high degree of electrophilicity due to the existence of the equilibrium of both isomers **1** and **1'** with the iminium benzotriazolide ion pair **2** [11] (*Scheme 1*). Studies from *Katritzky's* group have successfully applied this concept in their reactions with suitable reagents to provide an easy access to secondary and tertiary amines [12–14].

The high synthetic potential of alkanamine derivatives is connected also with many electronic applications like photon funnels or energy-transfer controllers [15], the concentration of conducting units being essential as well as the knowledge of the *Langmuir–Blodgett* film architecture. We undertook the study of the formation of single and two-component *Langmuir* and *Langmuir–Blodgett* films of synthesized heterocyclic molecules. Particular attention was paid to the films containing alkylheteroaromatic compounds mixed with docosanoic acid (DA), tricos-22-enoic acid (TA),

Scheme 1



11-mercaptoundecanoic acid (MUA), and gramicidine A (GrA) which are amphiphilic molecules facilitating the deposition.

Since the *Langmuir–Blodgett* technique allows the controlled, layer-by-layer deposition of ordered molecular films on solid substrates, the films constructed by means of this method are expected to be components for potential applications in sensorics, photonics, or photoelectronics [16].

Results and Discussion. – *Synthesis of 1H-Benzotriazole-1-methanamines 1a–l.* Benzotriazoles (Bt) are precursors in the synthesis of complex organic compounds including classes which are difficult to prepare [17][18]. This fact motivated us to synthesize by this way compounds **1a–l** (Scheme 2). One of the basic procedures connected with the synthesis of alkanamine derivatives is the reaction in which a benzotriazole (Bt) derivative is used as intermediate. Thus, the 1H-benzotriazole-1-methanamines **1a–l** were easily synthesized by the well-established condensation of 1H-benzotriazole, an aliphatic aldehyde, and a secondary amine, either in CH₂Cl₂ in the presence of anhydrous MgSO₄ at room temperature (**1d–g,i,j,l**) [18] or, in the case of aromatic aldehydes, in toluene under *Dean–Stark* conditions (for **1a–c,h,k**) [18]. The reaction under *Dean–Stark* conditions catalyzed by *p*-toluenesulfonic acid (TsOH) resulted in much better yield.

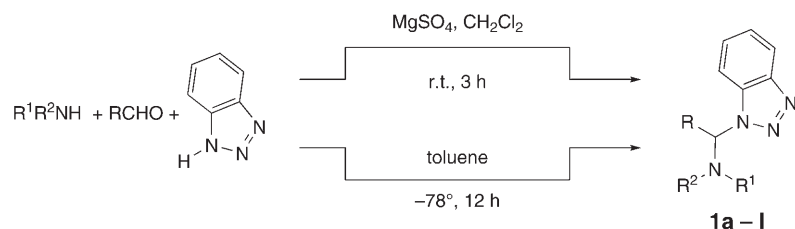
Synthesis of Alk-2-yn-1-amines. A group of alk-2-yn-1-amines **3** were obtained according to the standard procedure of lithiation of organic compounds [19] (Table, Scheme 3). The key step of this methodology was the deprotonation of the alkynes and formation of unstable lithio compounds, which at -78° in THF reacted with the 1H-benzotriazole-1-methanamines **1a–l** and finally gave alk-2-yn-1-amines **3a–t**. The reaction occurred with very good yield at -78° in THF with BuLi or lithium diisopropylamide (LDA), both bases giving similar results.

The ¹H- and ¹³C-NMR spectra and the elemental analyses of all synthesized compounds fully supported the structures.

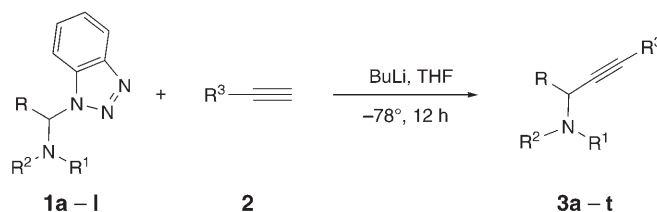
Biological interest of the prepared derivatives is connected with the potential inhibition character of **3a–t** as squalene-epoxidase inhibitors [20]. The amphiphilic character of the obtained compounds causes interest in aggregation and electroconductivity measurements.

Physicochemical Effects of Langmuir–Blodgett Films Build from Synthesized Materials. To obtain *Langmuir* films, the synthesized amphiphilic compounds 4-(1-phenylhept-2-yn-1-yl)morpholine (= MF 6; **3s**) and α -(oct-1-yn-1-yl)-*N,N*-bis(phenyl-

Scheme 2



1	R	NR ¹ R ²
a	4-MeC ₆ H ₄	morpholin-4-yl
b	4-ClC ₆ H ₄	morpholin-4-yl
c	naphthalen-1-yl	piperidin-1-yl
d	ⁱ Pr	morpholin-4-yl
e	ⁱ Pr	thiomorpholin-4-yl
f	ⁱ Pr	BN ₂ N
g	Me ₃ CCH ₂	morpholin-4-yl
h	Ph	BN ₂ N
i	Me ₃ CCH ₂	pyrrolidin-1-yl
j	Me ₃ CCH ₂	thiomorpholin-4-yl
k	Ph	morpholin-4-yl
l	ⁱ Pr	PhNMe

Scheme 3^a)

^a) For R¹, R², and R³, see Table.

methyl)benzenemethanamine FDF 8; **3t**) (Table) were dissolved in CHCl₃ (Aldrich; HPLC grade) and spread onto the H₂O surface of a Langmuir trough. Concentrations of solutions were maintained at ca. 1 mg/ml. All measurements were carried out according to our previous reports [19][21]. The films of desired composition were formed by dropwise spreading of the alkyamine derivative solution, with or without docosanoic acid (DA), tricos-22-enoic acid (TA), 11-mercaptoundecanoic acid (MUA), or gramicidine A (GrA), respectively, on high purity H₂O at 293 K. The binary systems were mixed to obtain molar compositions of the deposition mixture of 1:1, 1:2, and 10:1.

From the measured π -A isotherms of the synthesized derivatives MF 6 (**3s**) and FDF 8 (**3t**), it was clear that these unsymmetric structures form stable Langmuir and Langmuir-Blodgett films. The pressure-area isotherms for representative binary

Table. Synthesized Compounds **3**

	R	NR ¹ R ²	R ³	Yield [%]
3a	Me ₃ CCH ₂	N(CH ₂ CH ₂) ₂ O	Me(CH ₂) ₅	86
3b	4-MeC ₆ H ₄	N(CH ₂ CH ₂) ₂ O	Ph	89
3c	ⁱ Pr	N(CH ₂ CH ₂) ₂ O	Me(CH ₂) ₅	92
3d	ⁱ Pr	N(CH ₂ CH ₂) ₂ O	Ph	93
3e	Me ₃ CCH ₂	N(CH ₂ CH ₂) ₂ S	Me(CH ₂) ₅	95
3f	ⁱ Pr	Bn ₂ N	Me(CH ₂) ₅	90
3g	Me ₃ CCH ₂	N(CH ₂) ₄	4-MeC ₆ H ₄	92
3h	4-ClC ₆ H ₄	N(CH ₂ CH ₂) ₂ O	4-MeC ₆ H ₄	94
3i	Me ₃ CCH ₂	N(CH ₂ CH ₂) ₂ O	4-MeC ₆ H ₄	90
3j	Ph	Bn ₂ N	4-MeC ₆ H ₄	95
3k	Ph	Bn ₂ N	Bu	87
3l	4-ClC ₆ H ₄	N(CH ₂ CH ₂) ₂ O	Bu	88
3m	Me ₃ CCH ₂	N(CH ₂ CH ₂) ₂ S	Bu	94
3n	naphthalen-1-yl	N(CH ₂) ₅	Bu	83
3o	Ph	Bn ₂ N	Me(CH ₂) ₄	89
3p	naphthalen-1-yl	N(CH ₂) ₅	Me(CH ₂) ₄	87
3q	4-MeC ₆ H ₄	N(CH ₂ CH ₂) ₂ O	Me(CH ₂) ₄	98
3r	ⁱ Pr	PhNMe	Me(CH ₂) ₄	91
3s	Ph	N(CH ₂ CH ₂) ₂ O	Bu	97
3t	Ph	Bn ₂ N	Me(CH ₂) ₅	90

complexes of MF 6 (**3s**) and FDF 8 (**3t**) are shown on *Figs. 1* and *2*. The compression proceeds smoothly until the film collapses. Although pure MF 6 and FDF 8 form good *Langmuir* films, their *Langmuir-Blodgett* films are not stable because the transfer procedure occurs under a relatively low surface pressure.

Comparison of the π -*A* isotherms of *Figs. 1* and *2* shows also that when using binary films, it is possible to obtain much higher surface pressures and, therefore, closer

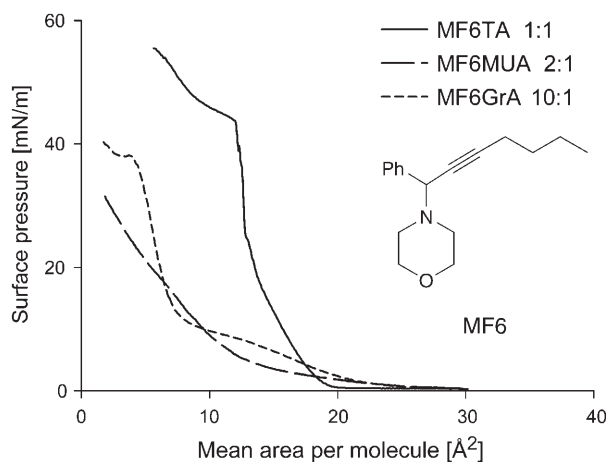


Fig. 1. π -*A* Isotherms of binary MF6 (**3s**) complexes with TA (tricos-22-enoic acid), MUA (11-mercaptoundecanoic acid), and GrA (gramicidine A)

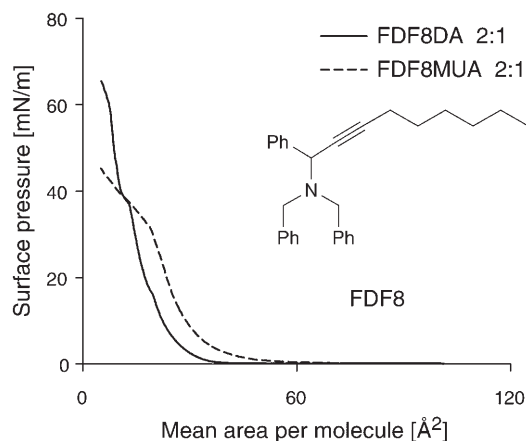


Fig. 2. π -A Isotherms of binary FDF8 (**3t**) complexes with DA (docosanoic acid) and MUA (11-mercaptoundecanoic acid)

packing, and MUA, TA, and gramicidine A facilitate this process in the most prosperous way. This is caused by an almost planar structure of the alkyamine moiety of the derivatives MF6 and FDF8, by the alkyl chain being almost vertical to the hydrophilic part of MF6 and FDF8, and by the very favorable properties of the used acids MUA or TA or of GrA which improve packing and *Langmuir-Blodgett*-film architecture. We observed also similar results (besides unfavorable results) with long-chain acids (tricos-22-enoic acid, docosanoic acid) as model amphiphile in the case of another, previously synthesized heterocyclic compound [19].

In Fig. 3, a computer-generated model of the MF6 (**3s**) molecule is presented (structure optimization in Gaussian03 at the AM1 theory level; the surface was generated by the Molekel 4.3 program under command fast surface [22]). If the average plane of all aromatic rings was laid almost flat on the water, the aliphatic chain would be elevated by nearly 90° . In our case, *i.e.*, of an amphiphilic (hydrophilic-hydrophobic) molecule, aromatic rings are the more hydrophilic part of it. In such an arrangement, the calculated area per molecule equals *ca.* 30 \AA^2 , which is also confirmed by the π -A isotherm (in the binary system).

Transfer of the *Langmuir* films of MF6 or FDF8 from the air/H₂O interface onto a substrate under a constant surface pressure of 10 mN/m allowed to achieve complete and good-quality *Langmuir-Blodgett* films, as confirmed by the UV/VIS spectrum of FDF8 (**3t**) on a quartz substrate (75 mm \times 19 mm \times 1.08 mm) (Fig. 4). The usefulness of the obtained films in electrical experiments was established by the stability of the deposited layers.

Conclusions. – We successfully synthesized a series of alkyamine derivatives by a typical, straightforward and convenient methodology starting from an aldehyde and an amine *via* a 1*H*-benzotriazole derivative. The obtained alkyamines could find applications, for example, in promising electro-active materials. The alkyamines **3s** and **3t**, mixed with substances facilitating film building, gave stable and good-quality

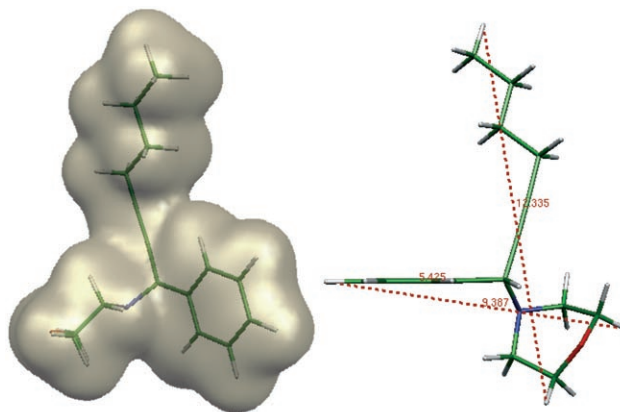
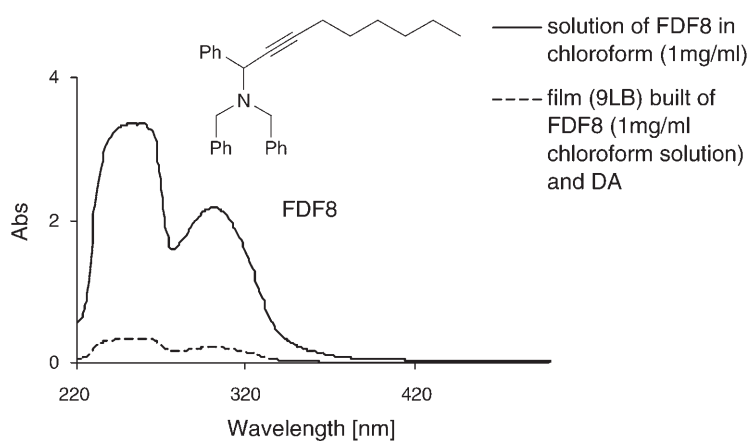


Fig. 3. Computer-generated models of MF6 (3s)

Fig. 4. UV/VIS Absorption spectra of a CHCl_3 solution and of a Langmuir–Blodgett film of FDF8 (3t)

Langmuir–Blodgett films. The electrical properties of a thin *Langmuir–Blodgett* film obtained with a synthesized alkyamine are in the course of evaluation.

We would like to thank Prof. Alan R. Katritzky from the Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, for valuable suggestions. This work was supported by a *Wrocław University of Technology Grant* (No. 332093).

Experimental Part

General. THF was used immediately after distillation from a soln. containing benzophenone/Na. Other starting materials, reagents, and solvents were used as received from suppliers. Column chromatography (CC): *Merck silica gel 60* (5386). M.p.: capillary melting point apparatus equipped with a digital thermometer. NMR Spectra: *Varian-VXR-300* spectrometer; at 300 (^1H) and 75 MHz (^{13}C) in CDCl_3 unless otherwise specified; δ in ppm, J in Hz.

General Procedure. To a soln. of an alkyne (2 mmol) in dry THF (10 ml), 1.6M BuLi in hexane (1.5 ml, 2.2 mmol) was added at -78° . The soln. was stirred at -78° for 1 h, and a soln. of the Bt derivative **1a–1** (2 mmol) in THF (10 ml) was added. The mixture was stirred for 12 h, while the temp. was allowed to rise to 20° . After quenching with H_2O (20 ml) and extraction with AcOEt (3×25 ml), the combined org. layer was washed with H_2O (25 ml) and dried ($MgSO_4$) and the solvent evaporated. The oily residue was subjected to CC (hexane/AcOEt 10:1 then 6:1): product **3a–t**.

4-[1-(2,2-Dimethylpropyl)non-2-yn-1-yl]morpholine (3a): 480.69 mg (86%). Colorless oil. 1H -NMR: 3.77–3.67 (*m*, 4 H); 3.35–3.31 (*m*, 1 H); 2.66–2.60 (*m*, 2 H); 2.50–2.43 (*m*, 2 H); 2.19 (*td*, $J = 7.0, 1.9, 2$ H); 1.55 (*d*, $J = 6.6, 2$ H); 1.53–1.28 (*m*, 8 H); 0.98 (*s*, 9 H); 0.89 (*t*, $J = 6.8, 3$ H). ^{13}C -NMR: 86.1; 78.1; 67.1; 54.2; 49.3; 46.9; 31.3; 30.3; 29.9; 28.5; 22.5; 18.6; 14.0. Anal. calc. for $C_{18}H_{33}NO$ (279.47): C 77.36, H 11.90, N 5.01; found: C 77.12, H 12.32, N 5.16.

4-[1-(4-Methylphenyl)-3-phenylprop-2-yn-1-yl]morpholine (3b): 518.69 mg (89%). Colorless microcrystals. M.p. $78.5–79.5^{\circ}$. 1H -NMR: 7.52–7.49 (*m*, 4 H); 7.33–7.29 (*m*, 3 H); 7.17 (*d*, $J = 7.8, 2$ H); 4.74 (*s*, 1 H); 3.77–3.68 (*m*, 4 H); 2.67–2.58 (*m*, 4 H); 2.35 (*s*, 3 H). ^{13}C -NMR: 137.4; 134.7; 131.7; 128.9; 128.5; 128.2; 128.1; 122.9; 88.2; 85.2; 67.1; 61.7; 49.8; 21.1. Anal. calc. for $C_{20}H_{21}NO$ (291.40): C 82.44, H 7.26, N 4.81; found: C 82.17, H 7.47, N 4.84.

4-(1-Isopropylnon-2-yn-1-yl)morpholine (3c): 462.61 mg (92%). Colorless oil. 1H -NMR: 3.77–3.66 (*m*, 4 H); 2.76 (*dt*, $J = 9.3, 1.9, 1$ H); 2.64–2.57 (*m*, 2 H); 2.45–2.38 (*m*, 2 H); 2.22 (*td*, $J = 7.0, 2.1, 2$ H); 1.81–1.72 (*m*, 1 H); 1.56–1.28 (*m*, 8 H); 1.02 (*d*, $J = 6.6, 3$ H); 0.96 (*d*, $J = 6.6, 3$ H); 0.89 (*t*, $J = 6.8, 3$ H). ^{13}C -NMR: 86.4; 67.1; 64.6; 49.8; 31.2; 29.7; 28.9; 28.4; 22.4; 19.9; 19.6; 18.5; 13.9. Anal. calc. for $C_{16}H_{29}NO$ (251.42): C 76.44, H 11.63, N 5.57; found: C 76.12, H 12.02, N 5.68.

4-(1-Isopropyl-3-phenylprop-2-yn-1-yl)morpholine (3d): 452.63 mg (93%). Colorless microcrystals. M.p. $68.5–69.5^{\circ}$. 1H -NMR: 7.46–7.41 (*m*, 2 H); 7.31–7.25 (*m*, 3 H); 3.80–3.69 (*m*, 4 H); 3.01 (*d*, $J = 9.62, 1$ H); 2.74–2.67 (*m*, 2 H); 2.51–2.48 (*m*, 2 H); 1.95–1.85 (*m*, 1 H); 1.11 (*d*, $J = 6.6, 3$ H); 1.03 (*d*, $J = 6.6, 3$ H). ^{13}C -NMR: 131.6; 128.2; 127.8; 123.3; 86.7; 86.5; 67.2; 65.1; 49.9; 29.8; 20.3; 19.7. Anal. calc. for $C_{16}H_{21}NO$ (243.35): C 78.97, H 8.70, N 5.76; found: C 79.31, H 8.86, N 5.81.

4-[1-(2,2-Dimethylpropyl)non-2-yn-1-yl]thiomorpholine (3e): 561.51 mg (95%). Colorless oil. 1H -NMR: 3.31–3.26 (*m*, 1 H); 2.90–2.84 (*m*, 2 H); 2.74–2.63 (*m*, 6 H); 2.19 (*td*, $J = 7.0, 1.9, 2$ H); 1.53 (*d*, $J = 6.6, 2$ H); 1.50–1.28 (*m*, 8 H); 0.96 (*s*, 9 H); 0.89 (*t*, $J = 6.7, 3$ H). ^{13}C -NMR: 85.7; 78.4; 55.3; 51.6; 47.0; 31.3; 30.3; 29.9; 28.9; 28.5; 28.2; 22.5; 18.6; 14.0. Anal. calc. for $C_{18}H_{33}NS$ (295.53): C 73.16, H 11.26, N 4.74; found: C 72.79, H 11.65, N 4.89.

N-(1-Isopropylnon-2-yn-1-yl)-N-(phenylmethyl)benzenemethanamine (3f): 650.84 mg (90%). Colorless oil. 1H -NMR: 7.44–7.38 (*m*, 4 H); 7.33–7.27 (*m*, 4 H); 7.24–7.18 (*m*, 2 H); 3.79 (*dd*, $J = 13.9, 2.5, 2$ H); 3.36 (*dd*, $J = 13.7, 3.7, 2$ H); 2.86 (*dd*, $J = 8.4, 2.0, 1$ H); 2.31–2.28 (*m*, 2 H); 1.89–1.83 (*m*, 1 H); 1.59–1.52 (*m*, 4 H); 1.36–1.34 (*m*, 4 H); 1.01–0.91 (*m*, 9 H). ^{13}C -NMR: 140.1; 128.8; 128.1; 126.7; 85.8; 59.2; 54.9; 31.4; 30.9; 29.3; 28.6; 22.7; 21.0; 19.9; 18.7; 14.1. Anal. calc. for $C_{26}H_{35}N$ (361.58): C 86.37, H 9.76, N 3.87; found: C 86.14, H 10.14, N 4.06.

1-[3,3-Dimethyl-1-[(4-methylphenyl)ethynyl]butyl]pyrrolidine (3g): 495.75 mg (92%). Orange oil. 1H -NMR: 7.30 (*d*, $J = 8.0, 2$ H); 7.09 (*d*, $J = 8.1, 2$ H); 3.80 (*dd*, $J = 9.2, 4.1, 1$ H); 2.77–2.66 (*m*, 4 H); 2.33 (*s*, 3 H); 1.80–1.76 (*m*, 4 H); 1.74–1.64 (*m*, 2 H); 1.03 (*s*, 9 H). ^{13}C -NMR: 137.6; 131.3; 128.9; 120.6; 88.4; 85.5; 51.0; 49.0; 48.9; 30.3; 30.0; 23.4; 21.4. Anal. calc. for $C_{19}H_{27}N$ (269.43): C 84.70, H 10.10, N 5.20; found: C 84.49, H 10.52, N 5.49.

4-[1-(4-Chlorophenyl)-3-(4-methylphenyl)prop-2-yn-1-yl]morpholine (3h): 612.58 mg (94%). Yellow microcrystals. M.p. $95–96^{\circ}$. 1H -NMR: 7.57 (*d*, $J = 8.4, 2$ H); 7.40 (*d*, $J = 8.0, 2$ H); 7.32 (*d*, $J = 8.4, 2$ H); 7.13 (*d*, $J = 8.0, 2$ H); 4.74 (*s*, 1 H); 3.76–3.67 (*m*, 4 H); 2.61–2.58 (*m*, 4 H); 2.35 (*s*, 3 H). ^{13}C -NMR: 138.5; 136.5; 133.4; 131.6; 129.8; 129.0; 128.3; 119.6; 88.9; 83.5; 67.1; 61.3; 49.7; 21.4. Anal. calc. for $C_{20}H_{20}ClNO$ (325.84): C 73.72, H 6.19, N 4.30; found: C 73.47, H 6.41, N 4.28.

4-[3,3-Dimethyl-1-[(4-methylphenyl)ethynyl]butyl]morpholine (3i): 513.77 mg (90%). Colorless microcrystals. M.p. $42.5–43.5^{\circ}$. 1H -NMR: 7.31 (*d*, $J = 8.1, 2$ H); 7.09 (*d*, $J = 7.8, 2$ H); 3.79–3.69 (*m*, 4 H); 3.56 (*dd*, $J = 7.9, 5.3, 1$ H); 2.76–2.69 (*m*, 2 H); 2.59–2.52 (*m*, 2 H); 2.32 (*s*, 3 H); 1.70–1.65 (*m*, 2 H); 1.03 (*s*, 9 H). ^{13}C -NMR: 137.7; 131.3; 128.9; 120.2; 87.2; 86.2; 67.0; 54.6; 49.4; 46.8; 30.3; 29.9; 21.3. Anal. calc. for $C_{19}H_{27}NO$ (285.43): C 79.95, H 9.53, N 4.91; found: C 79.91, H 9.81, N 4.86.

α -[*(4-Methylphenyl)ethynyl*]-*N,N*-bis(*phenylmethyl*)benzenemethanamine (**3j**): 762.96 mg (95%). Colorless microcrystals. M.p. 106.5–107.5°. ¹H-NMR: 7.30 (*d*, *J* = 7.7, 2 H); 7.52 (*d*, *J* = 8.0, 2 H); 4.93 (*s*, 1 H); 3.79 (*AB*, *J* = 13.5, 2 H); 3.54 (*AB*, *J* = 13.5, 2 H); 2.36 (*s*, 3 H). ¹³C-NMR: 139.6; 139.3; 138.3; 131.8; 129.1; 128.9; 128.2; 128.1; 127.4; 127.0; 120.2; 88.7; 83.9; 56.0; 54.6; 21.5. Anal. calc. for C₃₀H₂₇N (401.56): C 89.73, H 6.78, N 3.49; found: C 89.49, H 6.93, N 3.46.

α -[*(Hex-1-yn-1-yl)*]-*N,N*-bis(*phenylmethyl*)benzenemethanamine (**3k**): 639.52 mg (87%). Colorless oil. ¹H-NMR: 7.68 (*d*, *J* = 7.8, 2 H); 7.41–7.39 (*m*, 4 H); 7.30–7.25 (*m*, 6 H); 7.20–7.18 (*m*, 3 H); 4.69 (*s*, 1 H); 3.70 (*AB*, *J* = 13.5, 2 H); 3.44 (*AB*, *J* = 13.5, 2 H); 2.42 (*td*, *J* = 6.8, 1.9, 2 H); 1.68–1.52 (*m*, 4 H); 1.00 (*t*, *J* = 7.2, 3 H). ¹³C-NMR: 139.8; 139.7; 128.8; 128.3; 128.2; 127.9; 127.2; 126.9; 88.7; 74.6; 55.6; 54.5; 31.3; 22.1; 18.5; 13.7. Anal. calc. for C₁₅H₂₂NO₂S (367.54): C 88.23, H 7.95, N 3.81; found: C 88.10, H 7.86, N 3.61.

4-[*1-(4-Chlorophenyl)hept-2-yn-1-yl*]-morpholine (**3l**): 513.60 mg (88%). Yellow oil. ¹H-NMR: 7.50 (*d*, *J* = 8.4, 2 H); 7.30 (*d*, *J* = 8.4, 2 H); 4.49 (*s*, 1 H); 3.71–3.67 (*m*, 4 H); 2.51–2.48 (*m*, 4 H); 2.32 (*td*, *J* = 7.0, 2.1, 2 H); 1.59–1.42 (*m*, 4 H); 0.94 (*t*, *J* = 7.1, 3 H). ¹³C-NMR: 137.1; 133.2; 129.8; 128.1; 89.1; 74.6; 67.0; 60.9; 49.6; 31.0; 22.0; 18.4; 13.6. Anal. calc. for C₁₇H₂₂ClNO (291.82): C 69.97, H 7.60, N 4.80; found: C 69.66, H 7.79, N 4.95.

4-[*1-(2,2-Dimethylpropyl)hept-2-yn-1-yl*]-thiomorpholine (**3m**): 502.86 mg (94%). Colorless oil. ¹H-NMR: 3.24–3.18 (*m*, 1 H); 2.84–2.74 (*m*, 2 H); 2.66–2.63 (*m*, 6 H); 2.13 (*td*, *J* = 6.7, 1.9, 2 H); 1.46 (*d*, *J* = 6.7, 2 H); 1.43–1.31 (*m*, 4 H); 0.89 (*s*, 9 H); 0.85 (*t*, *J* = 7.1, 3 H). ¹³C-NMR: 85.3; 78.1; 55.2; 51.4; 46.9; 30.9; 30.1; 29.7; 28.0; 21.7; 18.1; 13.4. Anal. calc. for C₁₆H₂₉NS (267.48): C 71.85, H 10.93, N 5.24; found: C 71.47, H 11.37, N 5.39.

1-[*1-(Naphthalen-1-yl)hept-2-yn-1-yl*]-piperidine (**3n**): 507.08 mg (83%). Yellow oil. ¹H-NMR: 8.36 (*d*, *J* = 8.1, 1 H); 7.85 (*d*, *J* = 7.3, 1 H); 7.80 (*d*, *J* = 7.7, 1 H); 7.74 (*d*, *J* = 8.2, 1 H); 7.50–7.38 (*m*, 3 H); 5.17 (*s*, 1 H); 2.60–2.45 (*m*, 4 H); 2.35 (*td*, *J* = 6.8, 1.6, 2 H); 1.63–1.40 (*m*, 10 H); 0.94 (*t*, *J* = 7.1 Hz, 3 H). ¹³C-NMR: 134.9; 133.9; 131.9; 128.2; 128.1; 126.6; 125.5; 125.3; 125.1; 124.6; 88.5; 75.8; 60.0; 50.5; 31.2; 26.2; 24.6; 22.0; 18.5; 13.6. Anal. calc. for C₂₂H₂₇N (305.47): C 86.50, H 8.91, N 4.59; found: C 86.42, H 9.20, N 4.78.

α -[*(Hept-1-yn-1-yl)*]-*N,N*-bis(*phenylmethyl*)benzenemethanamine (**3o**): 679.19 mg (89%). Colorless oil. ¹H-NMR: 7.70 (*d*, *J* = 7.7, 2 H); 7.41–7.39 (*m*, 4 H); 7.33–7.26 (*m*, 6 H); 7.23–7.17 (*m*, 3 H); 4.69 (*s*, 1 H); 3.70 (*AB*, *J* = 13.5, 2 H); 3.44 (*AB*, *J* = 13.5, 2 H); 2.42 (*td*, *J* = 6.9, 2.1, 2 H); 1.70–1.63 (*m*, 2 H); 1.58–1.47 (*m*, 2 H); 1.45–1.37 (*m*, 2 H); 0.96 (*t*, *J* = 7.2, 3 H). ¹³C-NMR: 139.9; 139.8; 128.8; 128.3; 128.2; 127.9; 127.2; 126.9; 88.8; 74.7; 55.6; 54.5; 31.2; 28.9; 22.2; 18.8; 14.1. Anal. calc. for C₂₈H₃₁N (381.57): C 88.14, H 8.19, N 3.67; found: C 87.89, H 8.51, N 3.62.

1-[*1-(Naphthalen-1-yl)oct-2-yn-1-yl*]-piperidine (**3p**): 555.91 mg (87%). Yellow oil. ¹H-NMR: 8.35 (*d*, *J* = 8.1, 1 H); 7.84 (*d*, *J* = 7.1, 1 H); 7.80 (*d*, *J* = 8.5, 1 H); 7.74 (*d*, *J* = 8.2, 1 H); 7.49–7.38 (*m*, 3 H); 5.16 (*s*, 1 H); 2.53–2.52 (*m*, 4 H); 2.35–2.30 (*m*, 2 H); 1.64–1.31 (*m*, 12 H); 0.91 (*t*, *J* = 7.1, 3 H). ¹³C-NMR: 135.0; 133.9; 131.9; 128.2; 128.2; 126.7; 125.5; 125.3; 125.1; 124.7; 88.5; 75.9; 60.0; 50.5; 31.1; 28.8; 26.2; 24.6; 22.2; 18.8; 14.0. Anal. calc. for C₂₃H₂₉N (319.49): C 86.47, H 9.15, N 4.38; found: C 86.62, H 9.43, N 4.62.

4-[*1-(4-Methylphenyl)oct-2-yn-1-yl*]-morpholine (**3q**): 559.44 mg (98%). Colorless oil. ¹H-NMR: 7.42 (*d*, *J* = 8.0, 2 H); 7.13 (*d*, *J* = 8.0, 2 H); 4.47 (*s*, 1 H); 3.70–3.67 (*m*, 4 H); 2.53–2.49 (*m*, 4 H); 2.33 (*s*, 3 H); 2.29 (*td*, *J* = 7.0, 2.1, 2 H); 1.60–1.53 (*m*, 2 H); 1.45–1.30 (*m*, 4 H); 0.91 (*t*, *J* = 7.1, 3 H). ¹³C-NMR: 137.0; 135.4; 128.6; 128.3; 88.3; 75.5; 67.0; 61.3; 49.6; 31.0; 28.6; 22.1; 21.0; 18.6; 13.9. Anal. calc. for C₁₉H₂₇NO (285.43): C 79.95, H 9.53, N 4.91; found: C 79.58, H 9.92, N 5.17.

N-[*(1-Isopropyl)oct-2-yn-1-yl*]-*N*-methylbenzenamine (**3r**): 468.50 mg (91%). Yellow oil. ¹H-NMR: 7.25–7.20 (*m*, 2 H); 6.82 (*d*, *J* = 8.0, 2 H); 6.75–6.70 (*m*, 1 H); 4.04–4.01 (*m*, 1 H); 2.84 (*s*, 3 H); 2.17 (*td*, *J* = 6.9, 2.1, 2 H); 2.04–1.97 (*m*, 1 H); 1.50–1.44 (*m*, 2 H); 1.40–1.26 (*m*, 4 H); 1.09 (*d*, *J* = 6.6, 3 H); 0.93 (*d*, *J* = 6.6, 3 H); 0.88 (*t*, *J* = 7.1, 3 H). ¹³C-NMR: 150.5; 129.0; 117.2; 114.0; 85.2; 77.6; 59.2; 33.2; 32.2; 31.0; 28.6; 22.1; 20.0; 19.6; 18.6; 14.0. Anal. calc. for C₁₈H₂₇N (257.42): C 83.99, H 10.57, N 5.44; found: C 83.71, H 10.98, N 5.79.

4-[*(1-Phenyl)hept-2-yn-1-yl*]-morpholine (=MF6; **3s**): 499.32 mg (97%). Colorless oil. ¹H-NMR: 7.58–7.55 (*m*, 2 H); 7.37–7.26 (*m*, 3 H); 4.54 (*s*, 1 H); 3.73–3.69 (*m*, 4 H); 2.55–2.52 (*m*, 4 H); 2.33 (*td*, *J* = 7.0, 2.1, 2 H); 1.60–1.44 (*m*, 4 H); 0.95 (*t*, *J* = 7.2, 3 H). ¹³C-NMR: 138.5; 128.6; 128.1; 127.6; 88.7; 75.3;

67.2; 61.7; 49.8; 31.2; 22.1; 18.5; 13.7. Anal. calc. for C₁₇H₂₃NO (257.38): C 79.33, H 9.01, N 5.44; found: C 79.23, H 8.91, N 5.32.

α-(Oct-1-yn-1-yl)-N,N-bis(phenylmethyl)benzenemethanamine (=FDF8; **3t**): 712.06 mg (90%). Colorless oil. ¹H-NMR: 7.79–7.76 (*m*, 2 H); 7.52–7.50 (*m*, 4 H); 7.44–7.37 (*m*, 6 H); 7.33–7.30 (*m*, 3 H); 4.79 (*s*, 1 H); 3.80 (*AB*, *J* = 13.5, 2 H); 3.54 (*AB*, *J* = 13.5, 2 H); 2.53 (*td*, *J* = 6.8, 2.0, 2 H); 1.80–1.75 (*m*, 2 H); 1.68–1.66 (*m*, 2 H); 1.50–1.45 (*m*, 4 H); 1.04 (*t*, *J* = 7.0, 3 H). ¹³C-NMR: 139.8; 139.7; 128.8; 128.3; 128.2; 127.9; 127.2; 126.8; 88.8; 74.7; 55.6; 54.5; 31.4; 29.2; 28.6; 22.6; 18.9, 14.1. Anal. calc. for C₂₉H₃₃N (395.59): C 88.05, H 8.41, N 3.54; found: C 87.95, H 8.30, N 3.45.

General Procedure for Langmuir–Blodgett Deposition. The binary systems were mixed to achieve 1:1, 1:2, and 10:1 molar compositions of the deposition mixture. The π -*A* isotherms were measured by means of a commercial *Langmuir–Blodgett* trough (KSV, system 5000) by using a Pt hydrophilic *Wilhelmy* plate, on high-purity water at 295 K. The compression rates in our experiments ranged from 25 to 100 mm/min, depending on the rigidity of the films. *Langmuir–Blodgett* films were prepared by means of vertical emerging and dipping of the substrate at the surface pressure of *ca.* 10 mN/m.

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Received March 27, 2007