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

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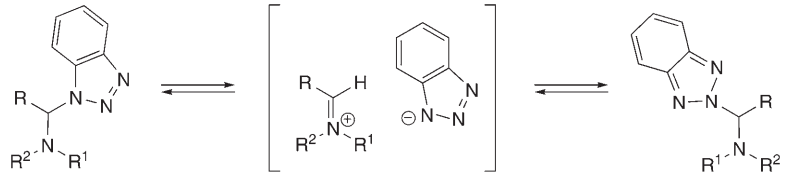
Reactions of readily available and stable benzotriazolemethanamines **1a**–**l**, obtained from aldehydes and secondary amines (*Scheme 2*), gave the expected alk-2-yn-1-amines **3a**–**t** (*Scheme 3*). The amphiphilic character of the synthesized products was responsible for physicochemical measurements. 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



1 **2** **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 1*H-*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 1*H*-benzotriazole-1-methanamines **1a**–**l** were easily synthesized by the well-established condensation of 1*H*-benzotriazole, an aliphatic aldehyde, and a secondary amine, either in CH_2Cl_2 in the presence of anhydrous $MgSO_4$ 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.

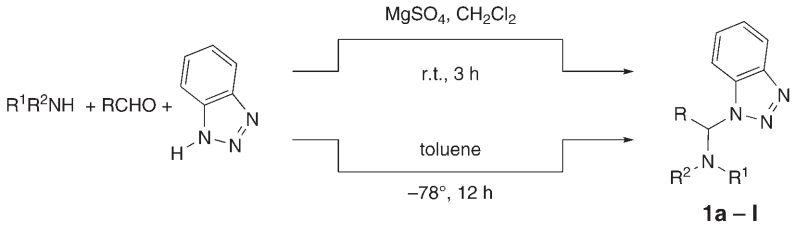
Synthesis of Alk-2-yn-1-amines. A group of alk-2-yn-1-amines **3** were obtained according to the standard procedure of lithiation of organic compounds [19] (*Table*, *Scheme 3*). The key step of this methodology was the deprotonation of the alkynes and formation of unstable lithio compounds, which at $-78°$ in THF reacted with the 1*H*-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 ^{1}H- and ^{13}C-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 electro-conductivity measurements.

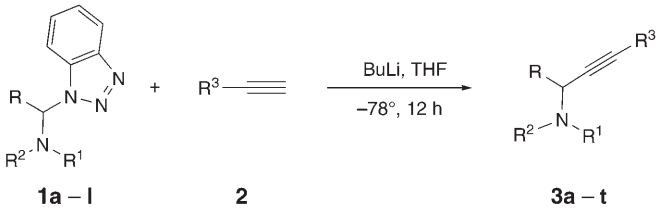
Physicochemical Effects of Langmuir–Blodgett *Films Build from Synthesized Materials.* To obtain *Langmuir* films, the synthesized amphiphilic compounds 4-(1-phenylhept-2-yn-1-yl)morpholine (= MF 6; **3s**) and α-(oct-1-yn-1-yl)-*N*,*N*-bis(phenyl-

Scheme 2



1	R	NR^1R^2
a	4-MeC_6H_4	morpholin-4-yl
b	4-ClC_6H_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_2N
g	Me_3CCH_2	morpholin-4-yl
h	Ph	Bn_2N
i	Me_3CCH_2	pyrrolidin-1-yl
j	Me_3CCH_2	thiomorpholin-4-yl
k	Ph	morpholin-4-yl
l	^{i}Pr	PhNMe

Scheme 3 [a])



[a]) For R^1, R^2, and R^3, see *Table*.

methyl)benzenemethanamine FDF 8; **3t**) (*Table*) were dissolved in $CHCl_3$ (*Aldrich*; HPLC grade) and spread onto the H_2O 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 alkynamine 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 H_2O 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^1R^2	R^3	Yield [%]
3a	Me_3CCH_2	$N(CH_2CH_2)_2O$	$Me(CH_2)_5$	86
3b	4-MeC_6H_4	$N(CH_2CH_2)_2O$	Ph	89
3c	^{i}Pr	$N(CH_2CH_2)_2O$	$Me(CH_2)_5$	92
3d	^{i}Pr	$N(CH_2CH_2)_2O$	Ph	93
3e	Me_3CCH_2	$N(CH_2CH_2)_2S$	$Me(CH_2)_5$	95
3f	^{i}Pr	Bn_2N	$Me(CH_2)_5$	90
3g	Me_3CCH_2	$N(CH_2)_4$	4-MeC_6H_4	92
3h	4-ClC_6H_4	$N(CH_2CH_2)_2O$	4-MeC_6H_4	94
3i	Me_3CCH_2	$N(CH_2CH_2)_2O$	4-MeC_6H_4	90
3j	Ph	Bn_2N	4-MeC_6H_4	95
3k	Ph	Bn_2N	Bu	87
3l	4-ClC_6H_4	$N(CH_2CH_2)_2O$	Bu	88
3m	Me_3CCH_2	$N(CH_2CH_2)_2S$	Bu	94
3n	naphthalen-1-yl	$N(CH_2)_5$	Bu	83
3o	Ph	Bn_2N	$Me(CH_2)_4$	89
3p	naphthalen-1-yl	$N(CH_2)_5$	$Me(CH_2)_4$	87
3q	4-MeC_6H_4	$N(CH_2CH_2)_2O$	$Me(CH_2)_4$	98
3r	^{i}Pr	PhNMe	$Me(CH_2)_4$	91
3s	Ph	$N(CH_2CH_2)_2O$	Bu	97
3t	Ph	Bn_2N	$Me(CH_2)_5$	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 $\pi-A$ 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

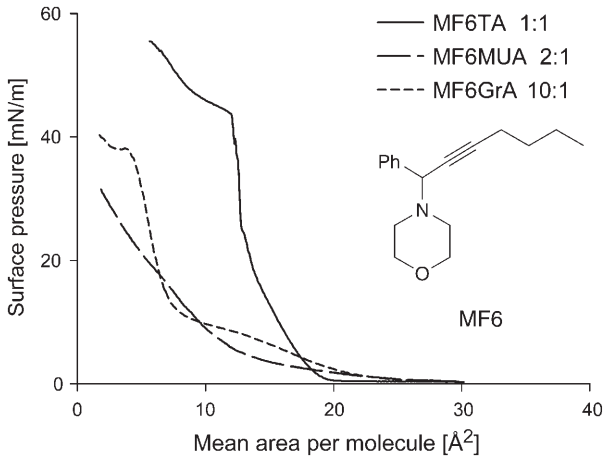


Fig. 1. $\pi-$A *Isotherms of binary MF6* (**3s**) *complexes with TA* (tricos-22-enoic acid), *MUA* (11-mercaptoundecanoic acid), *and GrA* (gramicidine A)

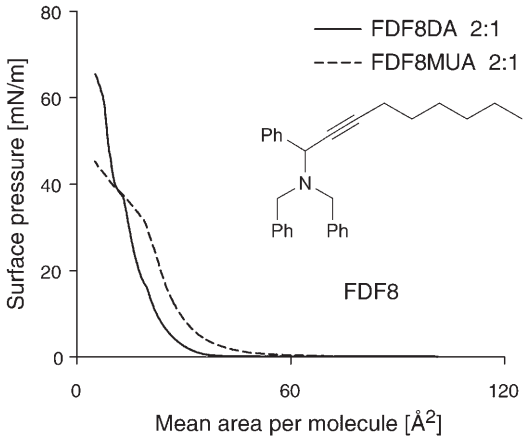


Fig. 2. π–A *Isotherms of binary FDF8* (**3t**) *complexes with DA* (docosanoic acid) *and MUA* (11-mercaptoundecanoic acid)

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 alkynamine moiety of the derivatives MF 6 and FDF 8, by the alkyl chain being almost vertical to the hydrophilic part of MF 6 and FDF 8, 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 MF 6 (**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 Å^2, which is also confirmed by the π–*A* isotherm (in the binary system).

Transfer of the *Langmuir* films of MF 6 or FDF 8 from the air/H_2O 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 FDF 8 (**3t**) on a quartz substrate (75 mm × 19 mm × 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 alkynamine derivatives by a typical, straightforward and convenient methodology starting from an aldehyde and an amine *via* a 1*H*-benzotriazole derivative. The obtained alkynamines could find applications, for example, in promising electro-active materials. The alkynamines **3s** and **3t**, mixed with substances facilitating film building, gave stable and good-quality

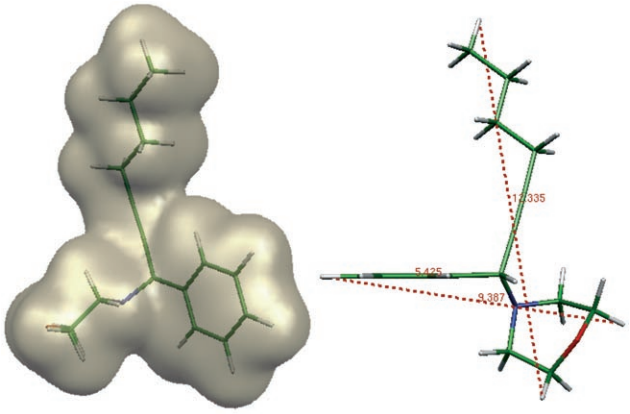


Fig. 3. *Computer-generated models of MF6* (**3s**)

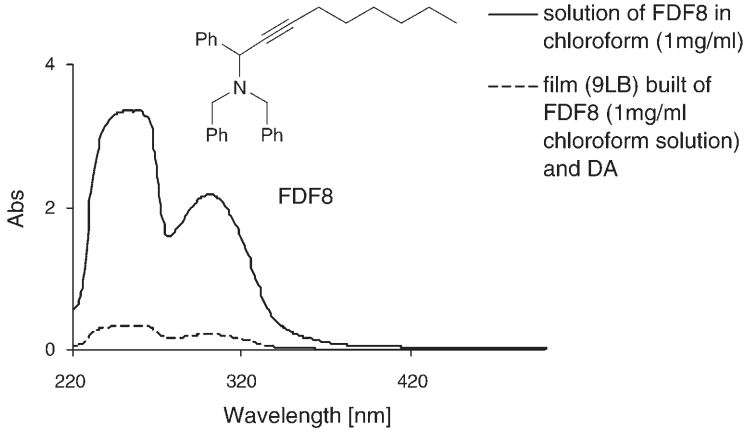


Fig. 4. *UV/VIS Absorption spectra of a $CHCl_3$ solution and of a* Langmuir–Blodgett *film of FDF8* (**3t**)

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

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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 (^{1}H) 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**–**l** (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. ^{1}H-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°. ^{1}H-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. ^{1}H-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°. ^{1}H-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. ^{1}H-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. ^{1}H-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. ^{1}H-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°. ^{1}H-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°. ^{1}H-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°. ^{1}H-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). ^{13}C-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 $C_{30}H_{27}N$ (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. ^{1}H-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). ^{13}C-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 $C_{15}H_{22}NO_2S$ (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. ^{1}H-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). ^{13}C-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 $C_{17}H_{22}ClNO$ (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. ^{1}H-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). ^{13}C-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 $C_{16}H_{29}NS$ (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. ^{1}H- 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). ^{13}C-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 $C_{22}H_{27}N$ (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. ^{1}H-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). ^{13}C-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 $C_{28}H_{31}N$ (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. ^{1}H-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). ^{13}C-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 $C_{23}H_{29}N$ (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. ^{1}H-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). ^{13}C-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 $C_{19}H_{27}NO$ (285.43): C 79.95, H 9.53, N 4.91; found: C 79.58, H 9.92, N 5.17.

N-*(1-Isopropyloct-2-yn-1-yl)*-N-*methylbenzenamine* (**3r**): 468.50 mg (91%). Yellow oil. ^{1}H-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). ^{13}C-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 $C_{18}H_{27}N$ (257.42): C 83.99; H 10.57, N 5.44; found: C 83.71, H 10.98, N 5.79.

4-(1-Phenylhept-2-yn-1-yl)morpholine (= MF6; **3s**): 499.32 mg (97%). Colorless oil. ^{1}H-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). ^{13}C-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 $C_{17}H_{23}NO$ (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. ^{1}H-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). ^{13}C-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 $C_{29}H_{33}N$ (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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