Supporting Information

Effect of *N*-Methylation on Dopamine Surface Chemistry

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Number of pages: 14

Number of figures: 8

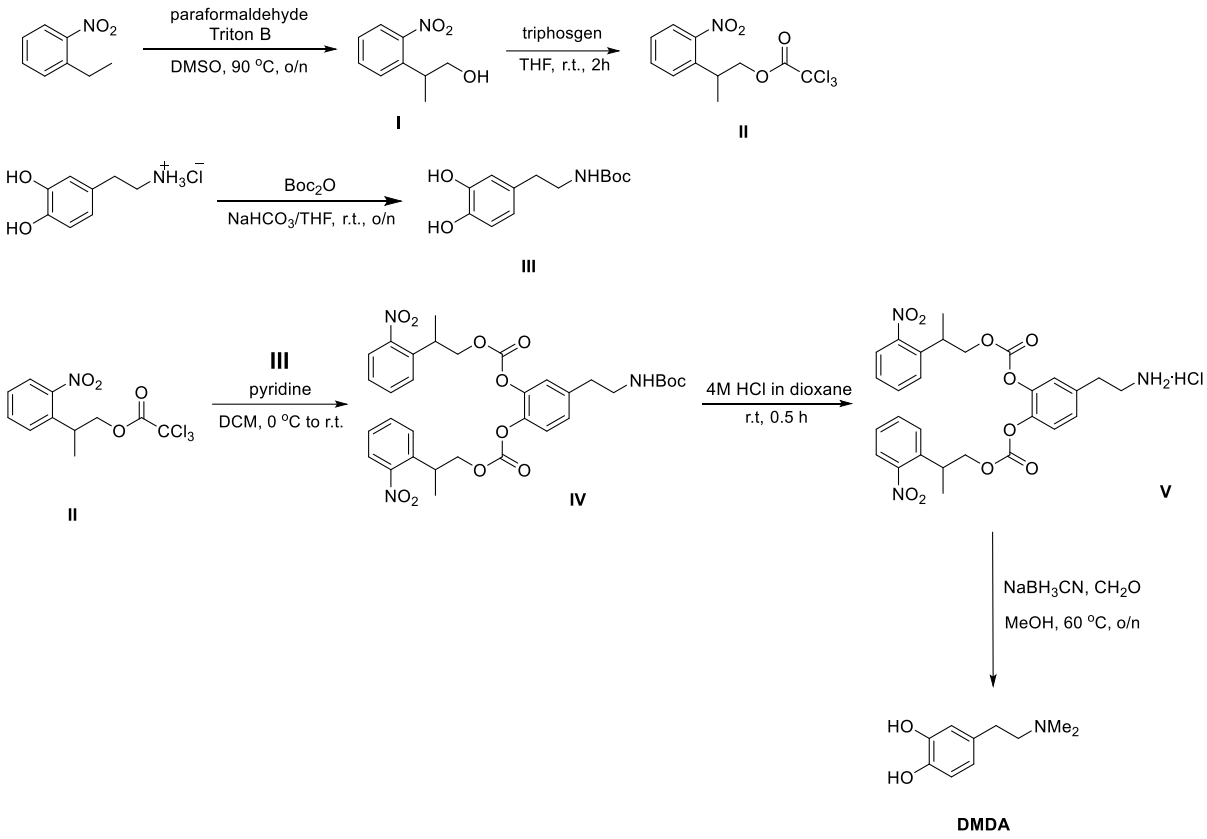


Figure S1. Schematic procedure for DMDA synthesis from 2-ethylnitrobenzene.

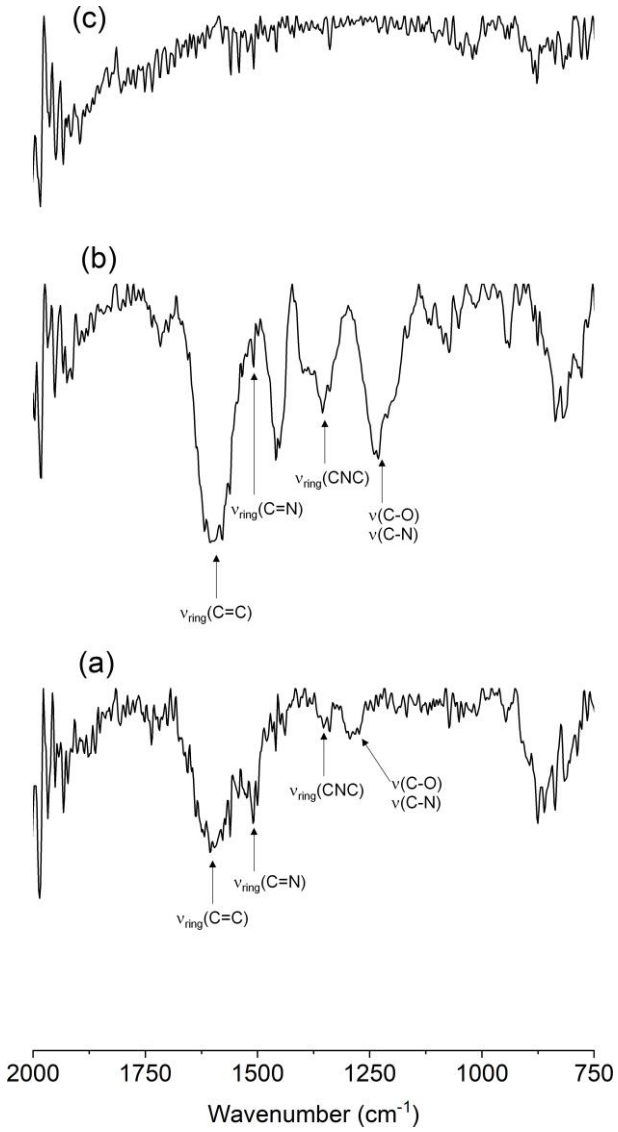


Figure S2. IR spectra of (a) DA-coated, (b) MDA-coated, and (c) DMDA-coated Ti/TiO_2 surfaces.

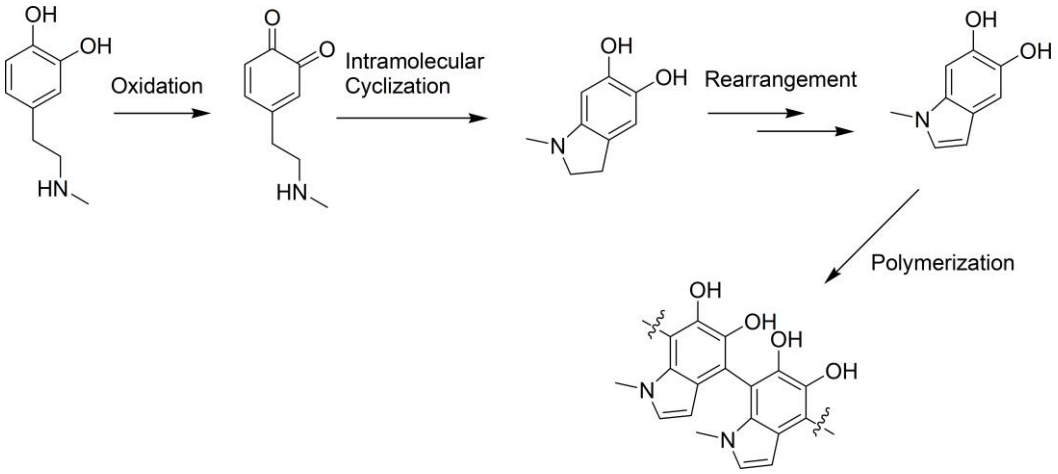


Figure S3. Proposed mechanism of the oxidative polymerization of MDA.

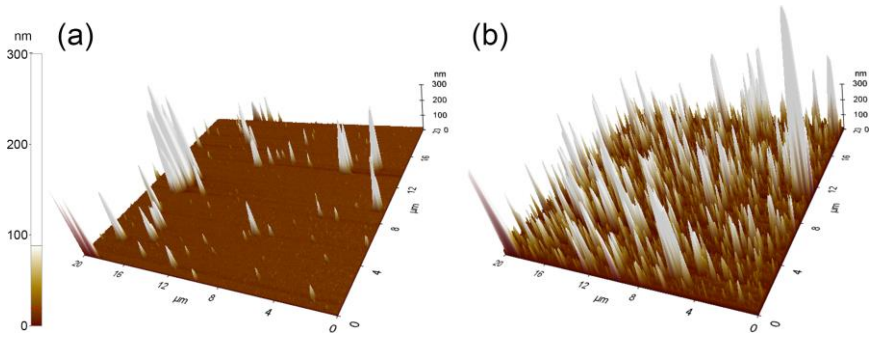


Figure S4. AFM images of (a) DA-coated and (b) MDA-coated Ti/TiO_2 surfaces.

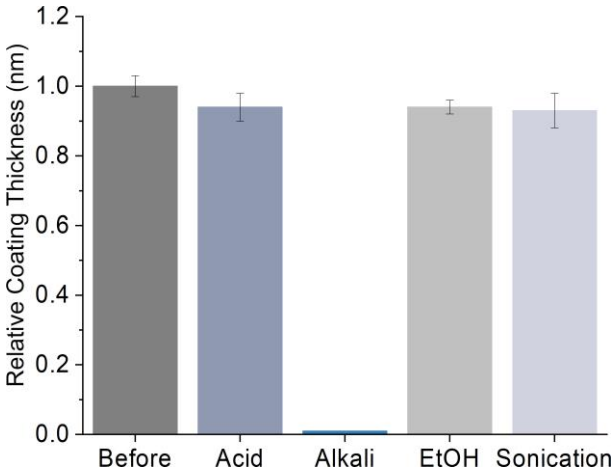


Figure S5. Relative coating thickness of MDA layers on Ti/TiO_2 surfaces before and after acid, alkali, ethanol (EtOH), and sonication treatments. Error bars display the 95% confidence limits.

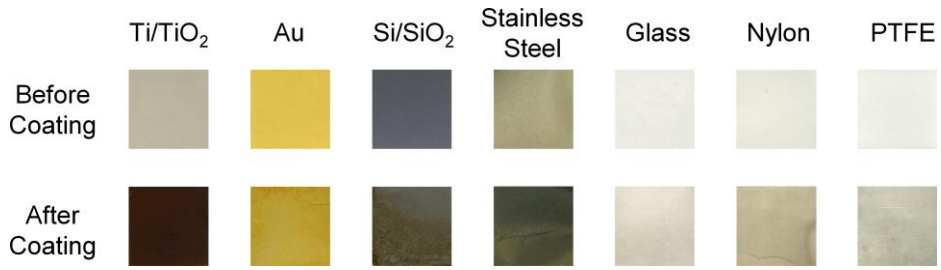


Figure S6. Photographs of various solid substrates before and after MDA coatings.

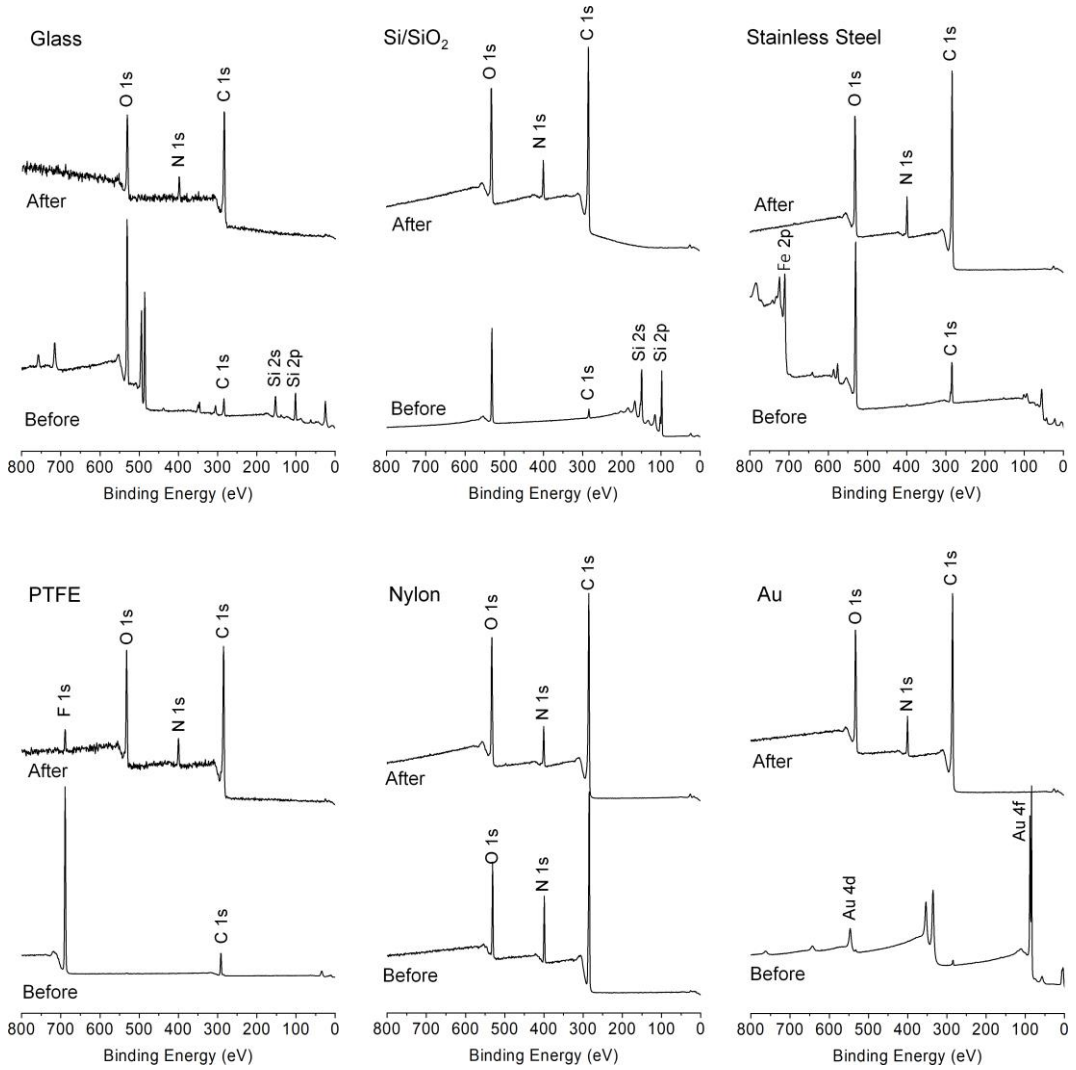


Figure S7. X-ray photoelectron spectra of glass, Si/SiO_2, stainless steel, PTFE, nylon, and Au surfaces before and after MDA coatings.

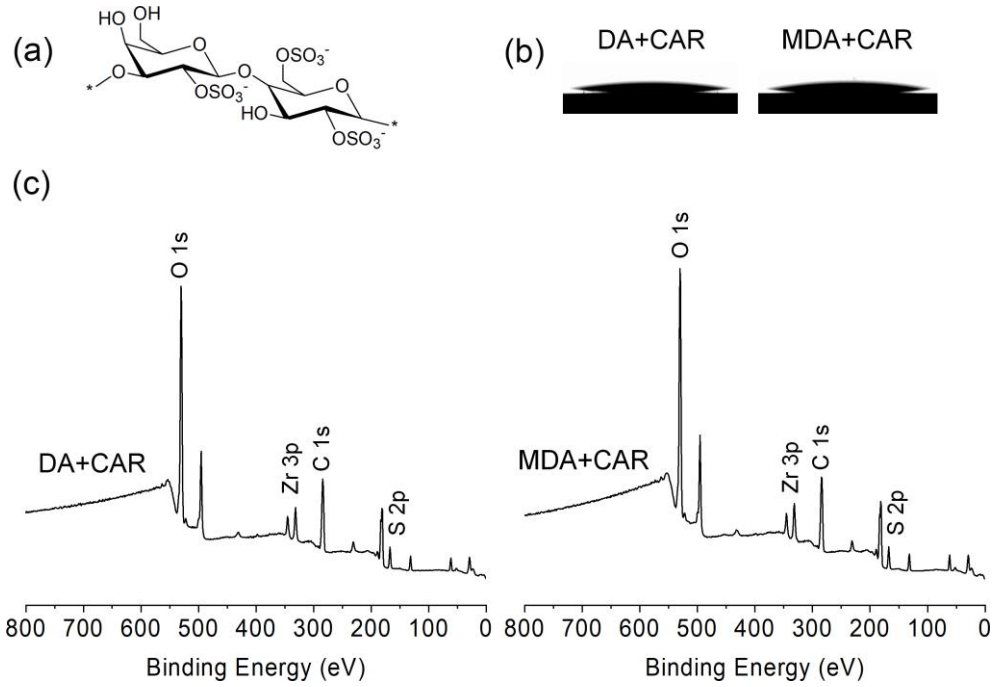
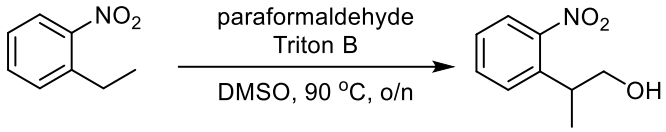


Figure S8. (a) Chemical structure of λ-carrageenan (CAR). (b) Water contact angle images and (c) XPS spectra of CAR-grafted DA and MDA coatings (solid substrate: Ti/TiO_2).

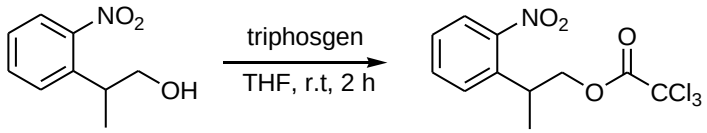
Synthesis of 2-(2-nitrophenyl)propanol (I)



I

After dissolve 2-ethylnitrobenzene (8.0 mL, 60 mmol) in dimethylsulfoxide (DMSO, 80 mL), Triton B (40% w/w in MeOH, 0.72 mL) and *para*-formaldehyde (740 mg, 20 mmol) were added to solution. The reaction mixture was refluxed for overnight at 90 °C. After completion (monitored by TLC), the reaction mixture was cooled to room temperature and neutralized with 1.0 M aqueous HCl solution. The organic layer was extracted with ethyl acetate (EtOAc, 3×2 5mL) and dried over $MgSO_4$. The solvent was removed under the reduced pressure. A dark red oil was obtained with the flash column chromatography. ^{1}H NMR (500 MHz, chloroform-*d*) δ: 1.24 (3H, d, *J* = 6.9 Hz), 1.98 (1H, s), 3.37-3.48 (1H, m), 3.68 (2H, m), 7.25-7.31 (1H, m), 7.40-7.43 (1H, m), 7.47-7.53 (1H, m), 7.65-7.68 (1H, m); ^{13}C NMR (125 MHz, chloroform-*d*) δ: 17.6, 36.4, 67.9, 124.1, 127.2, 128.2, 132.7, 138.1, 150.7.

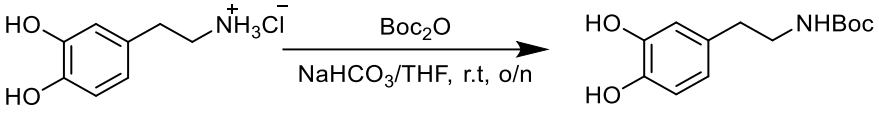
Synthesis of 2-(2-nitrophenyl)propyl 2,2,2-trichloroacetate (II)



I II

A solution of I (710 mg, 4.0 mmol) in THF (20 mL) was cooled to 0 °C. Then, a solution of triphosgen (15% w/w in toluene, 6.4 mL) was added to THF solution for 10 min (by dropwise). The reaction mixture was stirred for 2 h at room temperature. Excess of triphosgene was removed via N_2-flush. The solvent was subsequently removed under reduced pressure. After drying in high vacuum, the desired compound was obtained as brownish oil and was reacted immediately with *N*-Boc dopamine (**III**).

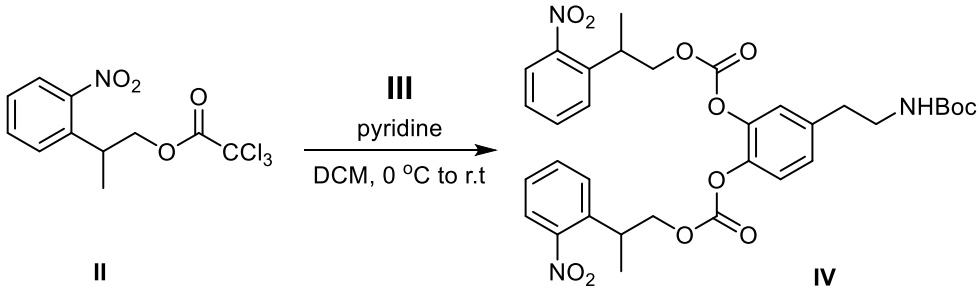
Synthesis of *N*-Boc dopamine (III)



III

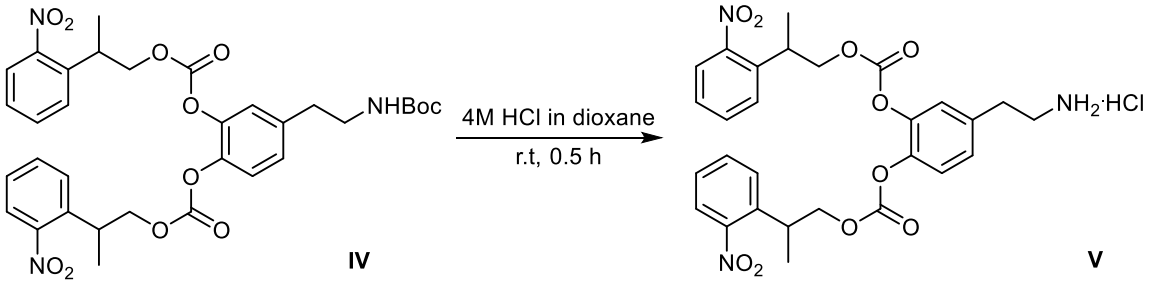
Boc_2O (632 mg, 2.86 mmol) was added to a solution of dopamine·HCl (500 mg, 2.60 mmol) in a mixture of THF (5.3 mL) and saturated aqueous $NaHCO_3$ solution (3.2 mL). The reaction mixture was stirred at room temperature for overnight. The aqueous layer was extracted with EtOAc (3×10 mL) and washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to yield as a white solid (623 mg, 99%). **III** was reacted immediately with **II** (without further purification).

Synthesis of *N*-Boc-(2-(2-nitrophenyl)propoxycarbonyl)$_2$ dopamine (IV)



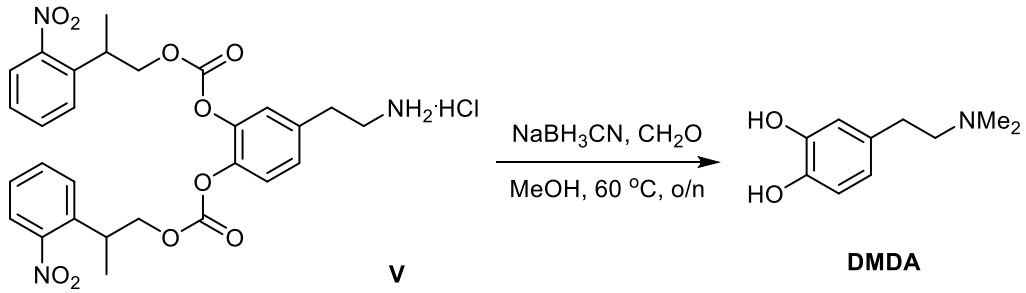
[Main reaction and storage of IV should be performed without light] After dissolve **III** (**9c**, 400 mg, 1.8 mmol) in dichloromethane (DCM, 4.0 mL), pyridine (0.40 mL, 8.0 mmol) was added slowly to the DCM solution at 0 °C. A solution **II** (972 mg, 4.0 mmol) in DCM (4.0 mL) was added to the mixture slowly (by dropwise). The reaction mixture was warmed up to room temperature and stirred overnight. After completion (monitored by TLC), the reaction mixture was transferred to a separatory funnel and diluted with DCM (50 mL). The organic layer was washed with brine (50 mL) and 10% aqueous $NaHCO_3$ solution (50 mL). Then, the organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. A brownish oil (0.52 g, 43%) is obtained by flash column chromatography (MeOH:DCM = 1:50). ^{1}H NMR (500 MHz, chloroform-*d*) δ: 1.37-1.39 (6H, t, *J* = 1.1 Hz), 1.42 (9H, s), 2.75-2.78 (2H, t, *J* = 6.9 Hz), 3.32-3.34 (2H, t, *J* = 6.3 Hz), 3.73-3.78 (2H, m), 4.36-4.43 (4H, m), 4.62 (1H, s, br), 7.03-7.13 (3H, m), 7.36-7.39 (2H, m), 7.47-7.49 (2H, m), 7.55-7.58 (2H, m), 7.76-7.78 (2H, m); ^{13}C NMR (125 MHz, chloroform-*d*) δ: 17.7, 28.4, 33.3, 35.6, 53.5, 72.4, 79.4, 123.0, 123.2, 124.4, 127.2, 127.7, 128.3, 128.3, 128.4, 132.8, 136.5, 136.6, 138.3, 140.7, 142.1, 150.1, 152.4, 152.5, 155.8.

Synthesis of (2-(2-nitrophenyl)propoxycarbonyl)$_2$ dopamine·HCl (V)



[Main reaction and storage of IV should be performed without light] IV (547 mg, 0.82 mmol) was added to 4 M HCl/dioxane (22 mL) solution, and the mixture was stirred at room temperature for 30 min. The solvent was removed under reduced pressure to obtain an ivory powder (222 mg, 68%). ^{1}H NMR (500 MHz, DMSO-d_6) δ: 1.30-1.31 (6H, d, J = 6.8 Hz), 2.94-2.95 (2H, t, J = 5.4 Hz), 3.03 (2H, s), 3.54-3.57 (2H, m), 4.37-4.43 (4H, m), 7.23-7.28 (3H, m), 7.49-7.53 (2H, m), 7.49-7.53 (2H, m), 7.68-7.72 (2H, m), 7.84-7.87 (2H, m) 8.30 (3H, s, br); ^{13}C NMR (125 MHz, DMSO-d_6) δ: 17.9, 17.9, 32.5, 33.3, 72.6, 72.6, 123.7, 123.7, 124.4, 124.4, 127.9, 128.5, 128.6, 129.0, 133.5, 133.6, 136.4, 136.4, 137.4, 141.0, 142.1, 150.4, 152.3, 152.3.

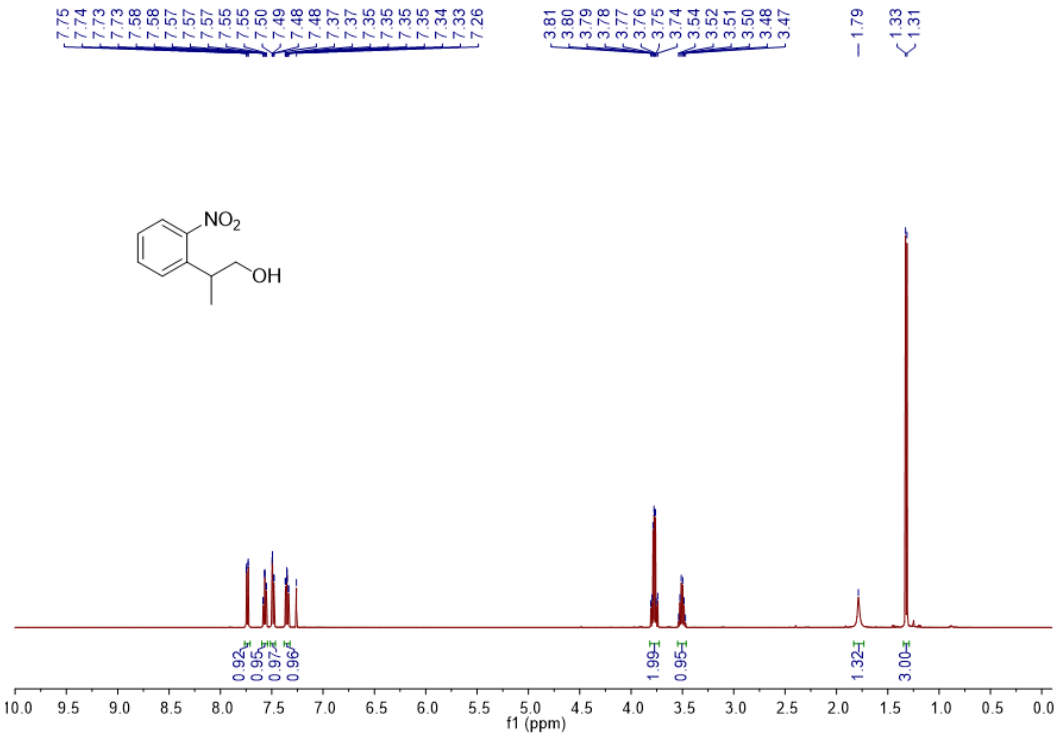
Synthesis of *N,N*-dimethyldopamine (DMDA)

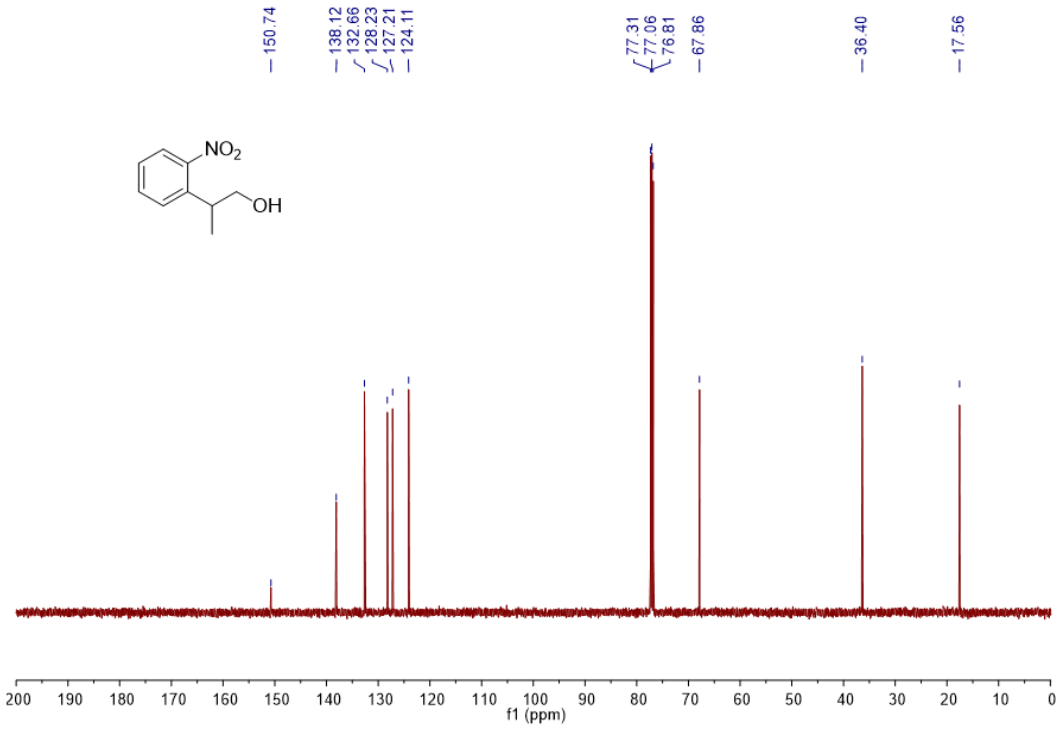


[Main reaction in normal condition with light for *in situ* deprotection] After dissolve **V** (471 mg, 0.831 mmol) in MeOH (1.45 mL), 36% aqueous formaldehyde solution (290 μL) and $NaBH_3CN$ (42.3 mg, 0.673 mmol) were added to the solution. Then, the reaction mixture was stirred at 60 ºC for overnight. After completion (monitored by TLC), the insoluble salts were filtrated out by Celite, and the organic solvent and residues were removed under the reduced pressure. A yellowish brown oil (32 mg, 21.3%) was obtained by flash column chromatography (EtOAc to MeOH). ^{1}H NMR (500 MHz, dimethyl sulfoxide-d_6): 2.73-2.74 (6H, m), 2.82-2.84 (2H, m), 3.11-3.15 (2H, m), 6.47-6.70 (3H, m), 8.98 (2H, br); ^{13}C NMR (125 MHz, dimethyl sulfoxide-d_6) δ: 29.3, 41.9, 48.6, 57.6, 115.9, 116.3, 119.3, 127.6, 144.1, 145.4. High Resolution MS (ESI) Calculated for [DMDA+H^+; $C_{10}H_{16}NO_2^+$] = 182.1176; Found = 182.1171.

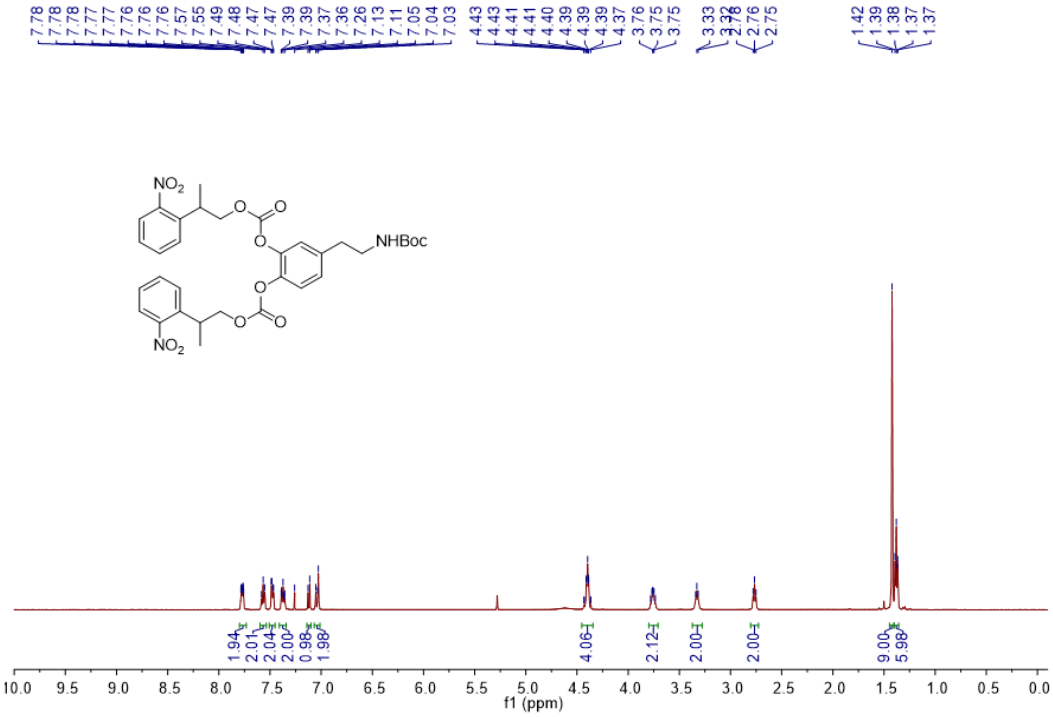
[Appendix: ^{1}H NMR and ^{13}C NMR]

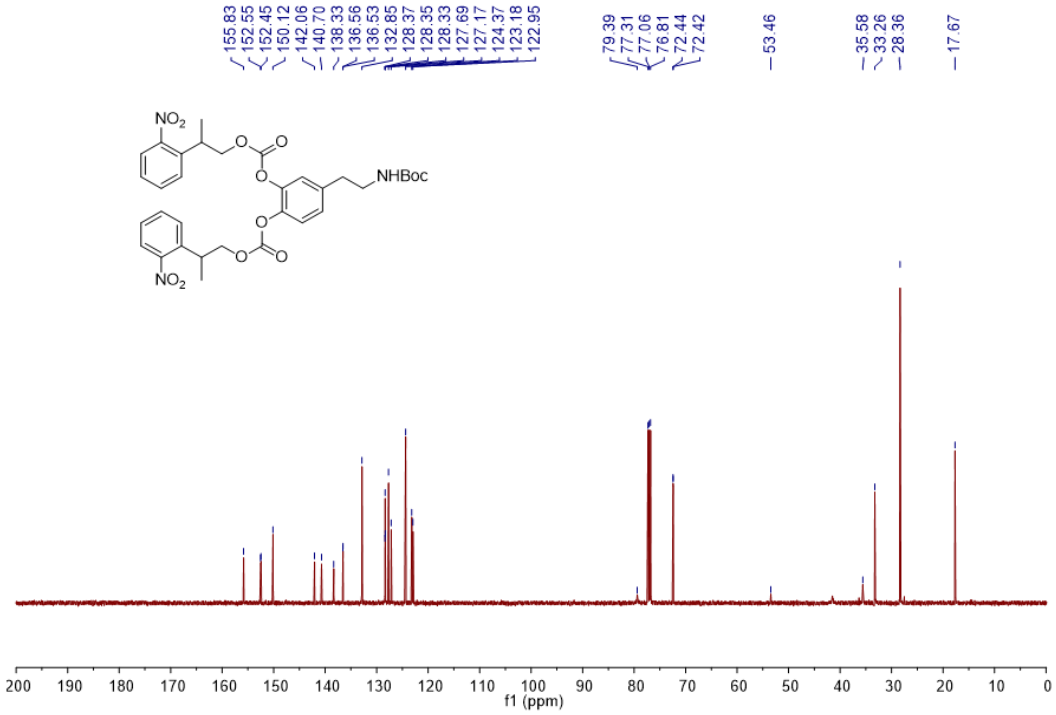
2-(2-Nitrophenyl)propanol (**I**)



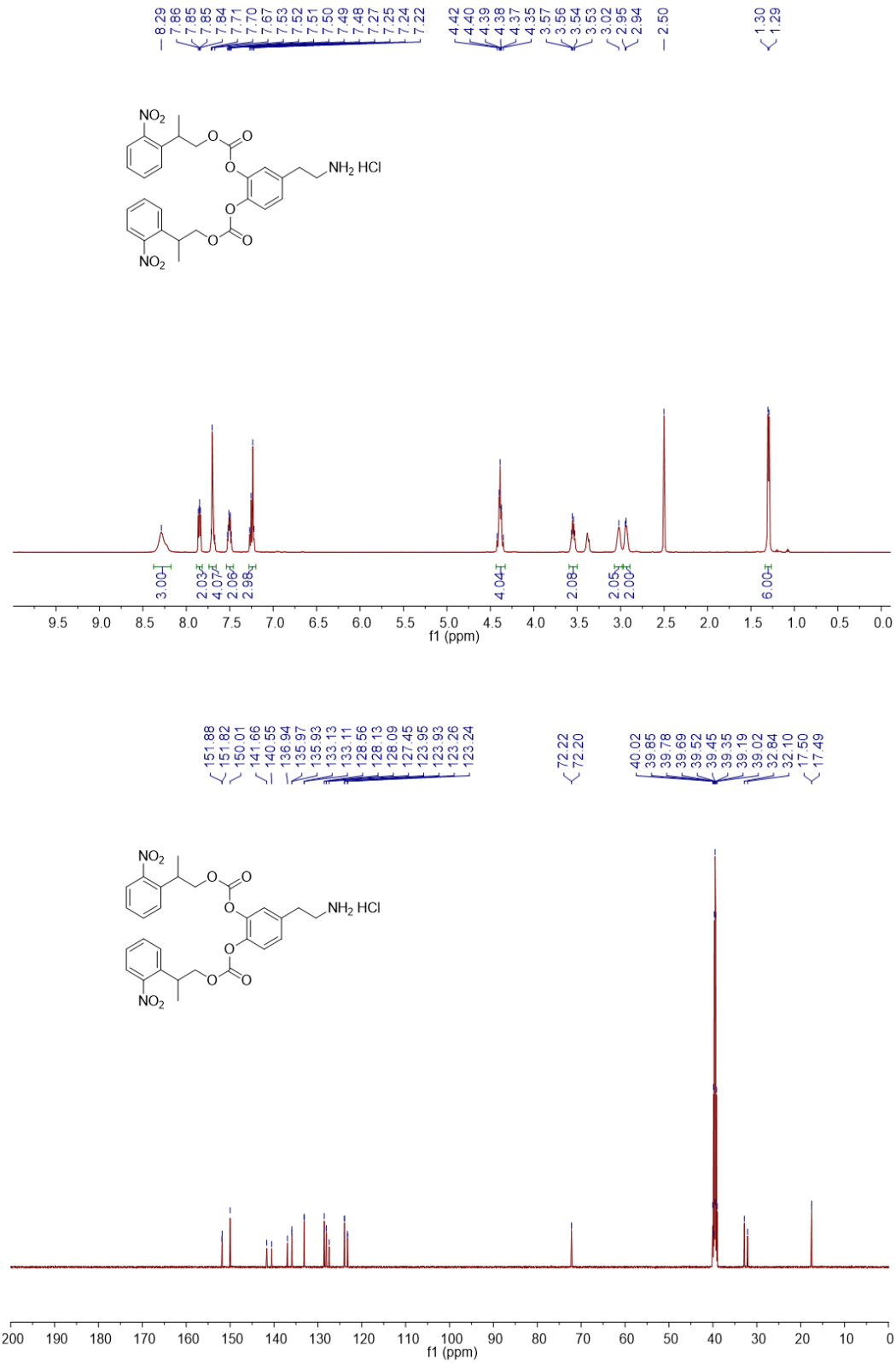


N-Boc-(2-(2-nitrophenyl)propoxycarbonyl)$_2$dopamine (**IV**)





(2-Nitrobenzyloxy)$_2$dopamine·HCl (**V**)



N,N-Dimethyldopamine (**DMDA**)