Supramolecular Comb Polymer Structure and Unique Mesomorphic Behavior Induced by Stacking Interactions Between Poly(2-Vinyl Pyridine) and Palladium Pincer Surfactants in the Solid State

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Synthetic details

The Pd-SCS surfactant was synthesized according to modified literature procedures.[1,2,3] Figure S1 shows the entire synthetic scheme.

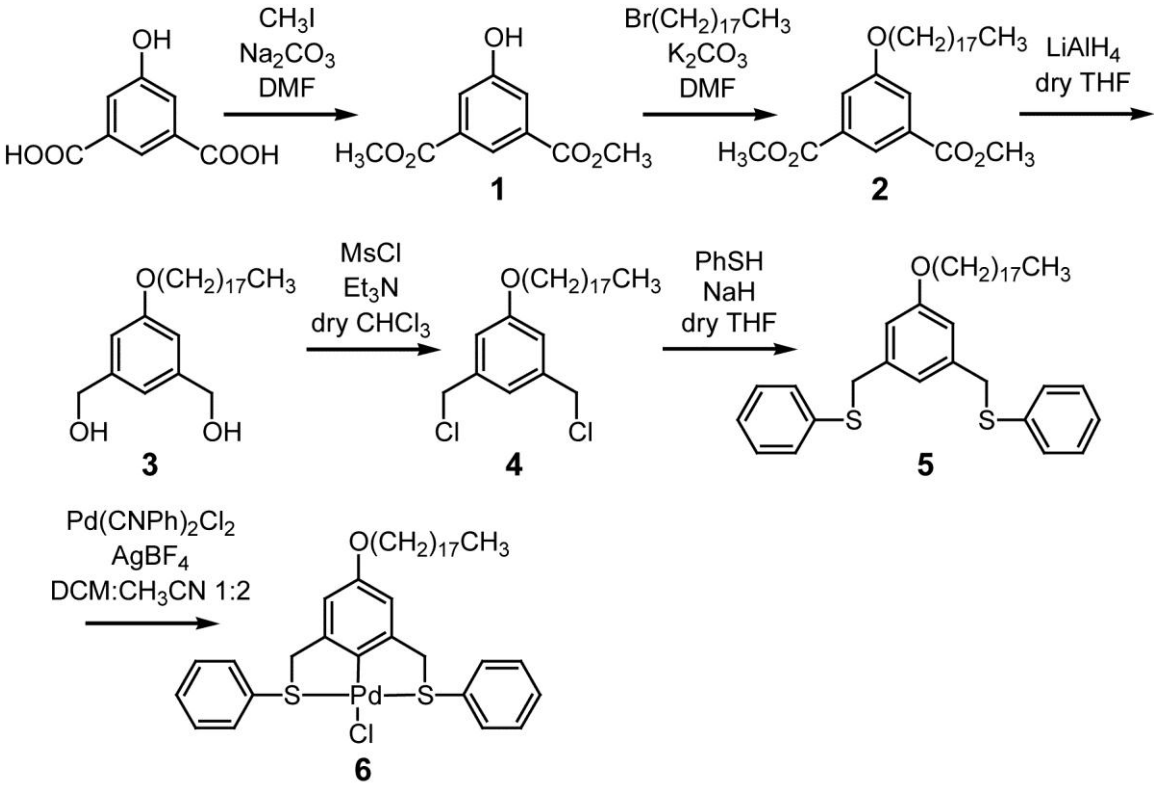

Figure S1. Pd-SCS synthesis.

Dimethyl 5-hydroxyisophthalate (1). To 2-hydroxyisophthalic acid dissolved in DMF, Na_2CO_3 (1 eq) was added slowly. After few minutes of mixing, methyl iodide (2 eq) was added. The mixture was stirred for 24 h at 40-50 ^oC, after which the solution was allowed to cool down to room temperature. The product was diluted in water, extracted with ethyl acetate, dried over Na_2SO_4 and filtered. Evaporation of the solution provided **1** as a white solid (77% yield). ^{1}H-NMR (400 MHz, δ_H ppm, $CDCl_3$) 8.26 (1 H, s, Ph), 7.76 (2 H, s, Ph), 3.95 (6 H, s, CH_3).

Dimethyl 5-(octadecyloxy)isophthalate (2). Compound **1**, K_2CO_3 (2.5 eq) and 11-bromooctadecane (1 eq) were dissolved in CH_3CN. The mixture was heated to reflux for 24 h, after which the solvent was evaporated and the product was re-dissolved in CH_2Cl_2 and washed with water. The organic layer was washed with 1M HCl solution, dried over Na_2SO_4, filtered and evaporated, resulting in white solid (98% yield). ^{1}H-NMR (400 MHz, δ_H ppm, $CDCl_3$) 8.26 (1 H, s, Ph), 7.74 (2 H, s, Ph), 4.03 (2 H, t, *J*=6.8, OCH_2), 3.94 (6 H, s, CO_2CH_3), 1.80 (2 H, m, OCH_2CH_2), 1.47 (2 H, m, CH_2), 1.25-1.40 (28 H, br s, CH_2), 0.88 (3 H, t, *J*=6.8, CH_2CH_3).

(5-(Octadecyloxy)-1,3-phenylene)dimethanol (3). $LiAlH_4$ (2 eq) was suspended in dry THF to create 1M solution to which **2** (1 eq), dissolved in dry THF, was added dropwise under nitrogen atmosphere. The reaction was heated to 40 ^{o}C for 24 h, cooled to room temperature, HCl solution (1 M) was added and the solvent was evaporated. The product was extracted in a soxhlet with a 1:1 v/v mixture of CH_2Cl_2:THF. Recrystallization from EtOH resulted in white solid (83% yield). ^{1}H-NMR (400 MHz, δ_H ppm, $CDCl_3$) 6.93 (1 H, s, Ph), 6.84 (2 H, s, Ph), 4.66 (4 H, s, CH_2OH), 3.98 (2 H, t, *J*=6.4, OCH_2), 1.76 (2 H, m, OCH_2CH_2), 1.47 (2 H, m, CH_2), 1.28-1.40 (28 H, br s, CH_2), 0.88 (3 H, t, *J*=6.8, CH_3).

1,3-Bis(chloromethyl)-5-(octadecyloxy)benzene (4). Compound **3** was dissolved in dry $CHCl_3$ under nitrogen atmosphere, after which triethyl amine (3 eq) and mesyl chloride (MsCl, 3 eq) were added. The reaction was refluxed overnight. After cooling, the solvent was evaporated and the product was purified by column chromatography (SiO_2, with 1:2 ethyl acetate:hexane as eluent). Recrystallization from EtOH resulted in white solid (80% yield). ^{1}H-NMR (400 MHz, δ_H ppm, $CDCl_3$) 6.97 (1 H, s, Ph), 6.88 (2 H, s, Ph), 4.54 (4 H, s, CH_2Cl), 3.97 (2 H, t, *J*=6.4, OCH_2), 1.76 (2 H, m, OCH_2CH_2), 1.45 (2 H, m, CH_2), 1.28-1.40 (28 H, br s, CH_2), 0.88 (3 H, t, *J*=6.8, CH_3).

(5-(Octadecyloxy)-1,3-phenylene)bis(methylene)bis(phenylsulfane) (5). Thiophenol (4 eq) was added to a stirred suspension of NaH (8 eq) in dry THF. The mixture was stirred for 1-1.5 hr to allow the formation of sodium thiophenolate. A solution of compound **4** in dry THF was added dropwise and the mixture was heated to 50 ^{o}C under nitrogen atmosphere overnight. The solvent was evaporated and the reaction mixture was re-dissolved in CH_2Cl_2. Excess NaH was neutralized with HCl solution (1 M). The organic layer was extracted with saturated solution of $NaHCO_3$ and brine, dried over Na_2SO_4, filtered and the solvent was evaporated. The product was purified by column chromatograph (SiO_2, 1:10 ethyl acetate:hexane as eluent) and then recrystallized from hexane or EtOH to give a white solid (75% yield). ^{1}H-NMR (400 MHz, δ_H ppm, $CDCl_3$) 7.22-7.25 (10 H, m, PhS), 6.81 (1 H, s, Ph), 6.70 (2 H, s, Ph), 4.03 (4 H, s, CH_2S), 3.84 (2 H, t, *J*=6.4, OCH_2), 1.71 (2 H, m, OCH_2CH_2), 1.41 (2 H, m, CH_2), 1.25-1.30 (28 H, br s, CH_2), 0.88 (3 H, t, *J*=6.8, CH_3).

(4-(Octadecyloxy)-2,6-bis(phenylthiomethyl)phenyl)palladium(II) chloride (6). The synthesis was performed according to the literature.[Error! Bookmark not defined.] The yellow product was purified by column chromatography (SiO_2, 200:3 CH_2Cl_2:MeOH as eluent) (72% yield). ^{1}H-NMR (400 MHz, δ_H ppm, $CDCl_3$) 7.81 (4 H, m, PhS), 7.36 (6 H, m, PhS), 6.60 (2 H, s, Ph), 4.55 (4 H, br s, CH_2S), 3.86 (2 H, t, *J*=6.4, OCH_2), 1.73 (2 H, m, OCH_2CH_2), 1.41 (2 H, m, CH_2), 1.25-1.30 (28 H, br s, CH_2), 0.88 (3 H, t, *J*=7.2, CH_3).

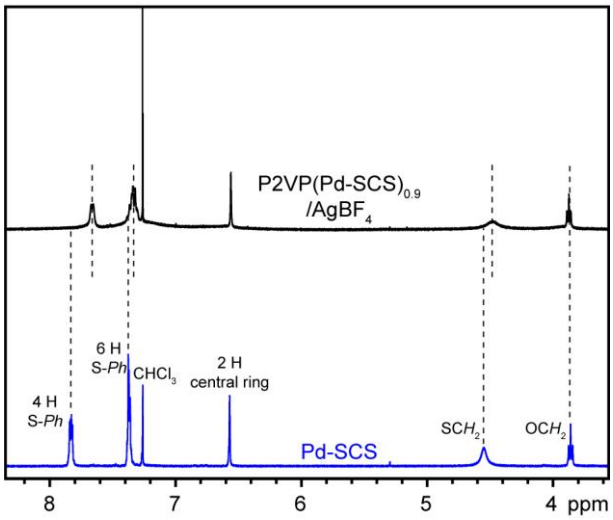

Figure S2. Low field portion of ^{1}H-NMR in $CDCl_3$ of pure Pd-SCS (blue) and P2VP(Pd-SCS)$_{0.9}$/$AgBF_4$ (black). Spectra are offset for clarity.

Table S1. ss-^{13}C-NMR assignment of Pd-SCS and P2VP based on DFT calculations.

Pd-SCS			
assignment	**δ_{exp} (ppm)**	**δ_{calc} (ppm)**	
C19	157	156.2	
C20,C24	111	110.6	106.1[a]
		101.6	
C21,C23	152	147.9	146.9[a]
	153	145.9	
C22	107	179.7	
C25	54	63.7	59.3[a]
		55.0	
C26	130	139.1	129.6[a]
		138.6	
C28,C30		126.8	
		128.4	
		126.6	
		127.5	
C27,C31		119.8	
		131.5	
		128.5	
		136.2	
C29		124.8	
		127.3	
C18	68	56.6	
C4-C17	30-40		
C16			
C3	25		
C2	23		
C1	15		

[a] Average calculated values.

P2VP		
assignment	**δ_{exp} (ppm)**	**δ_{calc} (ppm)**
C3	165	168.6
C7	150	149.2
C5	135	133.6
C4	122	118.4
C6		119.7
C2	40-45	51.3

References

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