Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Replacing amine by azide: Dopamine azide polymerization triggered by sodium periodate

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Keywords: **azide, catechol, polydopamine, polycatechols, polymerization,**

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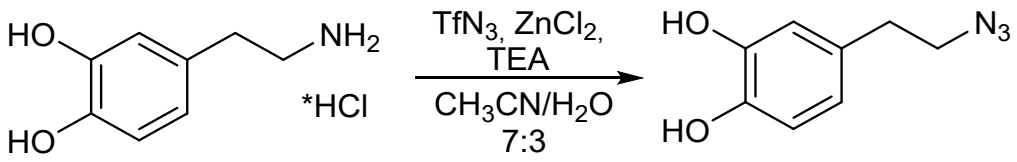
Synthesis of 4-(2-azidoethyl)benzene-1,2-diol



The compound was synthesized according to the procedure presented by Pagoti et al.[1] The trifluoromethanesulfonylazide (TfN_3) was prepared by addition trifluoromethanesulfonic anhydride (Tf_2O) (1.06 mL, 6.32 mmol, 1.2 eq.) to the suspension of sodium azide (1.0 g, 15.38 mmol, 2.0 eq) in 15 mL of CH_3CN in ice bath. The reaction temperature was maintained at 0 °C for 2 hours. Next dopamine hydrochloride (DA·HCl) (1.0 g (5.27 mmol, 1.0 eq.) was dissolved 25 mL of H_2O:CH_3CN (3:7) mixture under argon atmosphere followed by addition freshly prepared trifluoromethanesulfonyl azide (TfN_3), zinc chloride ($ZnCl_2$) (71.8 mg ,0.53 mmol, 0.1 eq.) and 2.21 mL (15.87 mmol, 3.0 eq.) of triethylamine (TEA). After 24 h, the crude mixture was filtered and concentrated on the rotary evaporator followed by extraction with ethyl acetate. The organic layer were dried over magnesium sulfate and evaporated to dryness. The product was purified by column chromatography using ethyl acetate:hexane 3:7 as eluent phase yielding 850 mg (79 %) of 4-(2-azidoethyl)benzene-1,2-diol as slightly darkish solid.

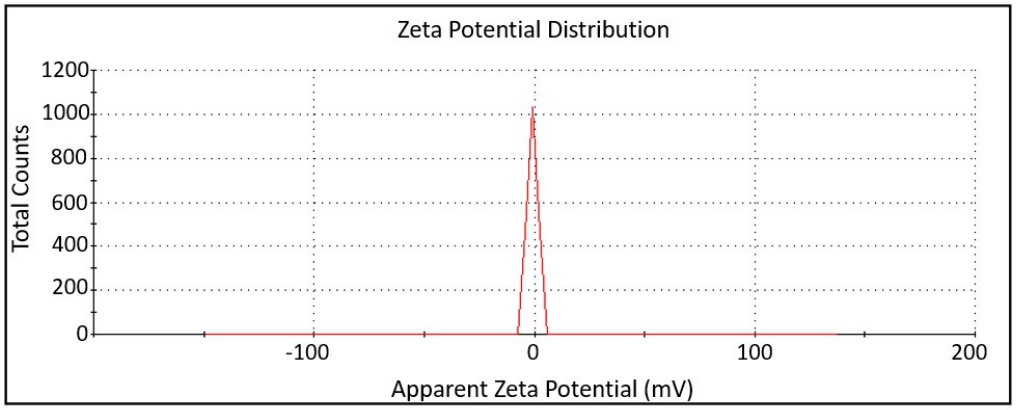


Figure S1. Zeta Potential of poly(dopaazide) particles in H_2O

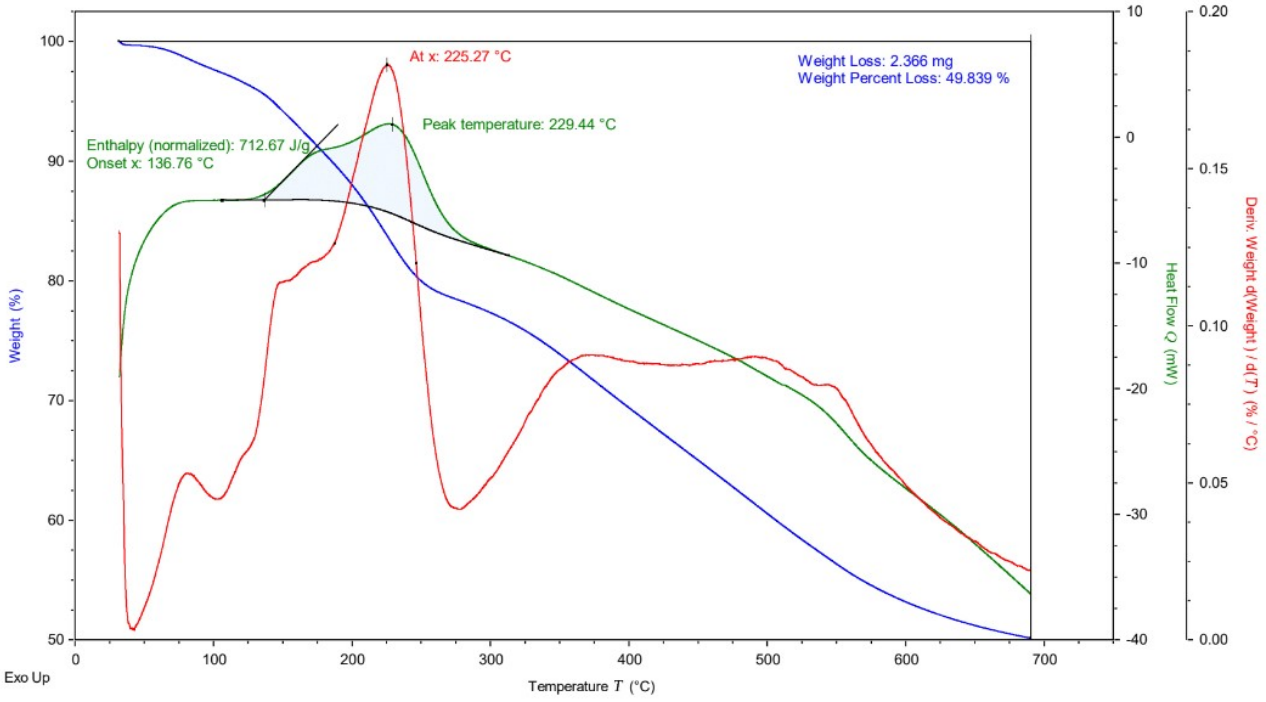


Figure S2. Thermal properties of poly(dopaazide) recoded by means of STA

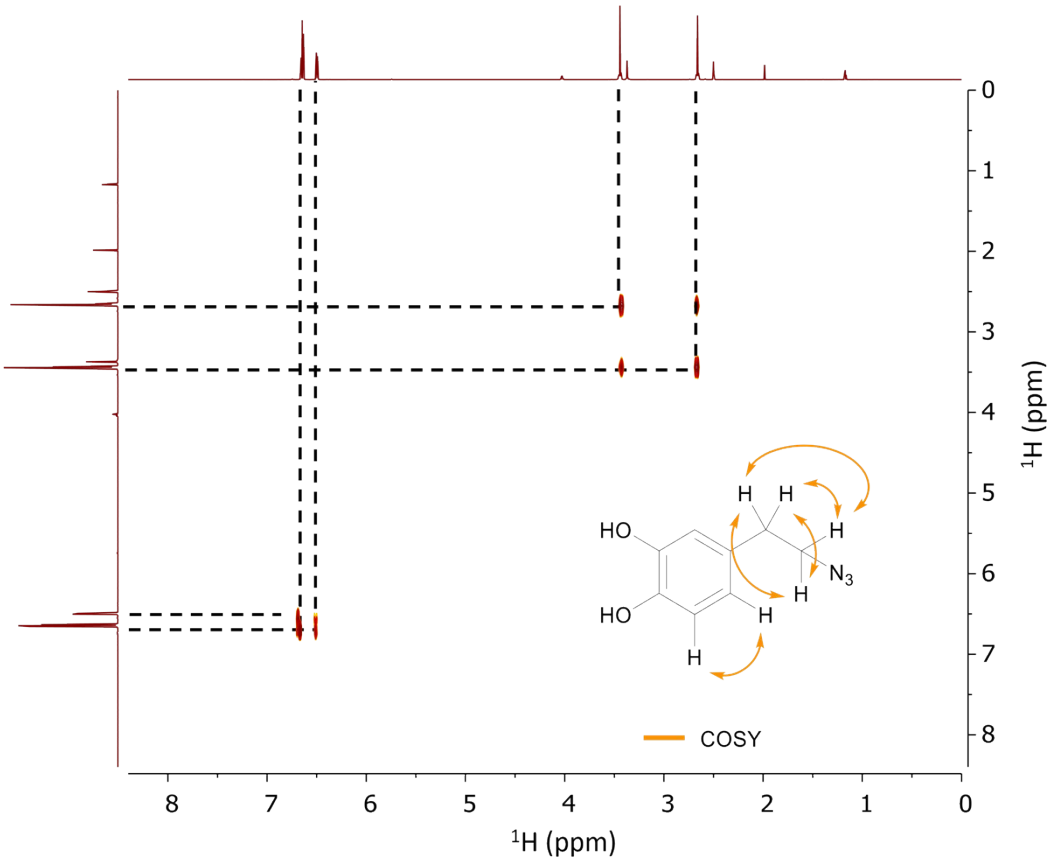


Figure S3. ^{1}H-^{1}H COSY spectrum of dopamine-azide (DMSO-d_6, 298 K).

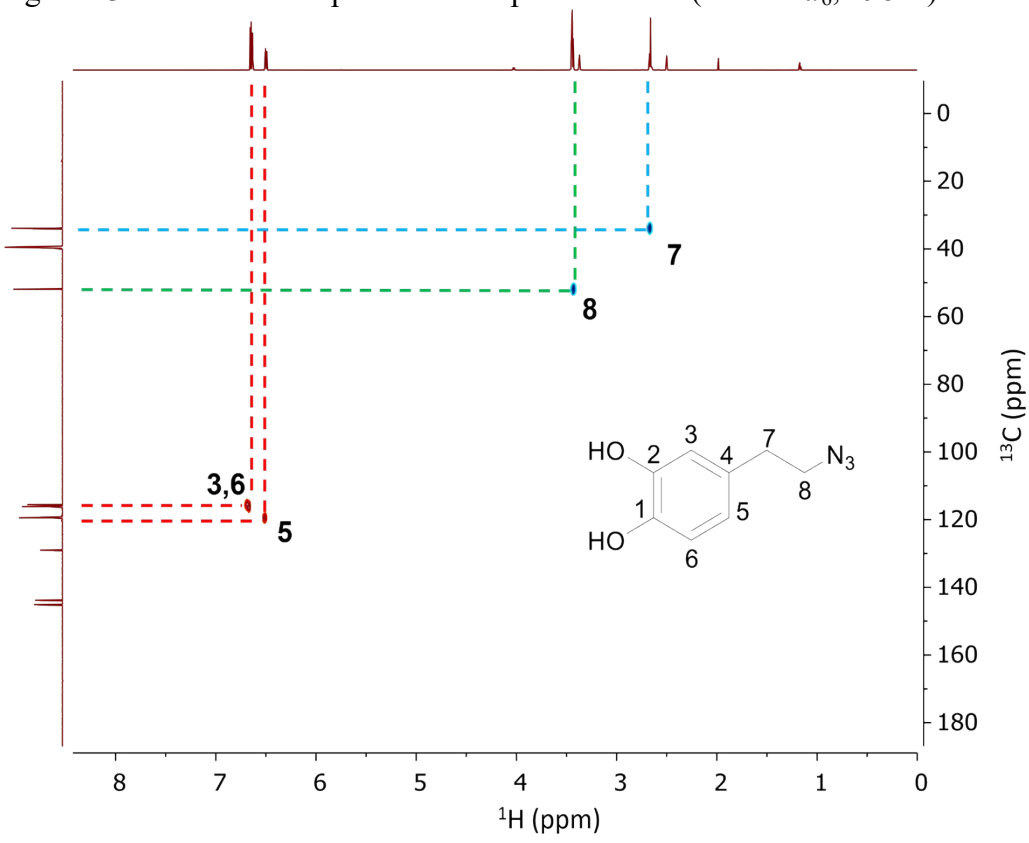


Figure S4. ^{1}H-^{13}C HSQC spectrum of dopamine-azide (DMSO-d_6, 298 K)

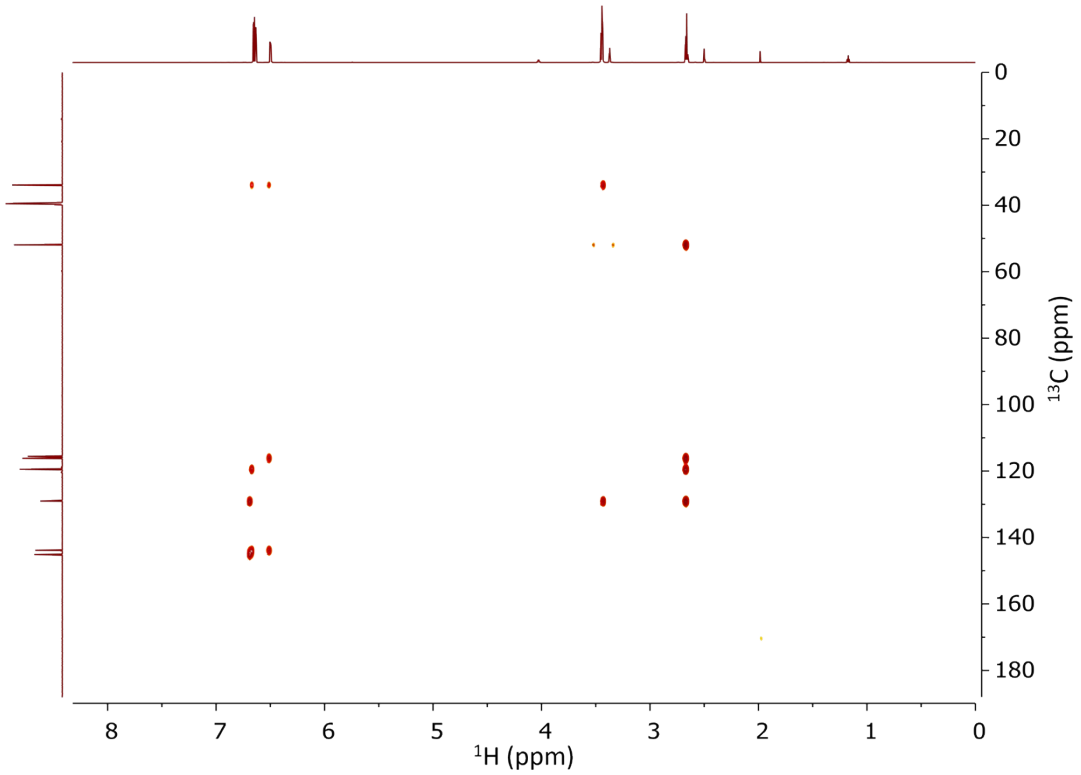


Figure S5. ^{1}H-^{13}C HMBC spectrum of dopamine-azide (DMSO-d_6, 298 K)

Figure S6. Experiment with different equivalents of $NaIO_4$. The left row corresponds to poly(dopaazide) and the right row presents PDA. Flask number: 1 and 10 (0.1 eq. $NaIO_4$), 2 and 9 (0.2 eq. $NaIO_4$), 3 and 8 (0.5 eq. $NaIO_4$), 4 and 6 (1.0 eq. $NaIO_4$), 5 and 6 (2.0 eq. $NaIO_4$)

After adding the periodate solution in water to the dopamine azide solution, an instantaneous color change from transparent to intense, clear orange was observed. Over time, the mixture turned cloudy, and the color became slightly lighter, dirty-orange. It was noticed that with more periodate added, the color of the mixture was darker and more brown than orange what suggest increased transformation speed of the intermediates. In the case of dopamine, the solution turned red immediately after adding the oxidant, gradually turning into cherry red, and finally turning a maroon color. As the concentration of periodate increased in the flask, the effect was the same as for the azide analog, i.e. a darker color was observed. The experiment was carried out for 24 h with oxygen access. The samples were purified by centrifugation and washed with water until the supernatant was transparent.

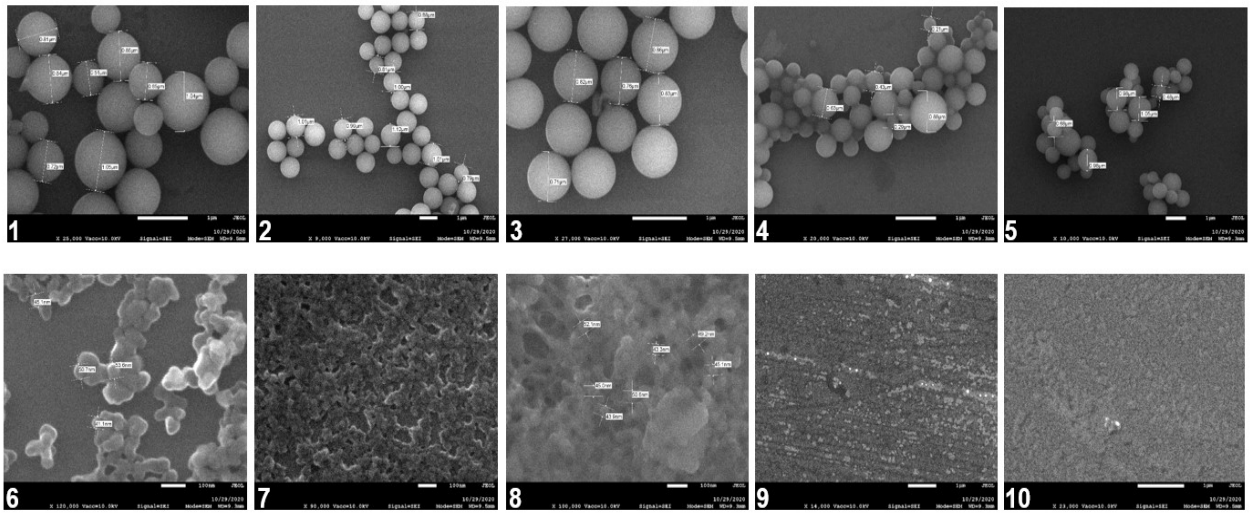


Figure S7. SEM pictures of poly(dopaazide) and PDA particles formed after 24 hours of polymerization with different equivalents of $NaIO_4$. The upper row corresponds to poly(dopaazide) and the bottom row presents PDA. Flask number: 1 and 10 (0.1 eq. $NaIO_4$), 2 and 9 (0.2 eq. $NaIO_4$), 3 and 8 (0.5 eq. $NaIO_4$), 4 and 6 (1.0 eq. $NaIO_4$), 5 and 6 (2.0 eq. $NaIO_4$)

Table S1 Contact angle (CA) measurement results for poly(dopaazide) and polydopamine (PDA)

Sample	**Initial CA**	**After 1 min**	**After 10 min**
Poly(dopaazide)/glass 24 h	62	58	36
Poly(dopaazide)/glass 48 h	70	67	47
Poly(dopaazide)/Si 48 h	77	53	32
PDA/glass 24 h	51	50	39
PDA/glass 48 h	62	60	38
PDA/Si 48 h	65	61	53

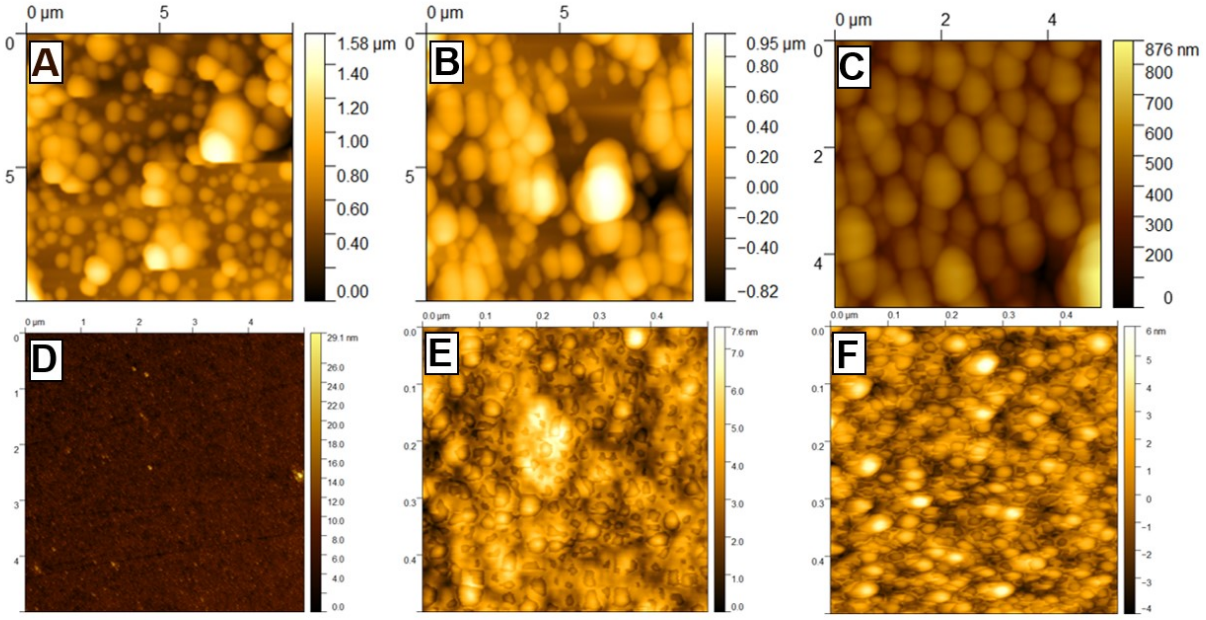
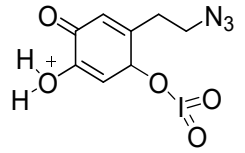
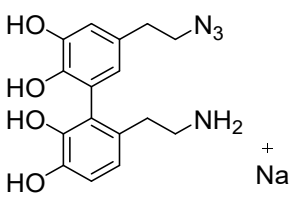
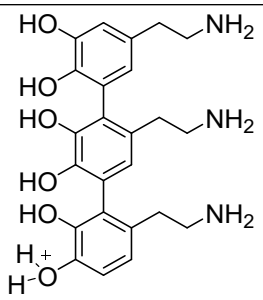
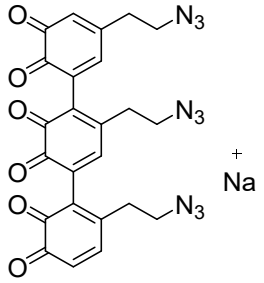
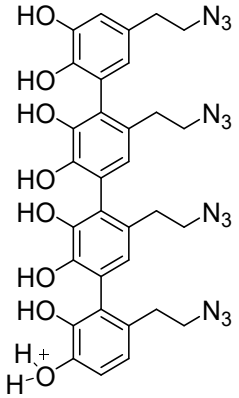
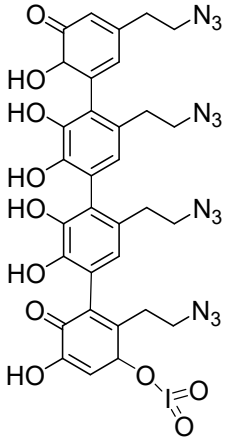
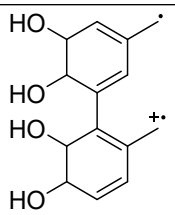
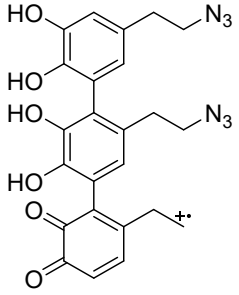
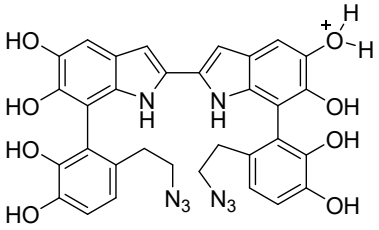
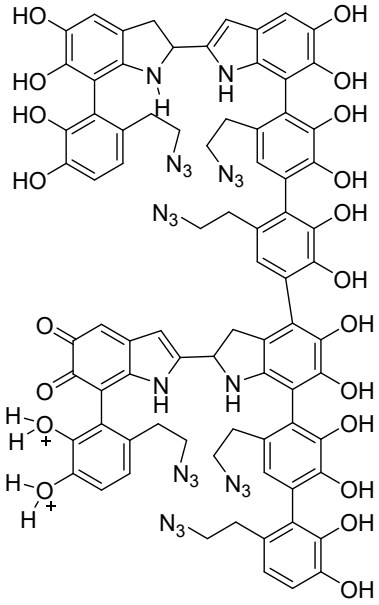


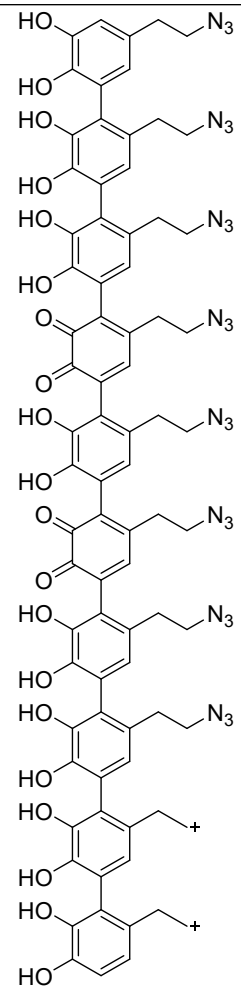
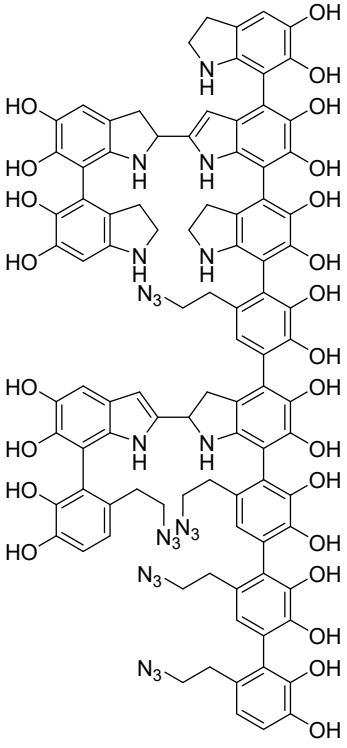
Figure S8. AFM pictures of coated substrates by poly(dopaazide) and PDA. A. poly(dopaazide)/glass 24 h, B. poly(dopaazide)/glass 48 h, C. poly(dopaazide)/Si 48 h, D. PDA/glass 24 h, E. PDA/glass 48 h, F. PDA/Si 48 h

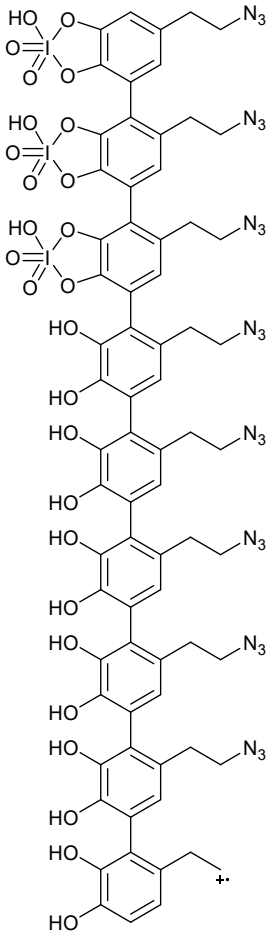
Table S2 Proposed structures of poly(dopaazide) predicted from mass spectrometry analysis

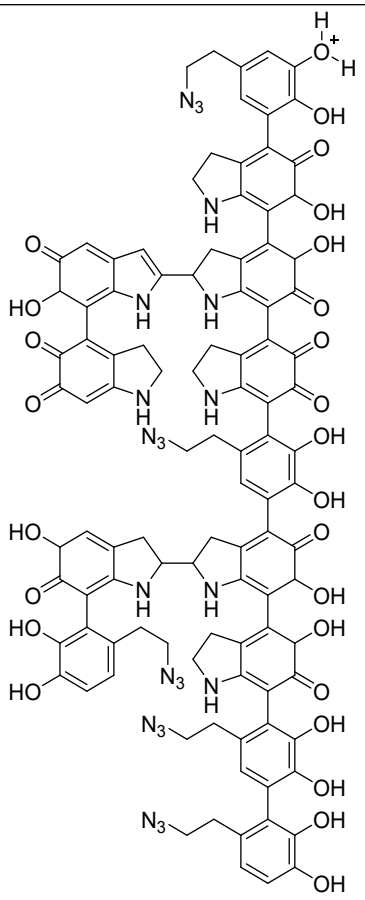
Mass predicted from ESI-MS in positive ion mode	**Mass found**	**Structure**
353.2670	353.9581 353.1227	 Exact Mass: 353.9581 or  Exact Mass: 330.1328 Exact Mass: 22.9892

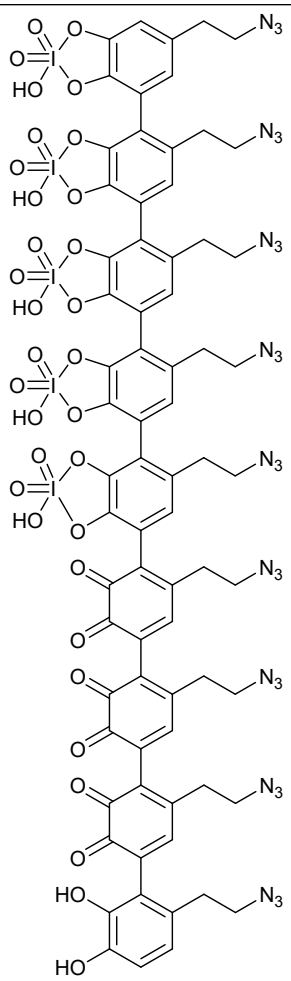
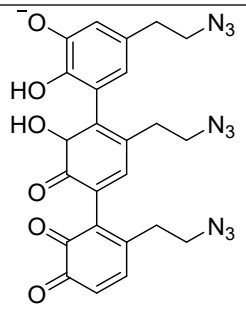
456.1425	456.2129	 Exact Mass: 456.2129
550.2056	550.1194	 Exact Mass: 527.1302 Exact Mass: 22.9892
711.5766	711.2382	 Exact Mass: 711.2382
884.4302	884.1123	 Exact Mass: 884.1123
Mass predicted from MALDI -MS in positive ion mode	**Mass found**	**Structure**

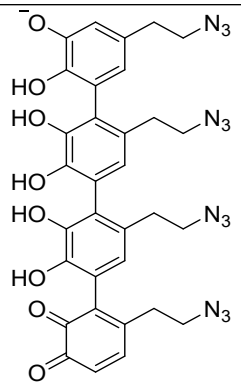
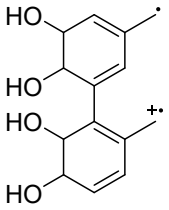
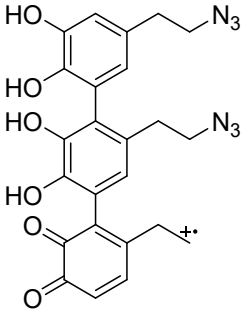
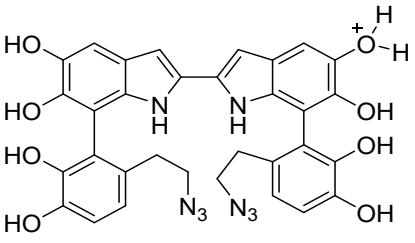
247.2295	247.0965	 Exact Mass: 247.0965
488.1690	488.1439	 Exact Mass: 488.1439
651.2294	651.1946	 Exact Mass: 651.1946
1656.2420	1656.4980	 Exact Mass: 1656.4969

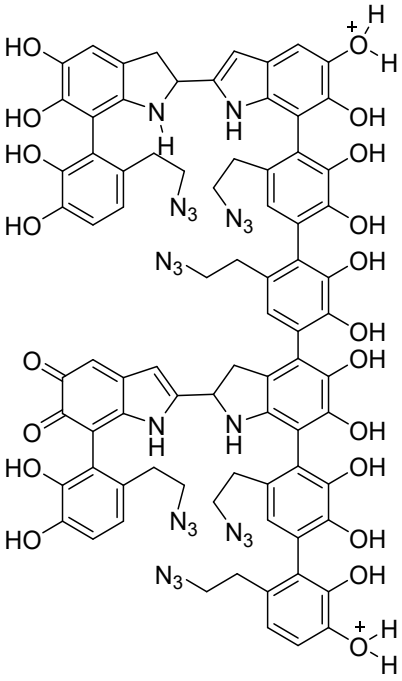
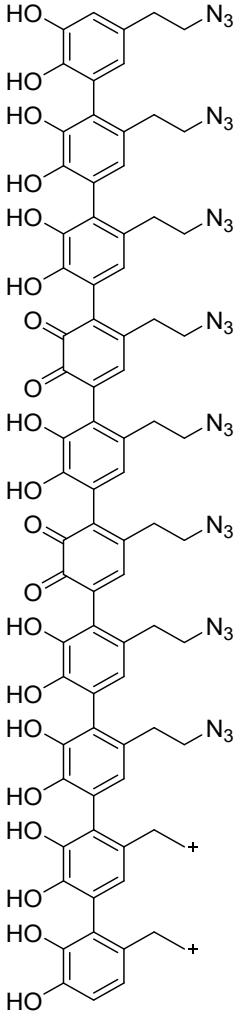
1684.2595	1684.5020	 Exact Mass: 1684.5031
1926.3296	1926.5872	 Exact Mass: 1926.5872

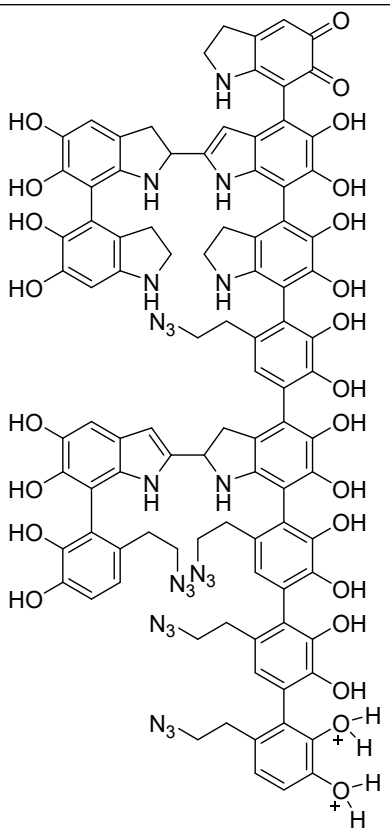
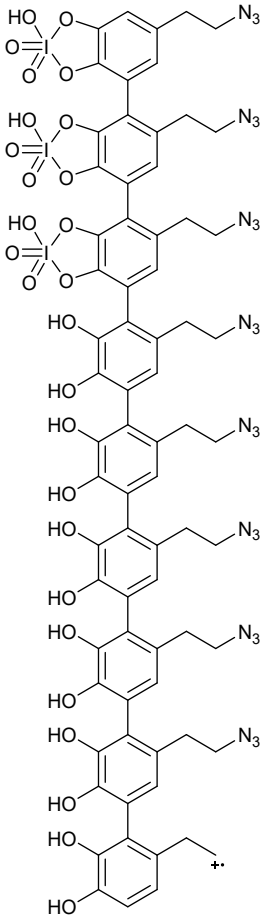
2074.3971	2074.1267 2074.6265	 Exact Mass: 2074.1267

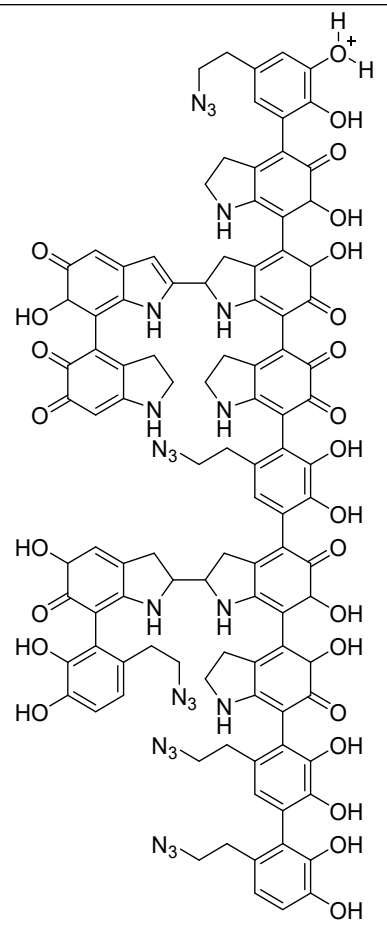
		 Exact Mass: 2074.6265

2482.5251	2482.8601	 Exact Mass: 2458.8601
Mass predicted from ESI-MS in negative ion mode	**Mass found**	**Structure**
530.1549	530.1542	 Exact Mass: 530.1542

707.2089	707.2080	 Exact Mass: 707.2080
Mass predicted from MALDI-MS in negative ion mode	**Mass found**	**Structure**
247.2295	247.0965	 Exact Mass: 247.0965
488.1690	488.1439	 Exact Mass: 488.1439
651.2294	651.1946	 Exact Mass: 651.1946

1656.2420	1656.4969	 Exact Mass: 1656.4969
1684.2595	1684.5031	 Exact Mass: 1684.5031

1926.3296	1926.5861	 Exact Mass: 1926.5861
2074.3971	2074.1267 2074.6265	 Exact Mass: 2074.1267

		 Exact Mass: 2074.6265

References

1. Pagoti, S., Dutta, D. & Dash, J. A magnetoclick imidazolidinone nanocatalyst for asymmetric 1,3-dipolar cycloadditions. *Adv. Synth. Catal.* **355**, 3532–3538 (2013).