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Supplementary Materials for

Progressive fuzzy cation-π assembly of biological catecholamines

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The PDF file includes:

Other Supplementary Material for this manuscript includes the following:

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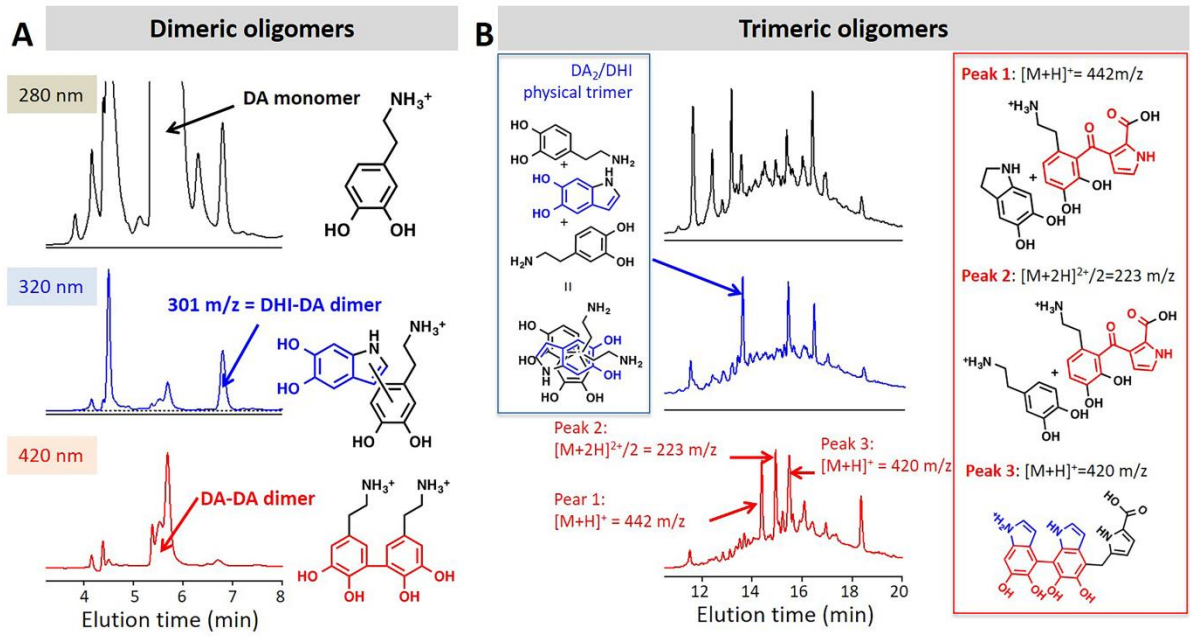


Fig. S1. Chemical structure of oligomers formed during polydopamine coating under St-Bc pH conditions analyzed by HPLC-MS with a C18 column. (**A**) Dimeric intermediates detected at approximately 4-8 min of elution time identified by both mass spectra and UV absorbance at 280 nm (black line), 320 nm (blue line), and 420 nm (red line). (**B**) Trimeric oligomers including the pre-defined (dopamine)$_2$/DHI (DA_2/DHI) physical trimer (blue box) and newly identified ones assigned as trimers containing partially opened/degraded DHI subunits (red box).

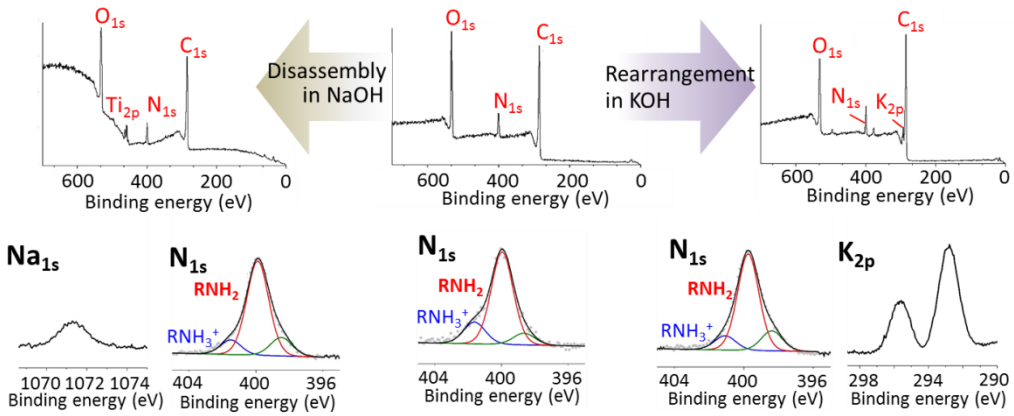


Fig. S2. XPS analyses of polydopamine-coated TiO_2 surfaces after 1 hour of strong base treatment. (i.e., 0.1 N NaOH (pH 11) and 0.1 N KOH (pH 11)). 1st row: survey scan and 2nd row: cation moieties (Na_{1s} and K_{1s}) and nitrogen ($-NH_3^+$ in blue, $-NH_2$ in red, and -NH- in green) species. The protonated amines ($-NH_3^+$) in the polydopamine-coated TiO_2 surface under Md-Bc existed above 35% (401.6-401.8 eV), whereas most protonated amines disappeared after both base treatments (below 8%).

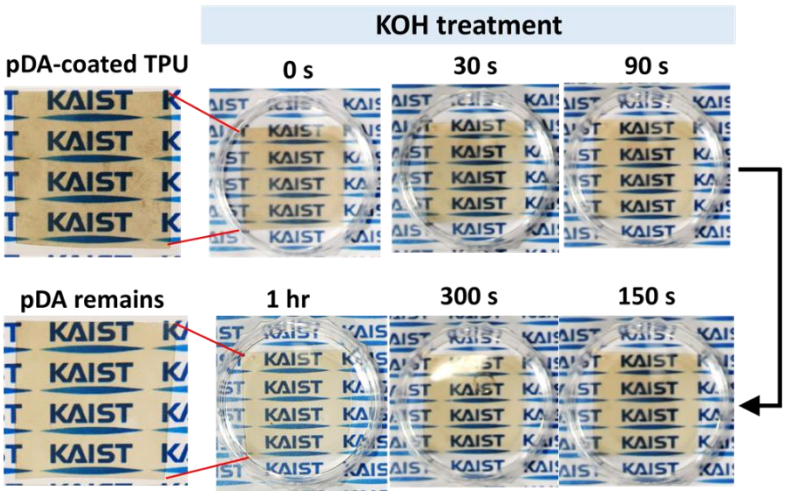
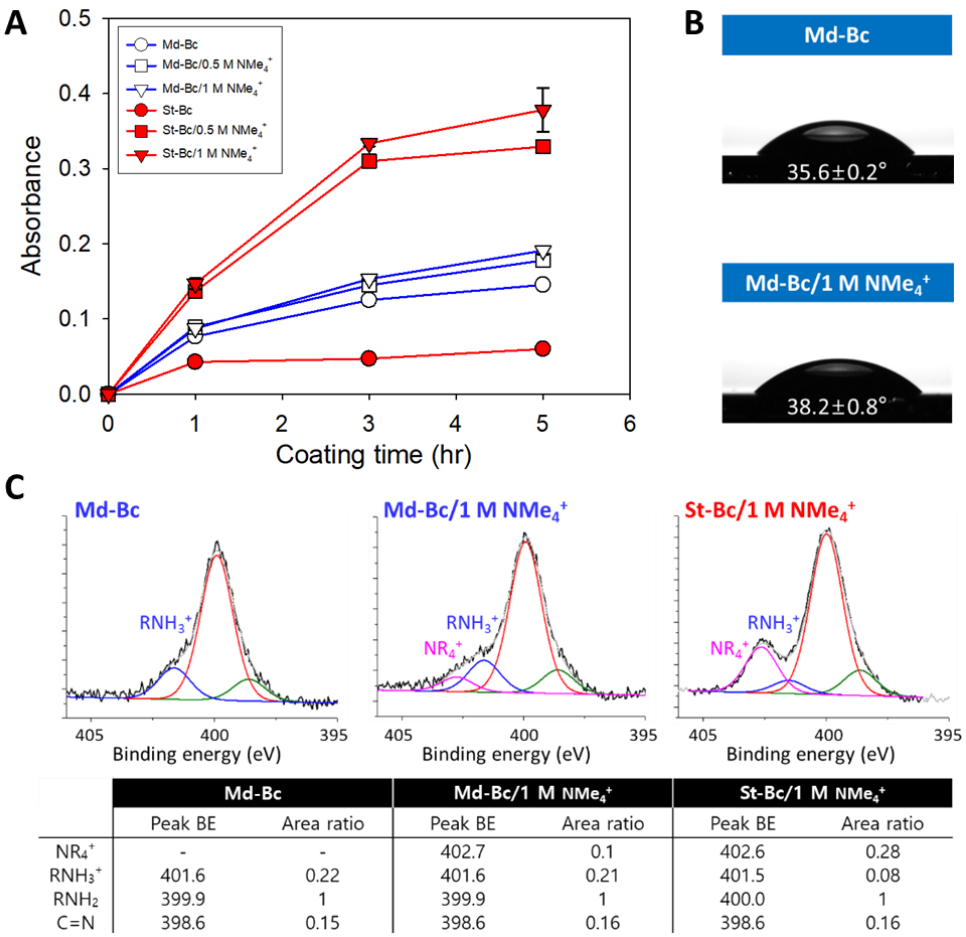


Fig. S3. Maintenance of polydopamine coating on a TPU film in 0.1 N KOH (pH 12) solution for 1 hour.



	Md-Bc		Md-Bc/1 M NMe_4^+		St-Bc/1 M NMe_4^+	
	Peak BE	Area ratio	Peak BE	Area ratio	Peak BE	Area ratio
NR_4^+	-	-	402.7	0.1	402.6	0.28
RNH_3^+	401.6	0.22	401.6	0.21	401.5	0.08
RNH_2	399.9	1	399.9	1	400.0	1
C=N	398.6	0.15	398.6	0.16	398.6	0.16

Fig. S4. Intercalation of NMe_4^+ on polydopamine coating with pH variations. (**A**) The initial polydopamine film growth rate monitored by UV absorption at 400 nm on a transparent glass substrate as the surface color becomes dark brown progressively (Blue lines: Md-Bc, Red lines: St-Bc / circle: no NMe_4^+, square: with 0.5 M NMe_4^+, reverse triangle: with 1 M NMe_4^+). (**B**) Wettability of polydopamine coated substrates in Md-Bc, with (bottom) and without (top) presence of NMe_4^+. (**C**) XPS N_{1s} high resolution analysis of polydopamine coating in Md-Bc (left), Md-Bc with NMe_4^+ (middle), and St-Bc with NMe_4^+ (right): pink line for NMe_4^+, blue line for R- NH_3^+, red line for R-NH_2, and green line for C=N. Peak binding energy (denoted as peak BE) and the area ratio of each nitrogen peak are summarized in a table below the XPS N_{1s} graphs.

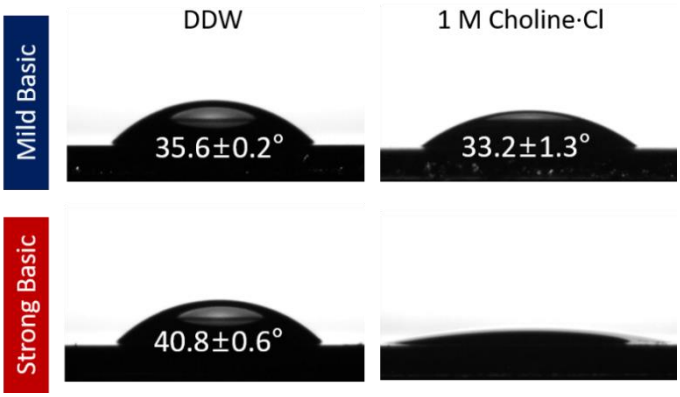


Fig. S5. Wettability of polydopamine-coated substrates in Md-Bc and St-Bc conditions in the presence and absence of 1 M choline, a precursor to neurotransmitter ACh.

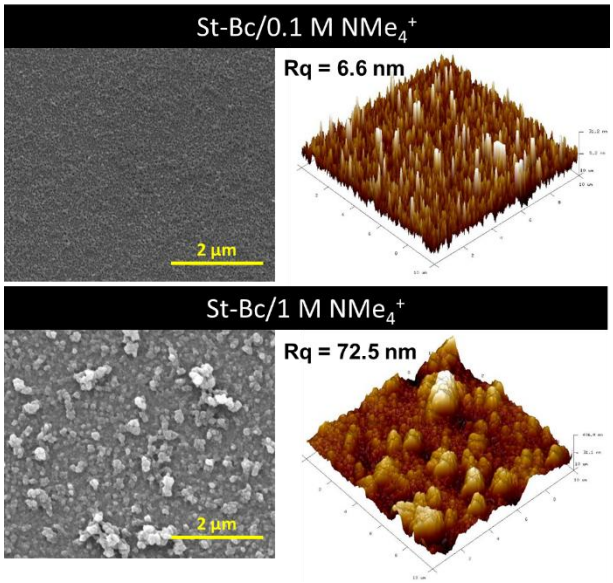


Fig. S6. Surface morphologies of the NMe_4^+-intercalated polydopamine functionalized surfaces at St-Bc with 0.1 M NMe_4^+ (top) and 1 M NMe_4^+ (bottom) by SEM and atomic force microscopy analyses.