Synthesis and Self-Assembly of a Heteroarm Star Amphiphile with 12 Alternating Arms and a Well-Defined Core

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Although star-shaped molecules have been known since the late 1940s, only recently did they become synthetically available. The progress was primarily due to recent advances in living anionic1 and radical polymerization.2 However, a number of challenges remain, including control over the structure of a core and the number of arms in such molecules.3 In addition, living polymerization conditions are very demanding, and that necessitates development of alternative synthetic approaches.4 Here, we demonstrate that a stepwise synthesis starting from commercially available linear precursors can produce well-defined starlike molecules with a precisely controlled number and position of arms. The amphiphile described here self-assembles into spherical and wormlike supermicelles5 in aqueous and methanol solutions, and forms reverse micelles in chloroform. This morphological diversity has not been previously observed in star-shaped amphiphiles and is believed to be a direct consequence of the well-defined molecular architecture.

The synthesis of amphiphile 1 consists of two parts: the preparation of a Y-shaped copolymer 3 and the synthesis of a hexafunctional core 4 (Scheme 1). Carboxyl-terminated polystyrene ($M_w = 2400$, PDI = 1.1) (Polymer Source, Inc.) was coupled with an excess of silyl-protected 3,5-dihydroxybenzoic acid under mild esterification conditions. Analogous coupling of 2 with poly(tert-butyl acrylate) followed by cleavage of the silyl group with DMAP afforded functional polymer 3 ($M_n = 7300$, PDI = 1.07). All products were obtained in high yields and were purified by flash chromatography. The second part of the synthesis involved preparation of an aromatic core which could offer a reduced steric hindrance and higher accessibility of the functional hydroxyl groups. The esterification reaction between silyl-protected 4′-hydroxy-biphenyl-4-carboxylic acid and hexahydroxybenzene, followed by deblocking of DTS under acidic conditions, produced hexafunctional core 4 in high yield and purity, as confirmed by MALDI mass spectrometry, $^1$H NMR, and $^{13}$C NMR.6 The key step of the overall synthesis was the coupling reaction between the core 4 and the Y-shaped copolymer 3. Remarkably, the esterification was found to proceed in nearly quantitative yield within just 1 h, and the product was easy to purify by conventional flash chromatography. The reaction was monitored by GPC, which demonstrated formation of a high molar mass product with a molecular weight of 35 100 and a very low polydispersity ($M_w/M_n = 1.07$). The final step involved deprotection of polycrylate arms under acidic conditions (TFA). Interestingly, the reaction can be monitored most effectively by $^{13}$C NMR because the resonance generated by the tertiary carbon of tert-butyl groups (80.9 ppm) does not overlap with other signals in the spectrum. The average length of polystyrene and poly(acrylic acid) arms in the resulting heteroarm amphiphile 1 was calculated from NMR spectra using biphenyl protons as the internal reference. The average molecular weight of 1 was determined by GPC in a 0.1 M solution of LiBr in DMF and was found to be 31 300 ($M_w/M_n = 1.14$).6

Compound 1 (Figure 1a) contains a well-defined hexabiphenyl core, six hydrophobic arms of polystyrene, and six hydrophilic arms of poly(acrylic acid). The arms are fairly short, and each type contains on average 25 monomer units. Thus, the starlike structure 1 has a rigid core and a flexible oligomeric shell. However, the shell is not compositionally uniform, and it is the shell itself which is amphiphilic (Figure 1a). Most importantly, all molecules have an identical hexafunctional core, and its size (4 nm) is comparable to the length of the arms (6 nm). This is in great contrast to the heteroarm high polymers,7 where the average size of the central...
core is negligible in comparison with the arms. Therefore, interactions of molecules 1 with selective solvents will be defined by the interplay of three structural elements, that is, a rigid hydrophobic core and two flexible subshells: hydrophilic (6 PAA arms) and hydrophobic (6 PS arms), respectively.

We conceived structure 1 on the basis of several simple assumptions. Interactions of molecule 1 (Figure 1a) with water should cause solvation of PAA arms, whereas PS chains would try to minimize their exposure to such a polar environment. However, the presence of a relatively large and rigid core would keep PS chains to minimize their exposure to such a polar environment. However, the presence of a relatively large and rigid core would keep PS chains spatially separated, and their mere collapse on the scale of the presence of a relatively large and rigid core would keep PS chains localized on the center of cylinders and PAA arms are localized on the periphery. In addition, very similar structures were found in methanol solutions.

Our recent investigation revealed that amphiphile 1 also forms reverse micelles in chloroform. Figure 2d shows a TEM image of one-dimensional structures which measure 17 ± 2 nm in width and up to 1 μm in length. NMR analysis of chloroform solutions demonstrated that the signals of PAA are significantly suppressed, unlike those from PS arms, which is indicative of reverse micellar aggregates. Static light-scattering experiments also confirmed the presence of micelles in chloroform solutions, and their radius of gyration (120 nm), apparent molecular weight (1.1 × 10^8 g/mol), and the second virial coefficient (4.6 × 10^-4 mol mL^2) were determined from the Zimm plot. In contrast, micelles were not observed in chloroform solutions of the star-shaped precursor PS–PtB₄Ar⁻core. Therefore, the self-assembly requires not only a well-defined molecular architecture but also the amphiphilicity of the shell.

It is worth noting that, regardless of solvent and the type of micelles, that is, spherical or cylindrical, regular or reverse, the hexabiphenyl cores of molecules 1 will always be confined at the interface between the solvophilic corona and the solvophobic core (Figure 1b). This brings to mind one potential application of such systems. If the cores, connecting the arms, were carriers of some function, that is, nanoparticles or catalytic centers, this micellization process would provide an effective way to organize them into well-defined zero- and one-dimensional arrays.

Supporting Information Available: Experimental details, 1H and 13C NMR spectra, GPC, SLS data, and TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(5) Strictly speaking, these aggregates cannot be called micelles because the PS core is below Tg. Such nonequilibrium structures are normally referred to as micelle-like aggregates. However, by convention currently adopted in the literature and for the sake of simplicity, we use the term micelle.
(6) See Supporting Information.
Supporting Information

**General.** Unless otherwise stated, all starting materials were obtained from commercial suppliers and used without further purification. The $^1$H NMR and spectra were recorded on solutions in CD$_2$Cl$_2$, D$_2$O, DMSO-$_d$_6, acetone-$_d$_6, methanol-$_d$_4, benzene-$_d$_6, and pyridine-$_d$_5 on a Varian Unity 300 (300 MHz) spectrometer. $^{13}$C NMR spectra were recorded at 75 MHz on a Varian Unity 300 spectrometer using the solvent carbon signals as internal references. Matrix assisted laser desorption ionization (MALDI) mass spectra were obtained on a Thermo BioAnalysis Dynamo MALDI mass analyser using dithranol silver trifluoroacetate as a matrix. GPC analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a dual λ absorbance detector (Waters 2487) using polystyrene standards and THF as an eluent. Transmission electron microscopy studies were performed on a JEOL 1200EX scanning/transmission electron microscope operating at 120 kV accelerating voltage. Samples were prepared by casting dilute solutions onto carbon-coated copper grids and negatively stained (if necessary) with 2 % aqueous solutions of uranyl acetate or phosphotungstate acid (PTA). Positive staining with ruthenium tetroxide was performed by placing TEM grids above aqueous solution of RuO$_4$ for 15-30 min in a closed chamber. Carboxyl-terminated polystyrene ($M_n$=2000, $M_w$/$M_n$=1.2) was purchased from Polymer Source, Inc. This polymer was additionally purified by flash chromatography on silica gel using a mixture of THF and CH$_2$Cl$_2$ (5:95 vol.) as an eluent, and was precipitated into excess methanol to reduce its polydispersity. The average molecular weight of the purified polystyrene was 2500 as measured by MALDI-TOF, whereas molecular weight estimated by GPC was 3200 ($M_w$/$M_n$=1.1). Poly($t$-butyl acrylate) with a molecular weight $M_n$=4200 ($M_w$/$M_n$=1.25) was also purchased from Polymer Source, Inc. and was used as received. 4-(N,N-dimethylamino)pyridinium-4-toluenesulfonate (DPTS) was prepared by mixing saturated THF solutions of DMAP (1 equiv) and $p$-toluenesulfonic acid monohydrate (1 equiv) at room temperature. The precipitate was filtered and dried under vacuum. The NMR analysis confirmed the structure of DPTS which was found to be the same as that reported previously. $^9$
**General procedure for esterification coupling reactions.** The acid (1.2 equiv), phehol or hydroxyl-terminated core (1 equiv), DPTS (1.6 equiv), and CH₂Cl₂ were combined in a flask with a stirring bar at room temperature. DIPC (2.5 equiv) was added after 2 minutes and the reaction was allowed to stir for several hours. The coupling reactions were monitored by TLC, GPC, and NMR. The mixture was then diluted by dichloromethane and 2-4 water extractions were used to quench the reaction and to remove DPTS. The crude product was purified by flash chromatography as outlined below.

**General procedure for the deprotection reaction using DMAP.** The dimethylthexylsilyl (DTS) protected acid (1 equiv) was dissolved in 30 % solution of DMAP in dichloromethane. The reaction was allowed to stir for 12 hours at room temperature. The mixture was diluted with CH₂Cl₂ and washed several times with 5 % aqueous solution of citric acid to completely eliminate DMAP. The organic layer was collected, dried, and concentrated in vacuo. The crude product was purified by flash chromatography as outlined in the following text.

**General procedure for the deprotection reaction using hydrofluoric acid (HF).** The DTS-protected phenol was dissolved in THF in a plastic vessel (10 wt. % solution). Hydrofluoric acid (49 % aq. solution) was added via syringe (20 equiv) and the reaction mixture was allowed to stir for 24 hours. The reaction was diluted by CH₂Cl₂ and quenched by saturated solution of sodium bicarbonate. The resultant mixture was washed several times with water and the crude product was purified by flash chromatography.

**3,5-Dihydroxy-dimethylthexylsilyl benzoate.** Morpholine (1.3 equiv) was added to a homogeneous solution of 3,5-dihydroxybenzoic acid (1 equiv) in DMF. Dimethylthexylsilyl chloride (1.1 equiv) was added via syringe upon rigorous stirring. The reaction mixture was allowed to stir exactly 5 minutes at room temperature, then diluted with CH₂Cl₂ and washed several times with water. The organic layer was collected, evaporated, and purified by column chromatography on silica gel (5% THF in CH₂Cl₂) to yield the product as a colorless liquid. R₇=0.43. Yield: 70 %. Caution: DTS group is not very stable and can be partially cleaved if the product is kept under vacuum for more than
several minutes. It is recommended to keep DTS-protected acids in a dilute CH₂Cl₂ solution (10 wt. %). ¹H NMR (300 MHz, CD₂Cl₂): δ 0.22 (s, 6H), 0.81 (m, 12 H), 1.62 (m, 1H), 6.61 (t, 1H, J = 2.1 Hz), 7.18 (d, 2H, J = 2.3 Hz).

Compound 2. Carboxyl-terminated polystyrene (1 equiv) was added to a 10 wt. % CH₂Cl₂ solution of 3,5-dihydroxy-dimethylthexylsilyl benzoate (10 equiv). DPTS (1.2 equiv) was added to the resulting solution and the mixture was stirred for 5 minutes before DIPC (1.5 equiv) was added via pipette. The reaction proceeded for 2 h, although complete disappearance of the activated polystyrene anhydrite spot on TLC (R_f=1 in dichloromethane) was observed in 15 min. The mixture was diluted in CH₂Cl₂ and washed with water 3 times. The product was purified by flash chromatography eluting with 5 % THF/CH₂Cl₂ mixture (R_f=0.5) to give 2 as a white glassy powder. Please note, some fractionation of the polymer product occurs as it passes through silica gel. In case of polystyrene, the high molar mass fractions come out of the column first. In order to decrease the overall polydispersity we intentionally cut off early and late fractions, which inevitably resulted in a decreased yield. Yield after column purification: 83 %. GPC (254 nm, THF) PDI=1.08, Mₙ=3500. ¹H NMR (300 MHz, CD₂Cl₂): δ 0.37 (s, 6H), 0.83 (m, 12 H), 1.2-2.1 (br m, 84 H), 6.3-7.5 (br m, 130 H). MALDI-TOF Mₙ=2881.

PS-PrBA-silyl benzoate. Compound 2 (1.1 equiv), carboxyl-terminated poly(t-butyl acrylate) (1 equiv), and DPTS (1.6 equiv) were dissolved in dichloromethane and DIPC was added upon rigorous stirring of the mixture. The coupling reaction was monitored by TLC and GPC and was found to be complete in 1 h. The mixture was diluted in CH₂Cl₂ and washed with water 3 times. The product was purified by flash chromatography eluting with 5 % THF/CH₂Cl₂ mixture (R_f=0.4) to give the product as a white glassy powder. In order to decrease the overall polydispersity we cut off early and late fractions, which resulted in a decreased yield. Yield after column purification: 65 %. GPC (254 nm, THF) PDI=1.09, Mₙ=7400. ¹H NMR (300 MHz, CD₂Cl₂): δ 0.41 (s, 6H), 0.85 (m, 12 H), 1.0-2.1 (br m, 370 H), 2.25 (br s, 25 H), 6.3-7.5 (br m, 140 H).
**Compound 3.** This compound was obtained following general procedure for deprotection of DTS esters with DMAP in dichloromethane. The product was purified by flash chromatography eluting first with CH$_2$Cl$_2$ gradually increasing to 7 % THF/CH$_2$Cl$_2$ mixture (R$_f$=0.55) to give 3 as a glassy solid. Yield: 90 %. GPC (254 nm, THF) PDI=1.07, M$_n$=7300. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): δ 1.0-2.1 (br m, 370 H), 2.25 (br s, 25 H), 6.3-7.5 (br m, 140 H).

![Figure S1. GPC trace of Y-shaped copolymer 3 (M$_n$= 7300, PDI=1.07).](image-url)
4'-dimethylthexylsilyloxy-biphenyl-4-carboxylic acid dimethylthexylsilyl ester. Morpholine (2.7 equiv) was added to a suspension of 4'-hydroxy-biphenyl-4-carboxylic acid in dichloromethane at room temperature. After stirring for 10 min, dimethylthexylsilyl chloride (2.5 equiv) was added via syringe and the reaction mixture was stirred for 3 hours. The flask content was then diluted with CH$_2$Cl$_2$ and washed 4 times with DI water. The organic layer was collected, evaporated and purified by flash chromatography on silica gel (30 % hexane in CH$_2$Cl$_2$) to yield double protected biphenyl as a colorless liquid. Yield: 93 %. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 0.27 (s, 6H, OSi(CH$_3$)$_2$), 0.43 (s, 6H, COOSi(CH$_3$)$_2$), 0.98 (br m, 24H, C(CH$_3$)$_2$CH(CH$_3$)$_2$), 1.71-1.82 (m, 2H, CH(CH$_3$)$_2$), 6.94 (d, 2H, $J$ = 8.67 Hz), 7.54 (d, 2H, $J$ = 8.67 Hz), 7.64 (d, 2H, $J$=8.54 Hz), 8.06 (d, 2H, $J$=8.55 Hz). $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$): $\delta$-3.18, -1.57, 16.47, 18.18, 19.75, 21.40, 23.01, 25.51, 33.89, 35.55, 120.13, 125.90, 127.78, 129.98, 132.27, 145.71, 156.60, 166.66.

4'-dimethylthexylsilyloxy-biphenyl-4-carboxylic acid. 4'-dimethylthexylsilyloxy-biphenyl-4-carboxylic acid dimethylthexylsilyl ester was dissolved in a mixture of THF, acetic acid and water (25: 67: 8 vol.) and stirred at room temperature for 24 h. The resulting mixture was diluted with CH$_2$Cl$_2$ and washed 3 times with water, 2 times with sodium bicarbonate saturated solution and one time with water. The organic layer was evaporated, and the crude product was recrystallized from 20 % CH$_2$Cl$_2$/hexane mixture to give the product as white needle-like crystals. Yield: 96 %. $^1$H NMR (300 MHz, acetone-$d_6$): $\delta$ 0.29 (s, 6H), 0.98 (br s, 12H), 1.78 (m, 1H), 7.00 (d, 2H, $J$ = 8.3 Hz), 7.65 (d, 2H, $J$ = 8.3 Hz), 7.75 (d, 2H, $J$= 8.06 Hz), 8.10 (d, 2H, $J$= 8.05 Hz).

Hexahydroxybenzene. Stannous chloride dihydrate (10g, 0.044 mol) was added to a boiling solution of tetrahydroxyquinone (1g, 0.0058 mol) in hydrochloric acid (20 mL of 2.4 N aqueous solution). After 30 min, an additional amount of HCl (25 mL of 12 N solution) was added and the mixture was boiled for another 30 min. The reaction mixture was then slowly cooled to room temperature and placed into refrigerator at –10 °C. The precipitate was filtered and the hexahydroxybenzene was collected on a Buchner funnel. The crude product was redissolved in hot
hydrochloric acid (45 mL of 2.4 N solution) containing stannous chloride dihydrate (0.3 g) and decolorizing carbon (0.1 g). The solution was filtered while hot, and the carbon was rinsed with boiling water. The solution was cooled in a refrigerator at –10 °C. The precipitate was collected and dried in vacuo to give the hexahydroxybenzene as a white crystalline solid. $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 128.01.

**DTS-protected hexabiphenyl core.** 4’-dimethylthexylsilyloxy-biphenyl-4-carboxylic acid (8 equiv) and DPTS (8 equiv) were added to a suspension of hexahydroxybenzene (1 equiv) in dichloromethane. DIPC (15 equiv) was added at room temperature and the reaction mixture was allowed to stir for 5 minutes. Small amount of DMF was then added to increase the solubility of hexahydroxybenzene and to accelerate the coupling reaction. The reaction was monitored by TLC and GPC and was found to be complete within 2 hours. The mixture was diluted with CH$_2$Cl$_2$ and washed with water 3 times. The organic layers were collected, dried and the crude product was purified by flash chromatography eluting with pure dichloromethane to first eliminate excess of the activated biphenyl acid (anhydrite which forms upon addition of DIPC, $R_f = 0.9$ in CH$_2$Cl$_2$) and then gradually increasing polarity of the eluent to 1 % THF/CH$_2$Cl$_2$ to give pure product as a white solid. Yield: 70 %.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ 0.28 (s, 6H), 0.98 (br s, 12H), 1.78 (m, 1H), 6.85 (d, 2H, $J = 8.24$ Hz), 7.35 (br s, 4H), 7.97 (br s, 2H). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ -1.96, 18.99, 20.53, 25.64, 34.72, 121.19, 126.93, 128.70, 131.60, 132.36, 135.43, 146.46, 156.93, 162.25.
Figure S2. $^{13}$C NMR spectrum of DTS-protected hexabiphenyl core.
Hexabiphenyl core (4). 20 wt. % solution of DTS-protected hexabiphenyl compound in THF was placed into a plastic container and excess (~50 equiv) hydrofluoric acid (49 % aq. solution of HF) was added via syringe upon rigorous stirring. The reaction was allowed to stir for 24 h at room temperature and then for 2 h at 50 °C. The mixture was cooled to room temperature, diluted with dichloromethane and quenched with aqueous saturated solution of sodium bicarbonate while in the plastic bottle. The organic layer was additionally washed 3 times with water and the product was precipitated into hexane. The precipitate was filtered and washed several times with pure dichloromethane to give compound 4 as a white solid (R_F=0.45 in 50 % THF/CH_2Cl_2). Yield: 98 %.

MALDI-TOF MS m/z 1358.45 [M+Li]^+. ^1H NMR (300 MHz, acetone-d_6): δ 6.86 (d, 2H, J= 8.67 Hz), 7.21 (d, 2H, J= 6.34 Hz), 7.36 (d, 2H, J=8.54 Hz), 7.90 (d, 2H, J=8.3 Hz), 8.73 (s, 1H, OH). ^13C NMR (100 MHz, DMSO-d_6 and acetone-d_6): δ 116.20, 125.42, 127.95, 128.01, 128.27, 130.91, 134.37, 145.86, 158.81, 161.05.
**Figure S3.** Aromatic region of $^1$H NMR spectrum of hexabiphenyl core 4 (see Scheme 1 in the text).
**Figure S4.** $^{13}$C NMR spectrum of hexabiphenyl core 4 (see Scheme 1 in the text).
**PS$_6$-PtBA$_6$-hexabiphenyl core.** Copolymer 3 (6.6 equiv) and DPTS (8 equiv) were added to a suspension of hexabipenyl core 4 in dichloromethane. After 5 min, DIPC (15 equiv) was added dropwise and the reaction mixture was allowed to stir at room temperature for 1 h. The completion of the coupling reaction was observed by TLC and GPC as the new sharp peak of a high molar mass product ($M_n$=35153) appeared in the GPC trace, whereas the peak of the starting material ($M_n$=7300) gradually disappeared. The new product had a slightly higher $R_f$ in comparison with the starting material 3 (0.7 versus 0.55 in 7 % THF/CH$_2$Cl$_2$, respectively). The reaction mixture was diluted with dichloromethane and washed 3 times with water. The crude product was purified by flash chromatography eluting with 7 % THF/CH$_2$Cl$_2$ to give the product as a glassy solid. Yield after column purification: 80 %. GPC (254 nm, THF) PDI=1.07, $M_n$=35153. $^1$H NMR (300 MHz, CD$_2$Cl$_2$): $\delta$ 1.0-2.1 (m, 2220H, CH$_2$ and CH of PS, CH$_2$ and CH$_3$ of PrBA), 2.26 (br s, 150H, CH of PrBA), 6.3-7.4 (br m, 850H, ArH of PS), 7.76 (br, 24H, Ar’H of biphenyls), 8.21 (d, 12H, $J$=8.3 Hz, Ar’H of biphenyls). $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$): $\delta$ 13.91, 20.24, 24.37, 26.33, 28.39, 28.45, 28.48, 30.67, 40.93, 41.13, 42.25, 42.64, 80.92, 126.22, 127.88, 128.01, 128.18, 128.23, 128.59, 145.95, 146.40, 174.13, 174.36, 174.56.
Figure S5. GPC trace of heteroarm star (PS₆-PtBA₆-hexabiphenyl core). $M_n=35153$, PDI=1.07.
Figure S6. $^1$H NMR spectrum of heteroarm star (PS$_6$-PtBA$_6$-hexabiphenyl core).
**PS₆-PAA₆-hexabiphenyl core (1).** PS₆-PrBA₆-hexabiphenyl core (0.91 g) was dissolved in a mixture of 10 mL of dichloromethane and 5 mL of THF. Trifluoroacetic acid (35 mL) was added dropwise upon rigorous stirring at room temperature. The reaction was monitored by ¹H NMR (reduction of a broad peak at 1.46 ppm) and by ¹³C NMR (disappearance of 80.92 ppm resonance which is generated by tertiary carbon of t-butyl groups). The deprotection proceeded for 48 h. The mixture was then diluted with 200 mL of 10 % THF/CH₂Cl₂ mixture and the excess of TFA was extracted with DI water (4 times), 5 % solution of sodium bicarbonate (one extraction), and DI water (two times). The organic layers were evaporated and dried in vacuo for 24 h at room temperature and 2 h at 50 °C to eliminate residual water and t-butyl alcohol to give 0.7 g of 1 as a white glassy solid. Yield: 98 %. GPC (270 nm, 0.1M solution of LiBr in DMF) PDI=1.14, Mₙ=31322. ¹H NMR (300 MHz, CD₂Cl₂/methanol-d₄ 65:35 vol.): δ 0.8-2.2 (br m, 870H, CH₂ and CH of PS, and CH₂ of PAA), 2.43 (br, 150H, CH of PAA), 6.3-7.4 (br m, 850H, ArH of PS), 7.54 (br, 24H, Ar’H of biphenyls), 8.08 (br, 12H, Ar’H of biphenyls). ¹³C NMR (100 MHz, CD₂Cl₂/methanol-d₄ 65:35 vol.): δ 14.37, 21.26, 22.94, 23.72, 26.26, 29.94, 32.16, 40.49, 40.57, 41.30, 42.03, 125.86, 127.92, 128.15, 128.23, 128.59, 145.48, 146.21, 176.26, 176.98, 177.34.

**Figure S7.** ¹H NMR spectrum of heteroarm star 1 (PS₆-PAA₆-hexabiphenyl core).
Figure S8. GPC trace of amphiphile 1 (PS₆-PAA₆-hexabiphenyl core). $M_n=31322$, PDI=1.14.
Figure S9. A photograph demonstrating the difference between the star-shaped polymer PS₆-PtBA₆-core and the amphiphile 1 obtained after the deprotection of polyacrylate arms (PS₆-PAA₆-core).

Left: PS₆-PtBA₆-core in water (insoluble); PS₆-PtBA₆-core in methanol (insoluble); PS₆-PtBA₆-core in chloroform (highly soluble).

Right: micellar solutions ($5 \cdot 10^{-5}$ M) of amphiphile 1 (PS₆-PAA₆-core) in water, methanol, and chloroform.
**Figure S10.** Low magnification TEM image of spherical micelles formed in water. The sample was cast from $3.3 \cdot 10^6$ M aqueous solution of amphiphile 1 (negative staining with 2 % solution of uranyl acetate in water). See also Figure 2a in the text.
Figure S11. TEM image of worm-like micelles formed in water at higher concentration. The sample was cast from $3.3 \cdot 10^{-5}$ M aqueous solution of amphiphile 1 (negative staining with 2 % solution of uranyl acetate in water). Both worm-like and spherical micelles coexist at this concentration (see also Figure 2c in the text).
Figure S12. Low and high magnification TEM images of worm-like and spherical micelles formed in methanol. The samples were cast from $3.3 \cdot 10^{-6}$ M methanol solution of amphiphile 1 (unstained samples).
Figure S13. Low and high magnification TEM images of one-dimensional structures formed in chloroform. The samples were cast from $3.3 \cdot 10^{-6}$ M chloroform solution of amphiphile 1 (negative staining with 2 % solution of PTA was used to generate contrast). See also Figure 2d in the text.
Figure S14. (A) Zimm plot for amphiphile 1 chloroform solutions at 30 °C.

Concentrations: $1.2 \cdot 10^{-6}$ M, $2.4 \cdot 10^{-6}$ M, $3.2 \cdot 10^{-6}$ M, and $5.1 \cdot 10^{-6}$ M.

Apparent molecular weight: $M_{w\ (app)} = (1.126 \pm 0.688) \times 10^8$ g/mol.

Radius of gyration: $R_g = 120.6 \pm 52.7$ nm.

2\textsuperscript{nd} virial coefficient: $(4.654 \pm 1.350) \times 10^{-4}$ mol mL/g\textsuperscript{2}.
Figure S15. Control experiment: TEM micrograph of a sample cast from $3.3 \times 10^{-6}$ M chloroform solution of PS$_6$-PtBA$_6$-core (negative staining with 2 % solution of uranyl acetate in water). Micelles have not been observed.