Electronic Supplementary Material (ESI) for Nanoscale.

A one step method for the functional and property modification of DOPA based nanocoatings

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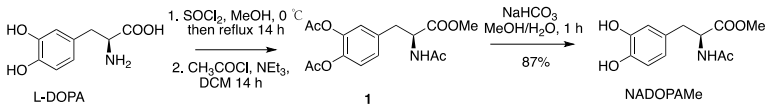
Supporting information

1. **Synthesis of *N*-Ac-3,4-dihydroxyphenylalanine methyl ester (NADOPAMe)**
2. **Coating Study and Characterization of Coating Films**
3. **Redox-Responsive Degradation and Release Study of NADOPAMe/10 film**

1. Synthesis of *N*-Ac-3,4-dihydroxyphenylalanine methyl ester (NADOPAMe)

NADOPAMe was synthesized following the reported method as shown **in Scheme S1**.[1,2] All other reagents and solvents were purchased from Sigma Aldrich or Alfa Aesar and were used without further purification unless otherwise specified. NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at 400 MHz for ^{1}H and at 100 MHz for ^{13}C with methanol-d_4 and chloroform-d as solvents. The chemical shifts are given in ppm, using the proton solvent residue signal (CD_3OD: δ 3.31) as a reference in the ^{1}H NMR spectrum. The deuterium coupled signal of the solvent was used as a reference in ^{13}C NMR (CD_3OD: δ 49.00). The following abbreviations were used to describe the signals: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet. Mass spectra were recorded on an Applied Biosystems MDS SCIEX API 2000 mass spectrometer using ESI-MS.



Scheme S1 The synthesis of NADOPAMe.

$SOCl_2$ (2.50 mL, 3.40 mmol) was added dropwise to a solution of L-DOPA (5.00 g, 2.50 mmol) in MeOH (10 mL) at 0 °C under nitrogen. The reaction mixture was refluxed overnight, following which the mixture was concentrated and re-dissolved in dry dichloromethane (DCM) (10 mL). To the mixture was added triethylamine (17.5 mL, 12.5 mmol) and acetyl chloride (9 mL, 12.5 mmol) and stirred overnight at room temperature. The reaction mixture was diluted with ethyl acetate (200 mL) and washed with water, brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to afford **1** as a white solid.

$NaHCO_3$ (1.87 g, 22.2 mmol) was added to a solution of DOPA derivative **1** (1.50 g, 4.44 mmol) in MeOH (10 mL) / H_2O (2 mL) mixture and stirred for 1 h. The reaction mixture was acidified with 3 N HCl and extracted with ethyl acetate (3 x 50 mL). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by column chromatography (3% MeOH/DCM, one drop of AcOH) to provide NADOPAMe (1.0 g,

87%), as a light yellow solid.

Characterization of NADOPAMe

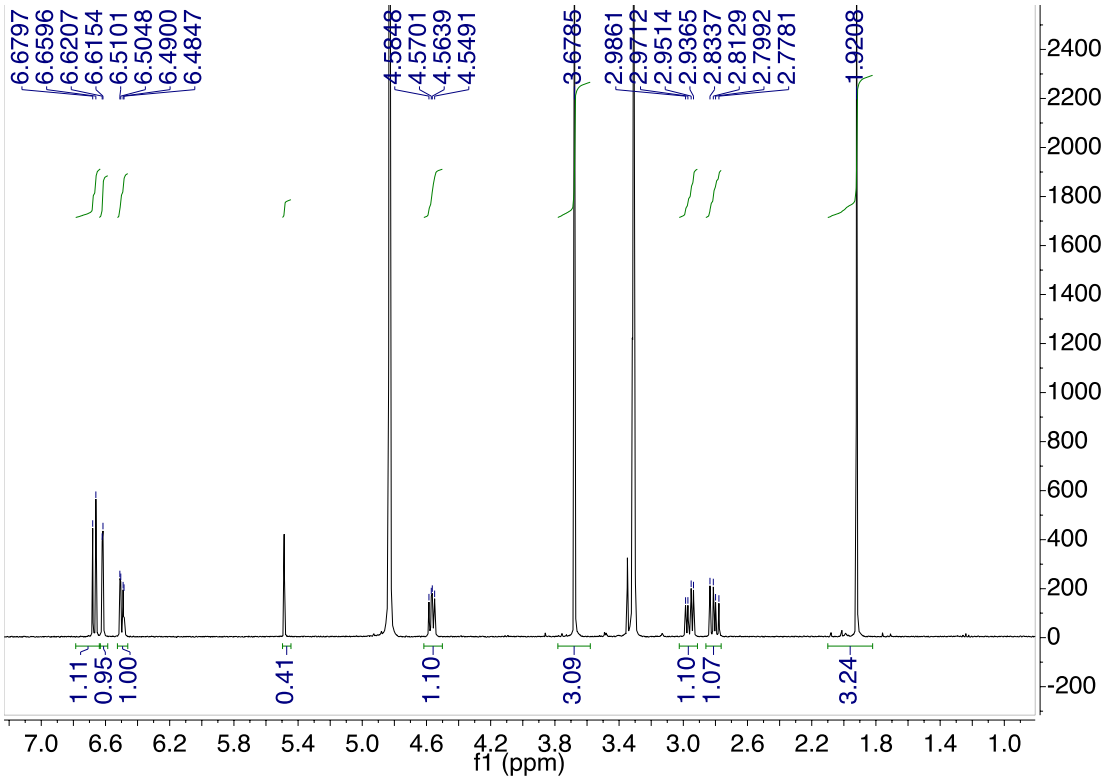
^{1}H NMR (400 MHz, CD_3OD) δ 6.67 (d, *J* = 8.0 Hz, 1H), 6.62 (d, *J* = 2.1 Hz, 1H), 6.50 (dd, *J* = 8.0, 2.1 Hz, 1H), 4.57 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.68 (s, 3H), 2.96 (dd, *J* = 13.9, 5.9 Hz, 1H), 2.81 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.92 (s, 3H).
^{13}C NMR (100 MHz, CD_3OD) δ 173.8, 173.1, 146.3, 145.3, 129.4, 121.5, 117.2, 116.3, 55.6, 52.6, 37.9, 22.2.
ESI-MS, *m/z* calcd for $C_{12}H_{16}NO_5$ $[M+H]^+$ 254.26, found 254.15.

References

1. A. Ishida, H. Fujii, T. Nakamura, T. Oh-ishi, K. Aoe, Y. Nishibata and A. Kinumaki, *Chem. Pharm. Bull.*, 1986, **34**.

2. A. Felim, G. Herrera, A. Neudoerffer, M. Blanco, J.-E. O'Connor and M. Largeron, *Chem. Res. Toxicol.*, 2010, **23**, 211-219.

Characterization of NADOPAMe



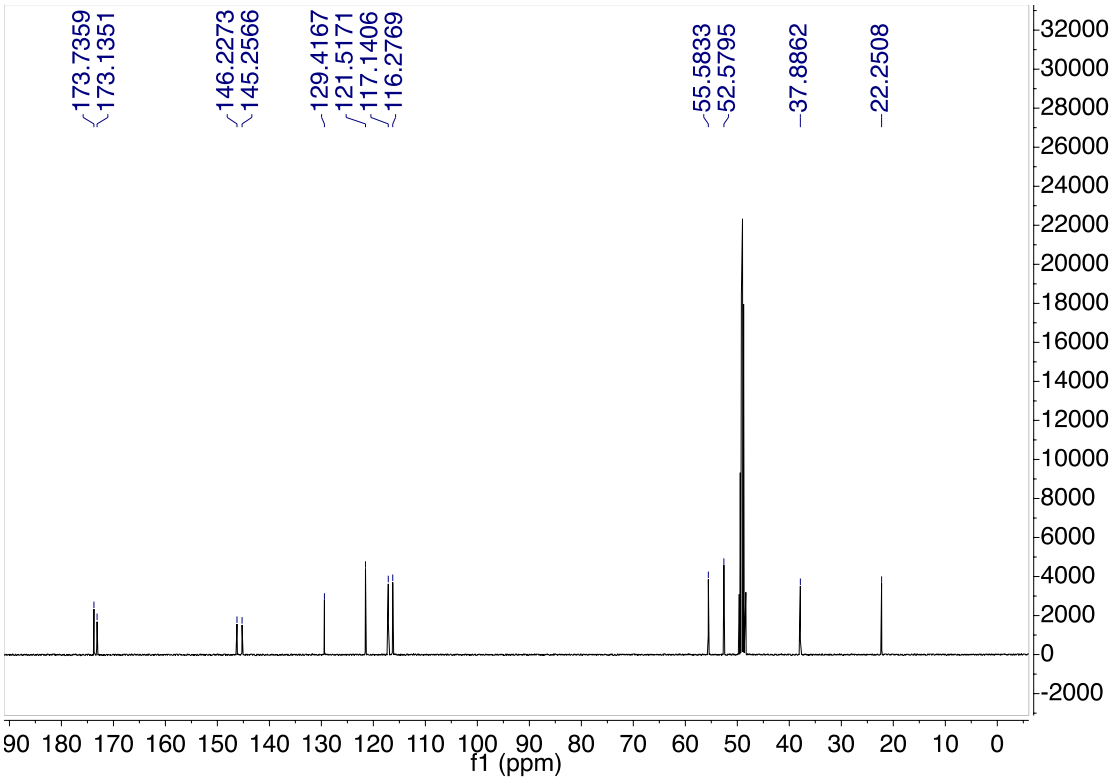


Fig. S1 ^{1}H-NMR and ^{13}C-NMR spectra of NADOPAMe in CD_3OD.

2. Coating Study and Characterization of Coatings

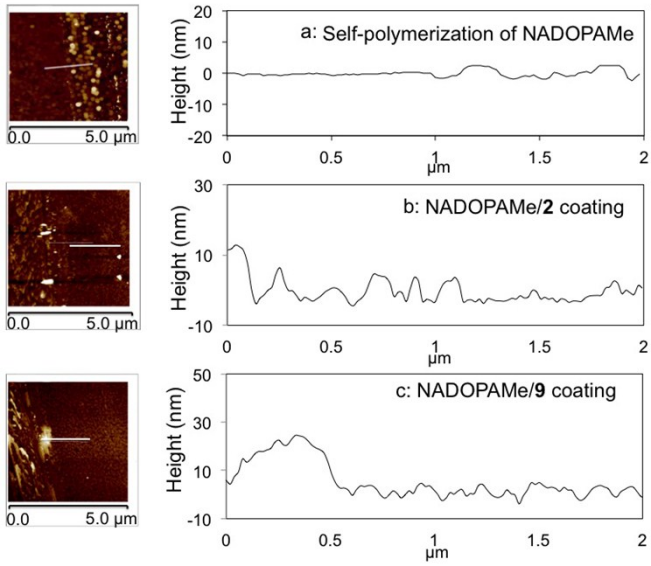


Fig. S2 AFM analysis of (a) coating of NADOPAMe without additives, (b) NADOPAMe/**2** coating and (c) NADOPAMe/**9** coating.

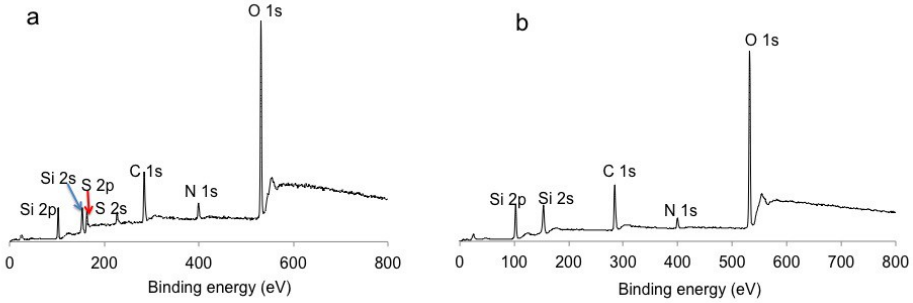


Fig. S3 XPS wide scan spectra of (a) NADOPAMe/**2** and (b) NADOPAMe/**9** on Si wafer.

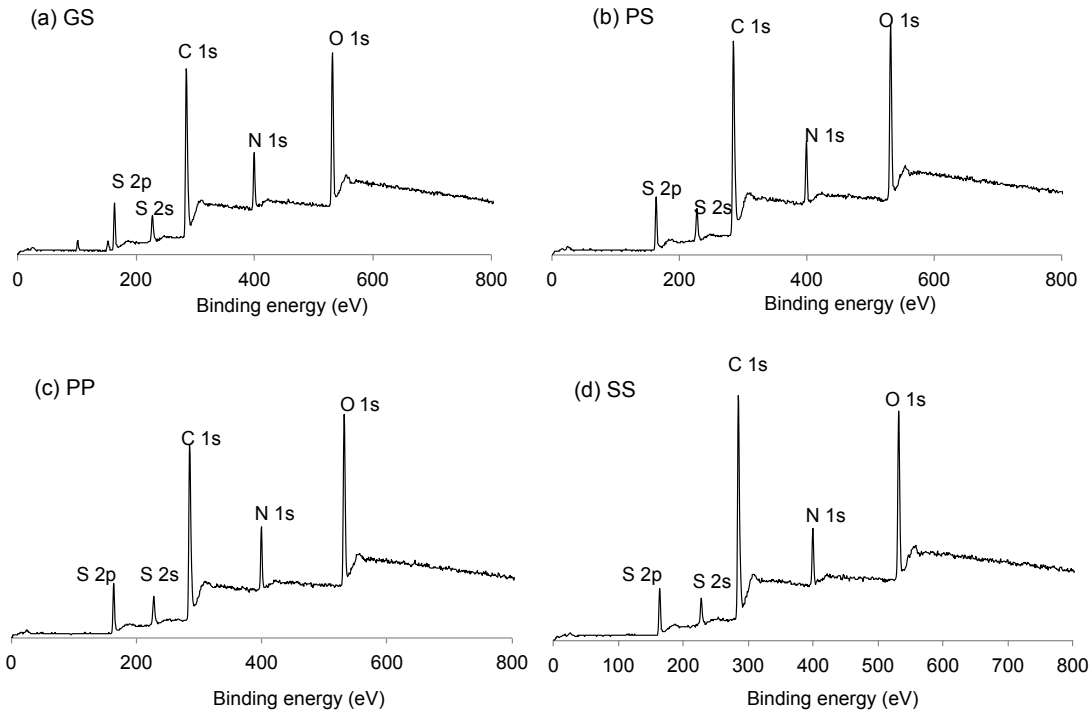


Fig. S4 XPS wide scan spectrum of NADOPAMe/**10** coated surfaces; (a) GS: glass, (b) PS: poly(lysine) slide, (c) PP: polypropylene, (d) SS: 304 stainless steel.

MALDI-TOF mass analyses:

The products from the self-polymerization of NADOPAMe and DOPA methyl ester, and the copolymerization mixtures in tris buffer pH 8.5 were collected respectively after 24 h and filtered. Those mixtures with suspended solids were reconstituted with 1mL of dimethylformamide (DMF) and then were filtered using a syringe filter (Microlab scientific, Nylon medium, 13 mm diameter and 0.22 µm pore size). 0.5 µL of the filtrates were spotted on a 384 well target plate and further crystallized with 0.5 µL of α–cyano-4-hydroxycinnamic acid (CHCA) in 0.1% (v/v) trifluoroacetic acid (TFA) and 50% (v/v) acetonitrile (ACN), which were subsequently subjected to MALDI-TOF/TOF mass analysis (4800 MALDI TOF/TOF Analyzer from Applied Biosystems, Framingham, MA, USA). The m/z data were manually acquired in the reflector mode using the Reflectron Method (accelerating voltage: 20000 V, laser intensity: 3300-3600 W/cm^2).

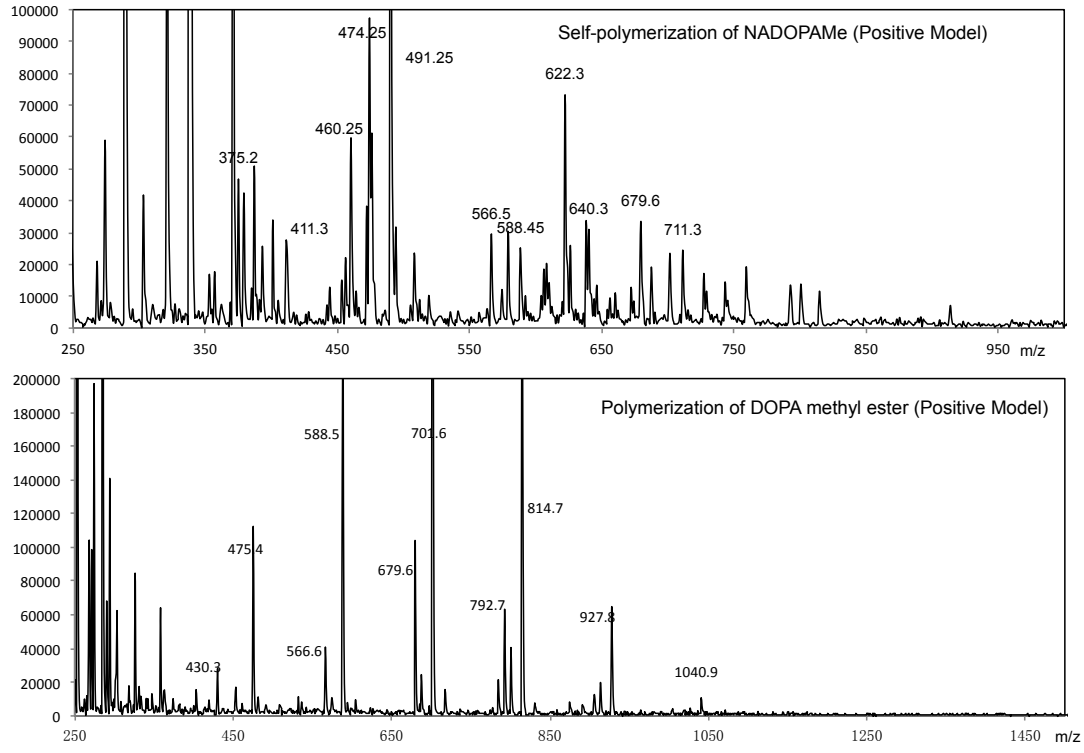


Fig. S5 Mass spectra of products from the self-polymerization of NADOPAMe and DOPA methyl ester in tris buffer (pH 8.5, 24 h).

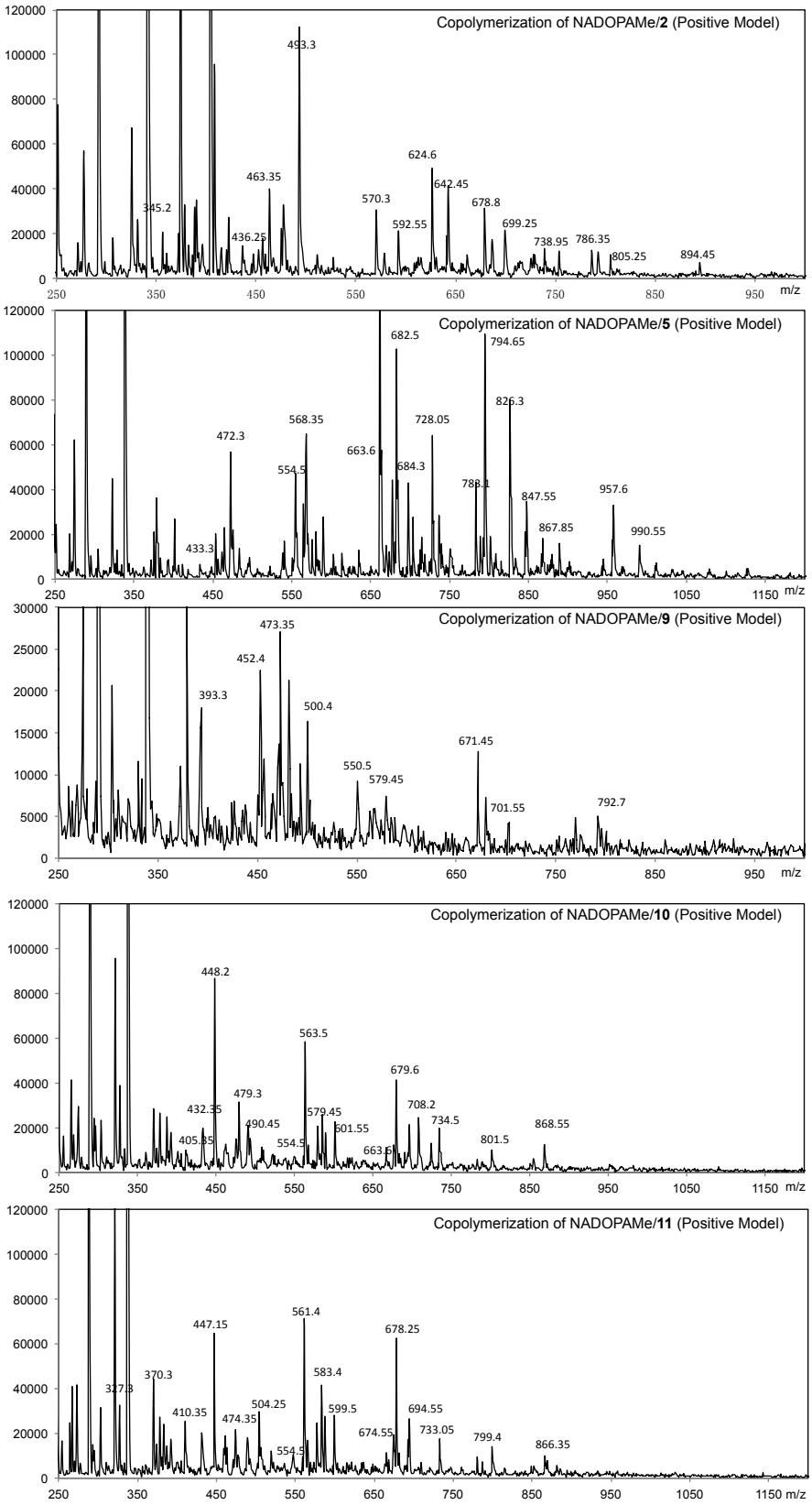
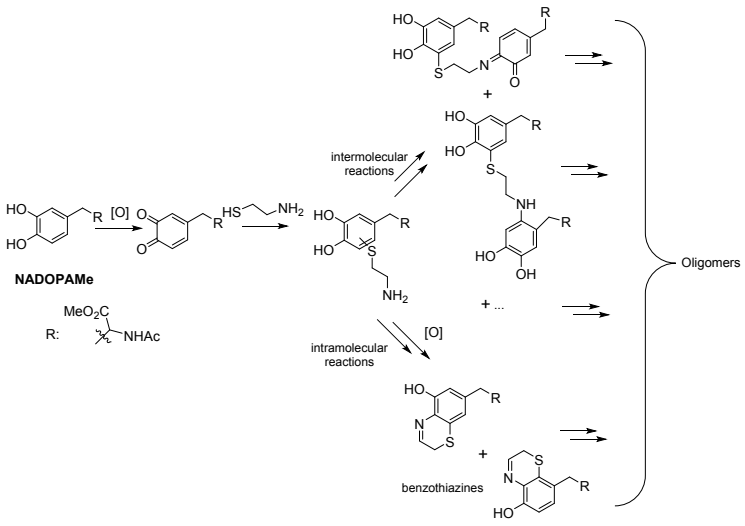
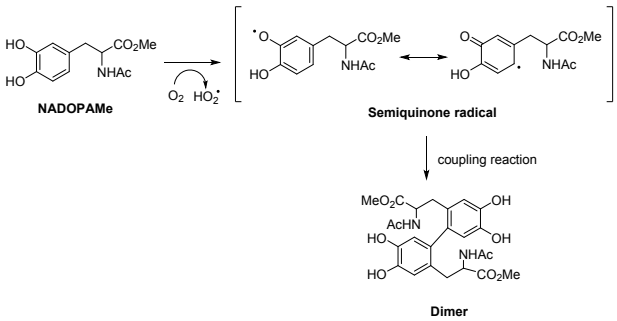


Fig. S6 Mass spectra of products from copolymerization of NADOPAMe and additives **2**，**5**，**9**，**10** and **11** in tris buffer (pH 8.5, 24 h).



Scheme S2 Possible intermediates and pathways that may be involved in the copolymerization of NADOPAMe and cysteamine 11



Scheme S3 A possible mechanism for the dimerization of NADOPAMe.

3. Redox-responsive Coating Degradation and Release of Loaded Compound

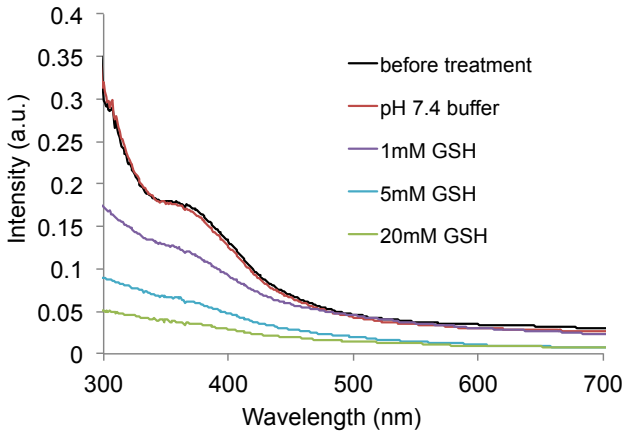


Fig. S7 UV-vis absorbance of NADOPAMe/**10** on polylysine slides before and after treatment with pH 7.4 buffer (8 h), 1mM (8 h), 5mM (8 h) and 20mM GSH (4 h) in buffer solution.

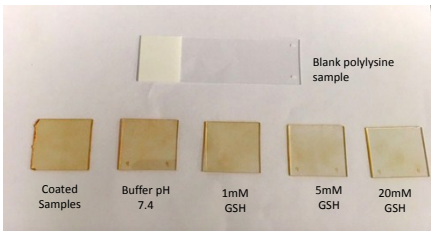


Fig. S8 Images of coatings on polylysine slides before and after treatment with pH 7.4 buffer (8 h), 1 mM (8 h), 5 mM (8 h) and 20 mM GSH (4 h) in tris buffer (10 mM, pH 7.4).