Supporting Information

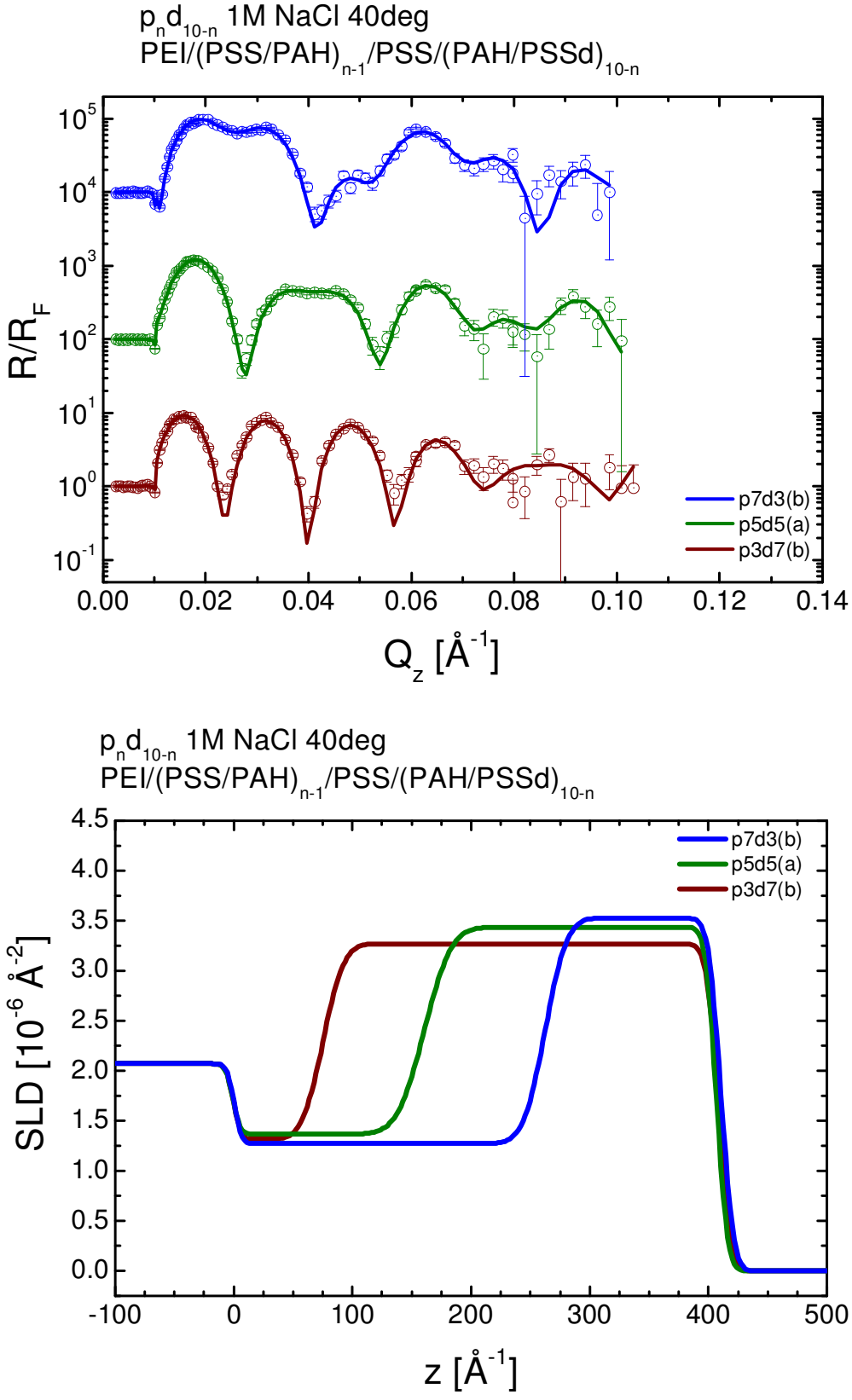

Fig. S1: Normalized reflectivity curves of PAH/PSS films consisting of 10 polyelectrolyte bilayers with corresponding scattering length density profiles. Depicted are the p_3d_7 (dark red), p_5d_5 (green) and p_7d_3 (blue) architecture, all films are prepared at 40°C and 1 M NaCl.

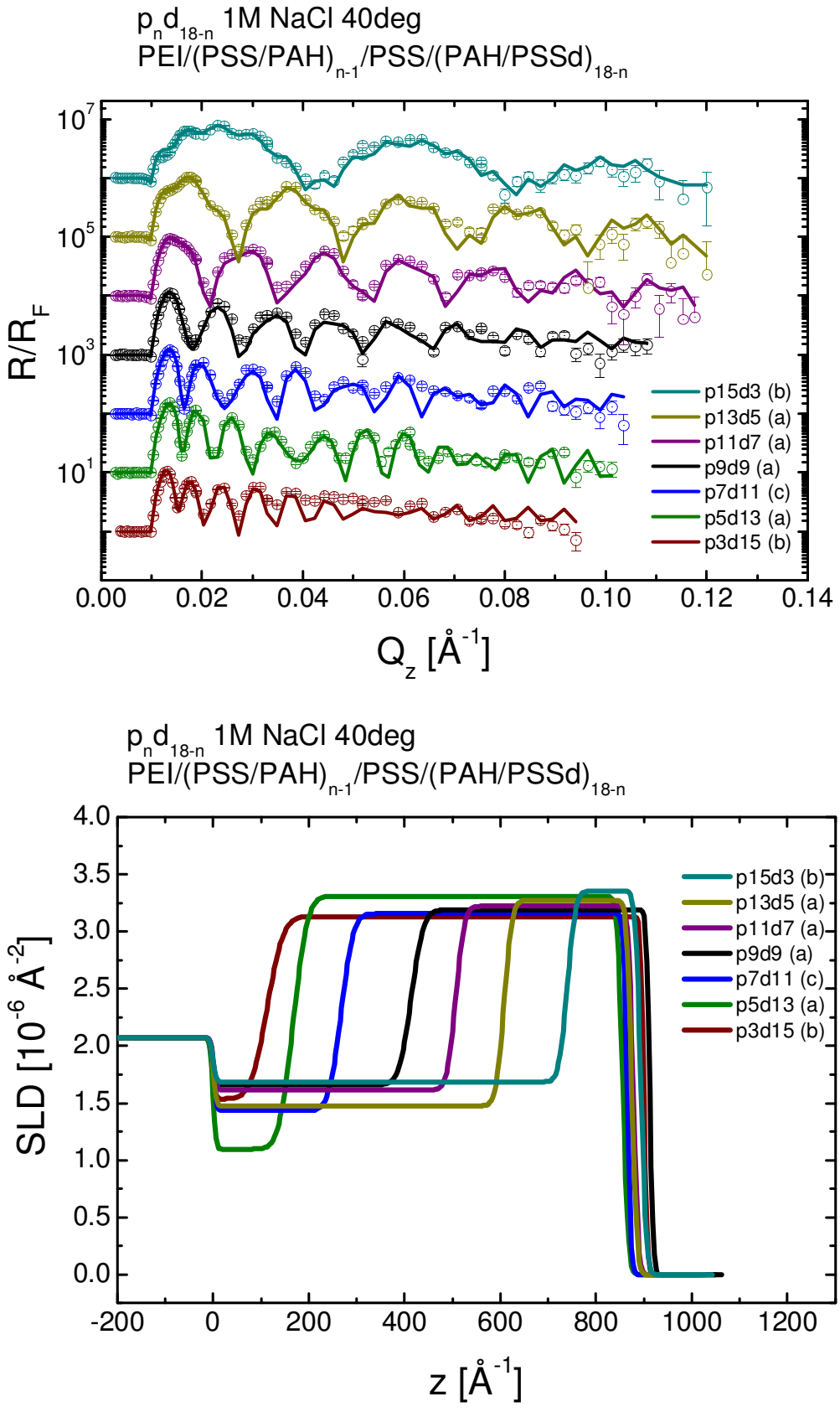

Fig. S2: Normalized reflectivity curves of PAH/PSS films consisting of 18 polyelectrolyte bilayers with corresponding scattering length density profiles. All films are prepared at 40°C and 1 M NaCl.

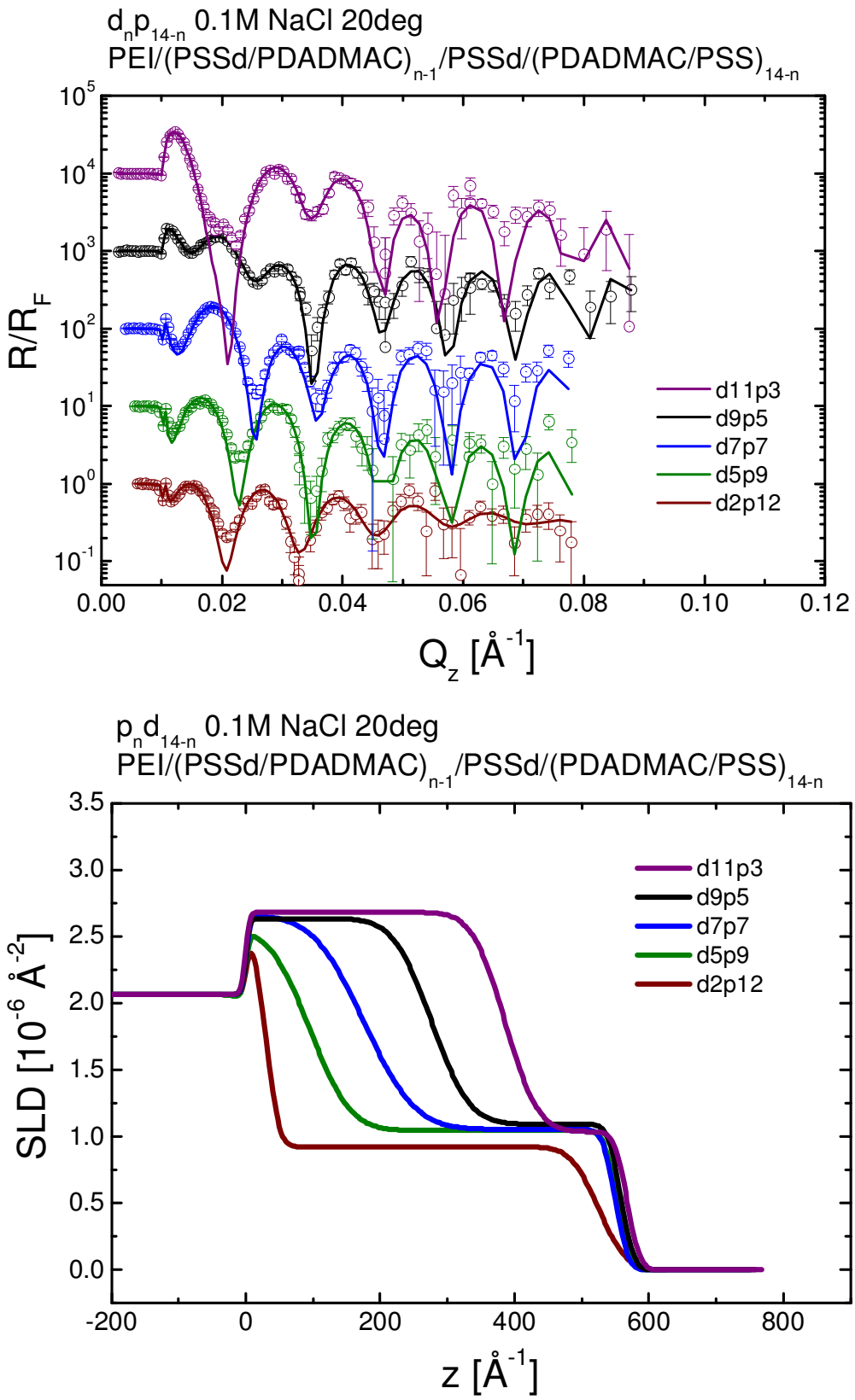

Fig. S3: Normalized reflectivity curves of PDADMAC/PSS films consisting of 14 polyelectrolyte bilayers with corresponding scattering length density profiles. Depicted are the d_2d_{12} (dark red), d_5p_9 (green), d_7p_7 (blue), d_9p_5 (black) and $d_{11}p_3$ (violet) architecture, all films are prepared at 20°C and 0.1 M NaCl.

Parameter Tables

210kDa PDADMAC: @ 0.1M NaCl, 20°C

	p_3d_{11}		p_5d_9		p_7d_7		p_9d_5		$p_{11}d_3$	
	prot.	deut.	prot.	deut.	prot.	deut.	prot.	deut.	prot.	deut.
D_{PEM} [Å]	64.46	521.50	102.4	464.6	184.2	377.9	270.7	283.8	364.5	177.7
D_{BL} [Å]	*21.48*	*47.41*	*20.48*	*51.62*	*26.31*	*53.99*	*30.08*	*56.76*	*33.14*	*59.23*
SLD [10^{-6}Å^{-2}]	1.780	2.633	1.361	2.669	1.266	2.666	1.22	2.633	1.164	2.557
n_{Water}	*-3.2*	*1.6*	*-1*	*1.5*	*-0.3*	*1.5*	*0*	*1.6*	*0.5*	*2*
σ_{int} σ_{air}	32.23	15.33	51.20	14.03	52.69	14.93	47.95	14.02	40.74	12.99
	$p_{12}d_2$									
	prot.	deut.								
D_{PEM} [Å]	407.7	118.9								
D_{BL} [Å]	*33.97*	*59.45*								
SLD [10^{-6}Å^{-2}]	1.167	2.594								
n_{Water}	*0.5*	*1.9*								
σ_{int} σ_{air}	34.56	11.89								

Table S1: Parameter tables for the Fits depicted in Figure 1, bottom. The free parameters are the thickness for the protonated and deuterated block (D_{PEM}), the corresponding scattering length densities SLD, and the internal roughness σ_{int} and the film/air roughness σ_{air}. The water content and the average bilayer thickness in the respective blocks are derived quantities.

PAH/PSS @ 1M NaCl, 40°C

14 BL			p_5d_9		p_7d_7		p_9d_5		$p_{11}d_3$	
			prot.	deut.	prot.	deut.	prot.	deut.	prot.	deut.
D_{PEM} [Å]			180.7	488.8	287.9	373.4	392.5	256.7	495.3	153.7
D_{BL} [Å]			*36.14*	*54.31*	*41.13*	*53.34*	*43.57*	*51.34*	*45.02*	*51.23*
SLD [10^{-6}Å^{-2}]			1.63	3.32	1.69	3.38	1.60	3.36	1.50	3.41
n_{Water}			*-0.3*	*1.8*	*-0.5*	*1.6*	*-0.2*	*1.7*	*0.3*	*1.5*
σ_{int} σ_{air}			19.07	8.82	16.4	8.07	13.16	9.47	12.48	8.78

Table S2: Parameter tables for the Fits depicted in Figure 1, center. The symbols are explained in the Caption to Table 1.

PAH/PSS @ 1M NaCl, 40°C

10BL	p_3d_7		p_5d_5		p_7d_3	
	prot.	deut.	prot.	deut.	prot.	deut.
D_{PEM} [Å]	75.4	333.6	161.3	246.3	262.0	148.3
D_{BL} [Å]	*25.12*	*47.66*	*32.26*	*49.26*	*37.43*	*49.43*
SLD [10^{-6}Å^{-2}]	1.31	3.27	1.37	3.43	1.27	3.52
n_{Water}	*1.4*	*2.0*	*1.0*	*1.5*	*1.6*	*1.2*
σ_{int} σ_{air}	13.81	8.21	18.02	7.27	14.49	8.30

Table S3: Parameter tables for the Fits depicted in Figure S1. The symbols are explained in the Caption to Table S1.

PAH/PSS @ 1M NaCl, 40°C

18 BL		p_3d_{15}		p_5d_{13}	
		prot.	deut.	prot.	deut.
D_{PEM} [Å]		102.8	774.7	167.6	688.8
D_{BL} [Å]		*34.26*	*51.64*	*33.52*	*52.98*
SLD [10^{-6}Å^{-2}]		1.70	3.37	1.10	3.31
n_{Water}		*-0.6*	*1.6*	*2.8*	*1.8*
σ_{int}	σ_{air}	25.62	8.07	23.44	9.35
		p_7d_{11}		p_9d_9	
		prot.	deut.	prot.	deut.
D_{PEM} [Å]		266.3	597.8	266.3	597.8
D_{BL} [Å]		*38.04*	*54.34*	*38.04*	*54.34*
SLD [10^{-6}Å^{-2}]		1.43	3.16	1.43	3.16
n_{Water}		*0.7*	*2.3*	*0.7*	*2.3*
σ_{int}	20.49	6.53	20.49	6.53	9.22
18 BL		$p_{11}d_7$		$p_{13}d_5$	
		prot.	prot.	prot.	deut.
D_{PEM} [Å]		505.5	267.0	267.0	607.5
D_{BL} [Å]		*45.95*	*46.73*	*46.73*	*53.40*
SLD [10^{-6}Å^{-2}]		1.62	1.48	1.48	3.27
n_{Water}		*-0.2*	*0.4*	*0.4*	*1.9*
σ_{int}	14.72	13.56	13.56	13.56	8.58
18 BL		$p_{15}d_3$			
		prot.	prot.		
D_{PEM} [Å]		740	740		
D_{BL} [Å]		*49.33*	*49.33*		
SLD [10^{-6}Å^{-2}]		1.69	1.69		
n_{Water}		*-0.5*	*-0.5*		
σ_{int}	13.97	13.97			

Table S4: Parameter tables for the Fits depicted in Figure S2. The symbols are explained in the Caption to Table S1.

210kDa PDADMAC: @ 0.1M NaCl, 20°C

14BL		d_5p_9		d_7p_7		d_9p_7		d_9p_5		$d_{11}p_3$	
		deut.	prot.	deut.	prot.	deut.	prot.	deut.	prot.	deut.	prot.
D_{PEM} [Å]		96.19	454.8	171.3	378.1	294.6	385.9	277.9	277.3	390.8	180.7
D_{BL} [Å]		*19.23*	*50.53*	*24.47*	*54.01*	*32.77*	*55.08*	*30.81*	*55.58*	*35.52*	*60.23*
SLD [10^{-6}Å^{-2}]		2.569	1.047	2.639	1.052	2.633	1.075	2.628	1.016	2.634	0.958
n_{Water}		*1.5*	*1.5*	*1.6*	*1.9*	*1.6*	*1.2*	*1.8*	*1.7*	*1.6*	*3.8*
σ_{int}	σ_{air}	48.95	15.0	59.18	7.92	57.36	10.72	41.49	6.71	37.23	6.72

Table S5: Parameter tables for the Fits depicted in Figure S3. The symbols are explained in the Caption to Table S1.

PAH/PSS @ 1 M NaCl, 40°C

19BL		$p_3(d_1p_3)_4$		
		p_3	d_1	p_3
D_{PEM} [Å]		127	49.97	149.91
D_{BL} [Å]		*42.33*	*49.97*	*49.97*
SLD [10^{-6}Å^{-2}]		1.26	3.33	1.40
n_{Water}		*1.7*	*1.8*	*0.9*
σ_{int}	σ_{air}	16.3		17.3

Table S6: Parameter assignment for the fit to the superstructure with a constant internal roughness, cf. Fig. 4. Another assumption is that each bilayer has the same thickness except the precursor zone. Free parameters are given in the first, third and last row.