Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Design of poly(*N*-isopropylacrylamide) coated MnO_2 nanoparticles for thermally regulated catalytic decomposition of H_2O_2

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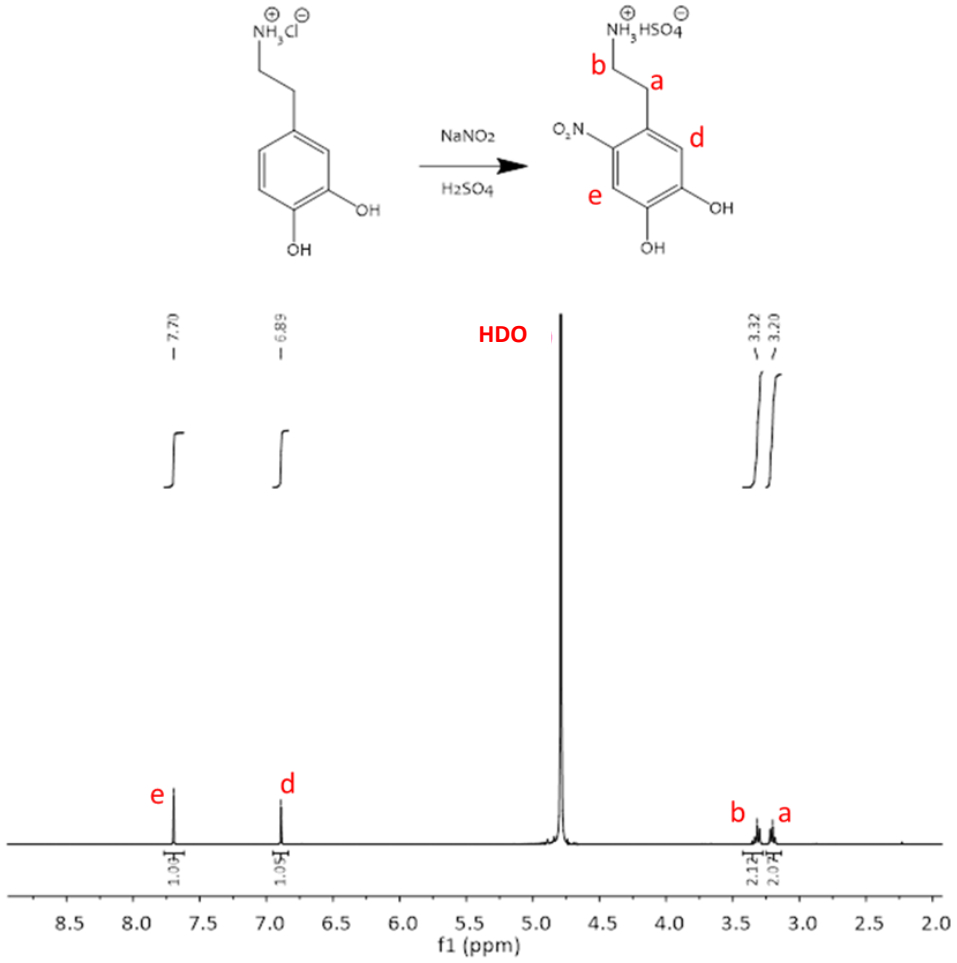

Figure S1. ^{1}H NMR spectrum of nitrodopamine hydrogensulfate measured in D_2O.

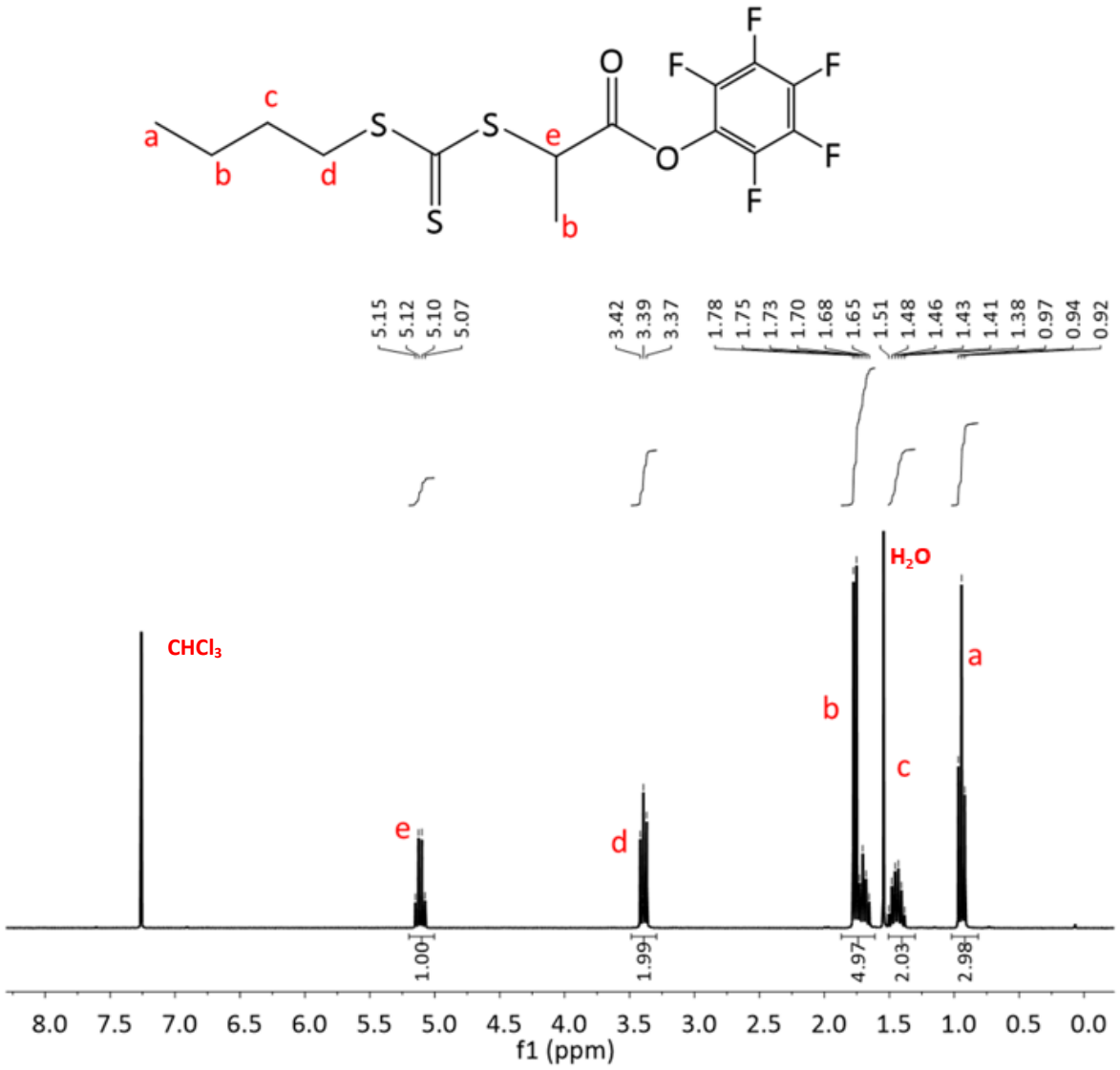

Figure S2. ^{1}H-NMR spectrum of pentafluorophenol (PFP) containing CTA measured in $CDCl_3$.

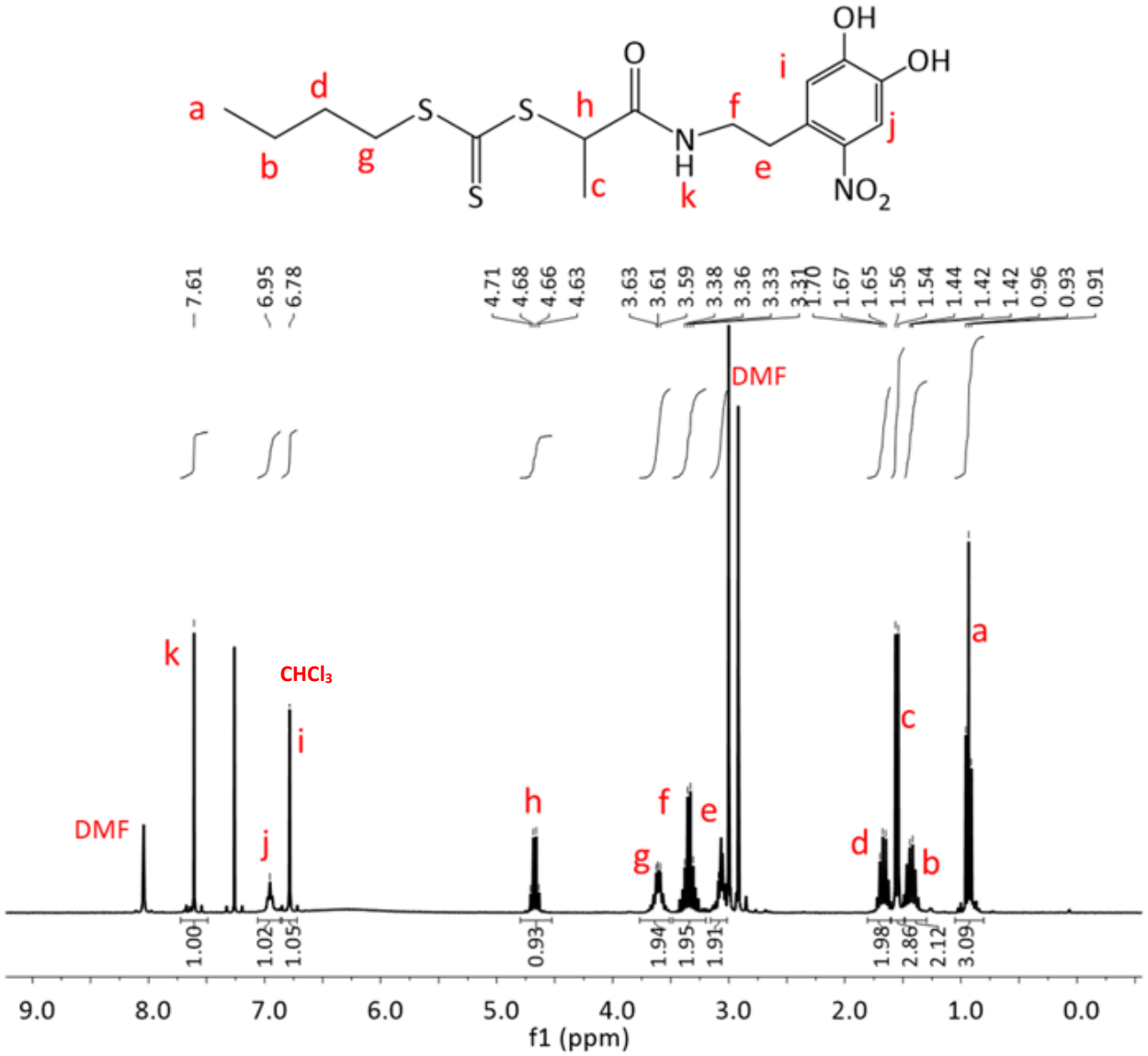

Figure S3. ^{1}H NMR spectrum of Nitro DOPA-CTA measured in $CDCl_3$.

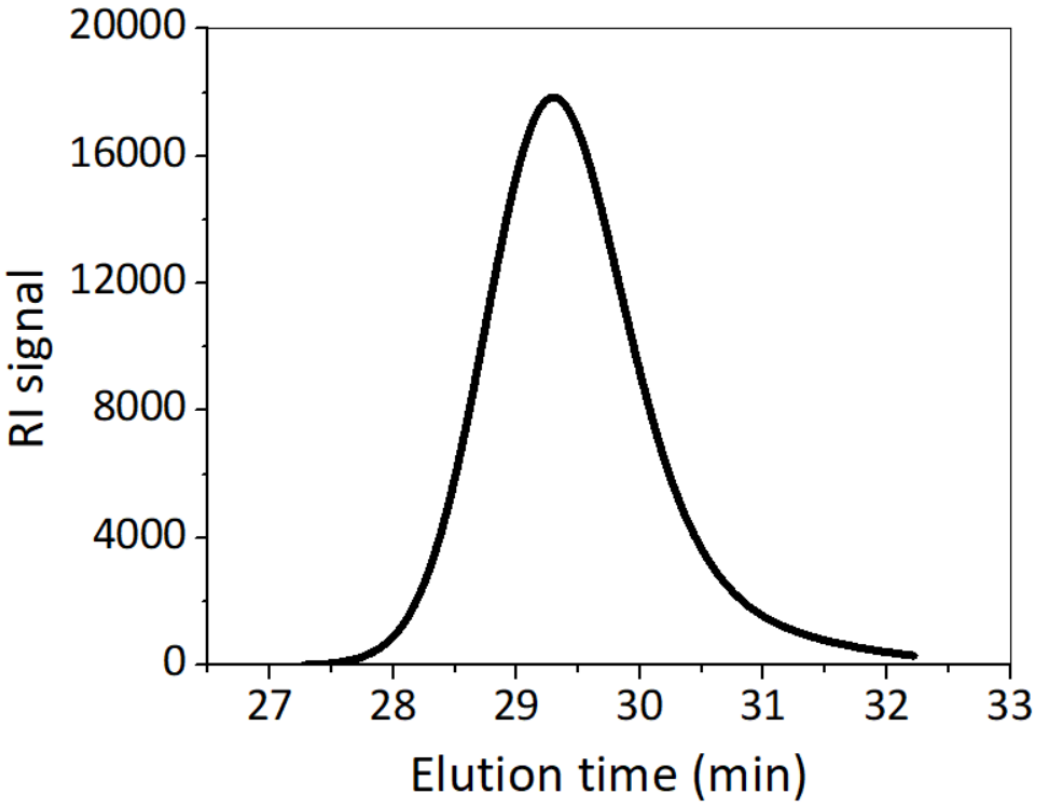

Figure S4. SEC RI trace of PNIPAM in DMAc containing 50 mM of LiCl at 50 °C.

Figure S5. Photographs of plastic cuvettes containing $KMnO_4$ and MnO_2NPs in water.

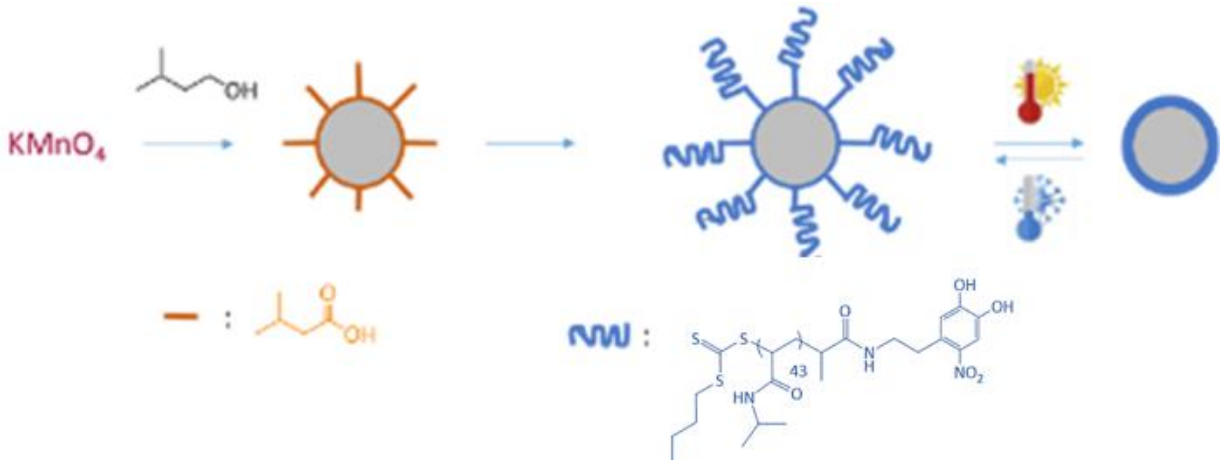

Figure S6. Schematic representation for the preparation of PNIPAM@MnO_2NPs and thermoresponsive behavior.

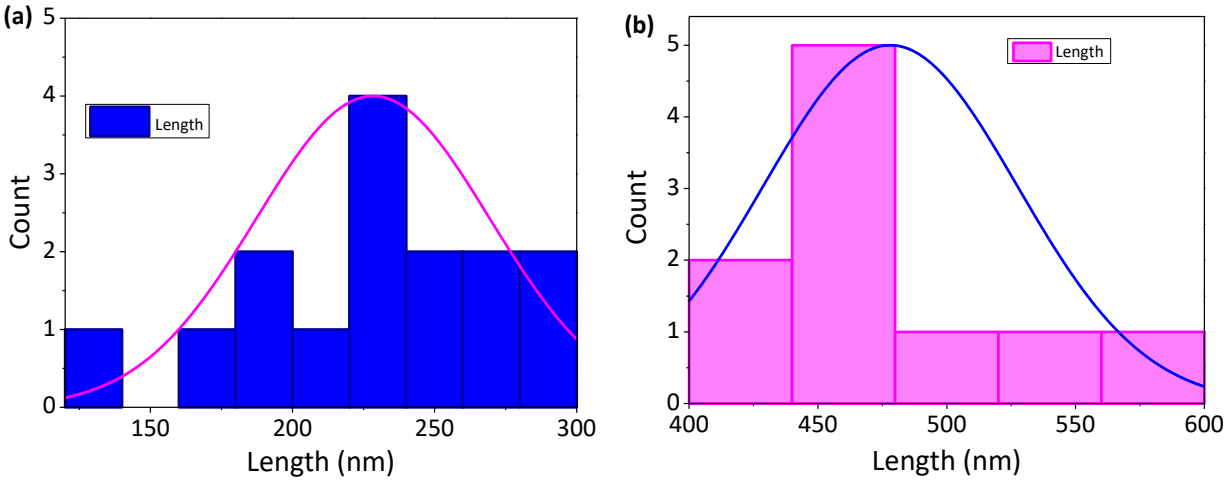

Figure S7. (a) Analysis of length of the MnO_2NPs from SEM Images at 1 µm scale, (b) Analysis of length of the PNIPAM modified MnO_2NPs from SEM Images at 1 µm scale.

Table S1. EDX data for MnO_2 NPs.

Element	***Net Counts***	***Weight %***	***Atom %***	***Formula***
C	1360	16.78	26.65	C
O	4292	52.62	62.73	O
Mn	2835	30.60	10.62	Mn
Total		100.00	100.00	

Table S2. EDX data for PNIPAM@MnO_2 NPs.

Element	***Net Counts***	***Weight %***	***Atom %***	***Formula***
C	2945	31.32	37.51	C
N	372	22.57	23.18	N
O	1002	42.55	38.26	O
S	152	0.62	0.28	S
Mn	206	2.94	0.77	Mn
Total		100.00	100.00	

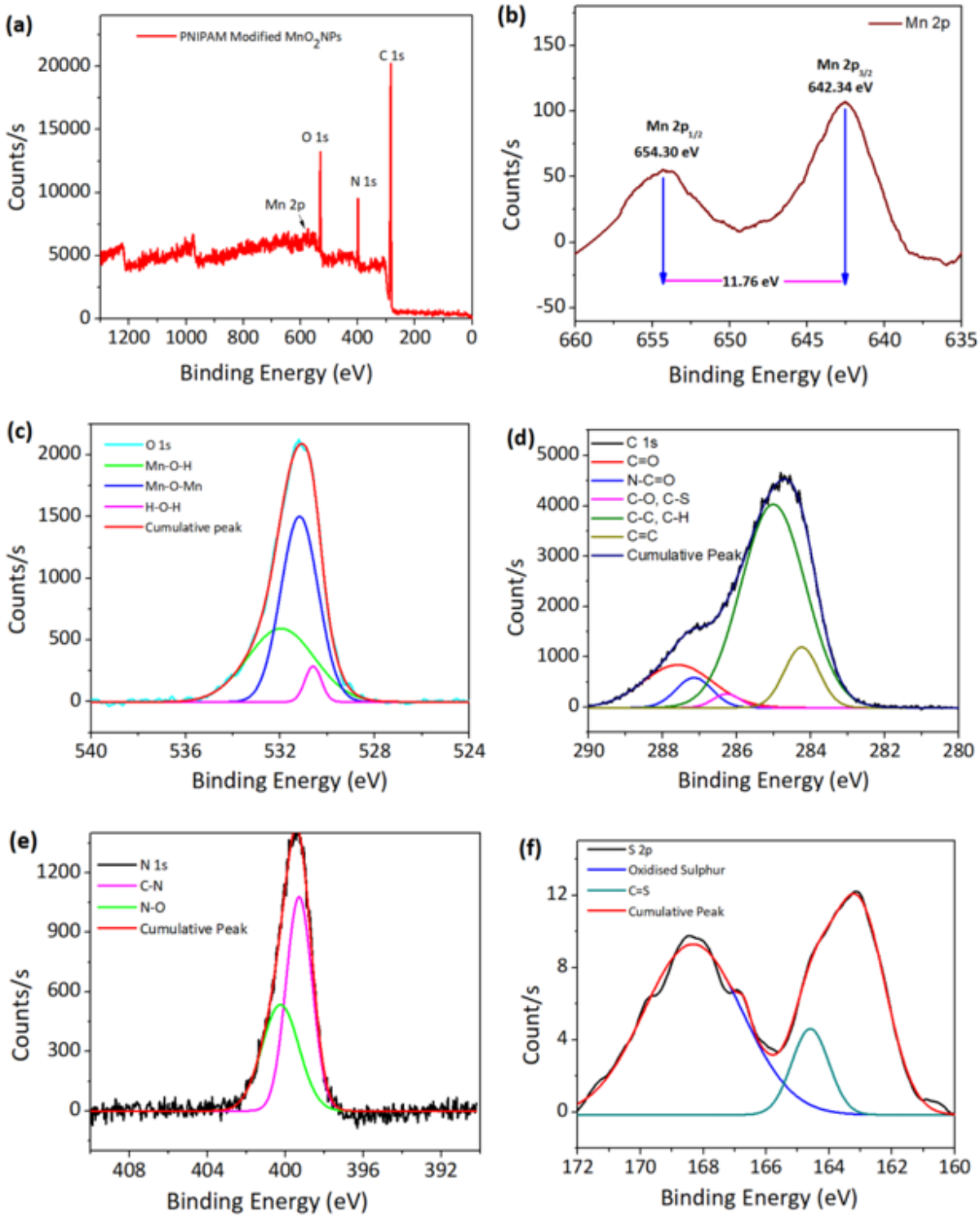

Figure S8. XPS-spectra (a) Overall PNIAM@MnO_2NPs, (b) Mn 2p,(c) O 1s, (d) C1s, (e) N 1s and (f) S 2p orbitals.

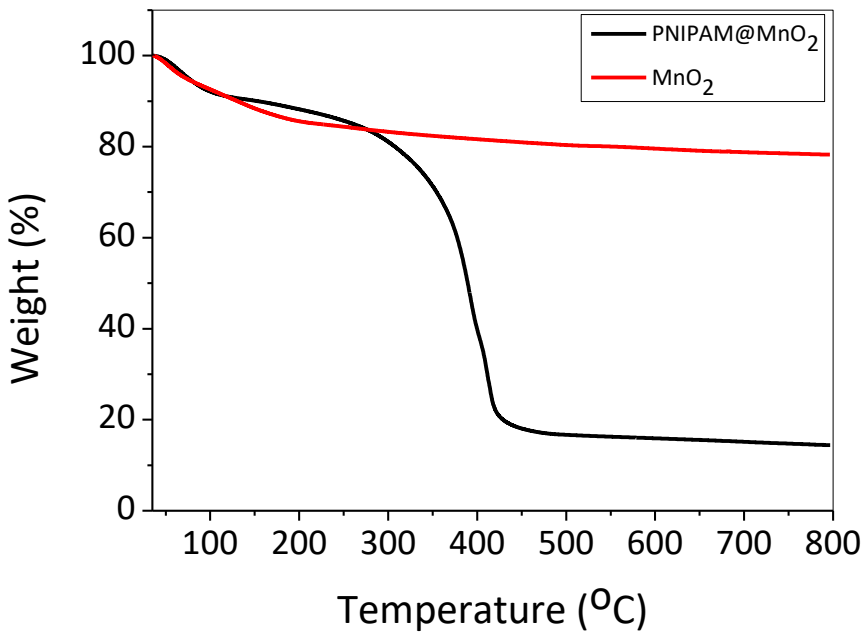

Figure S9. TGA graph for MnO_2NPs and PNIPAM@MnO_2NPs.

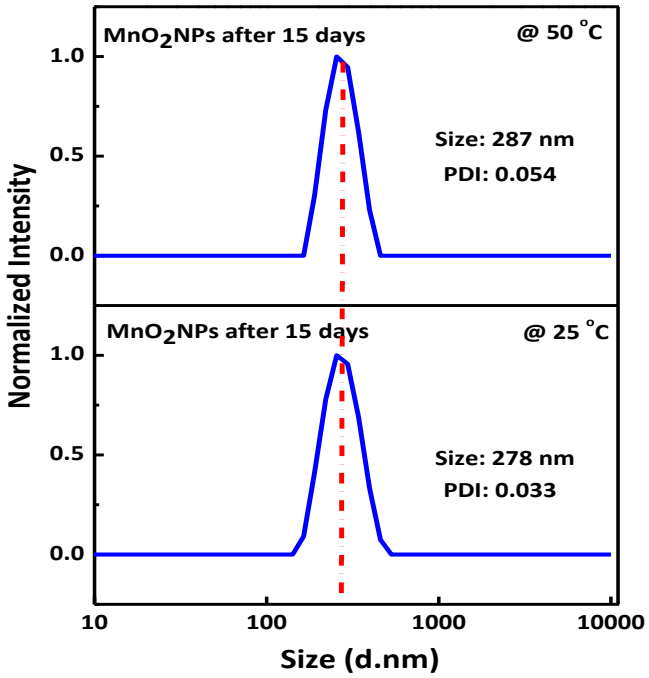

Figure S10. Stability of the MnO_2NPs measured *via* DLS at 0.2 mg/mL concentration in water.

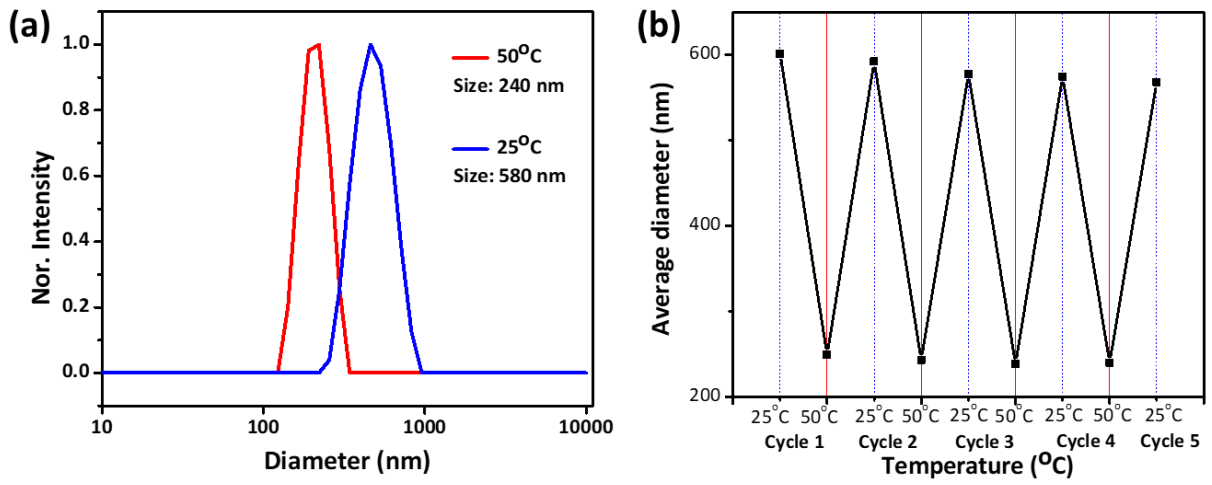

Figure S11. (a) DLS data for PNIPAM@MnO_2NPs 25 °C and 50 °C, (b) reversible DLS measurement at 25 °C and 50 °C for 5 consecutive cycles at 0.1 mg/mL concentration in water.

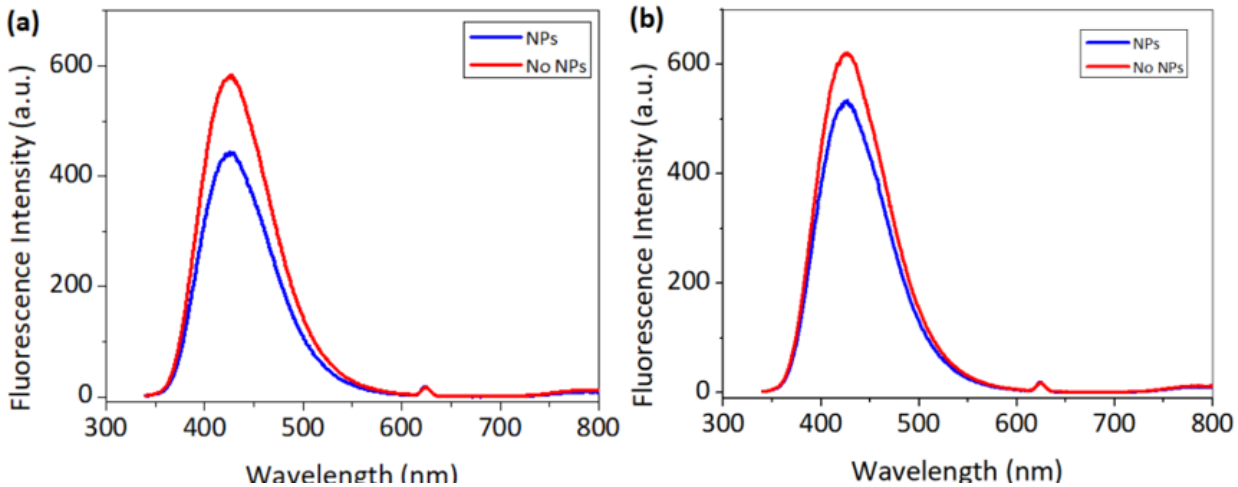

Figure S12. Comparison of fluorescent intensity without and with 10 µL PNIPAM@MnO_2NPs after 5 min in presence of 50 µL HRP, 50 µL HVA and 50 µL H_2O_2 in 2340 µL PBS at two different temperatures (a)10 °C and (b) 50 °C respectively ($\lambda_{Ex.}$ = 312 nm).

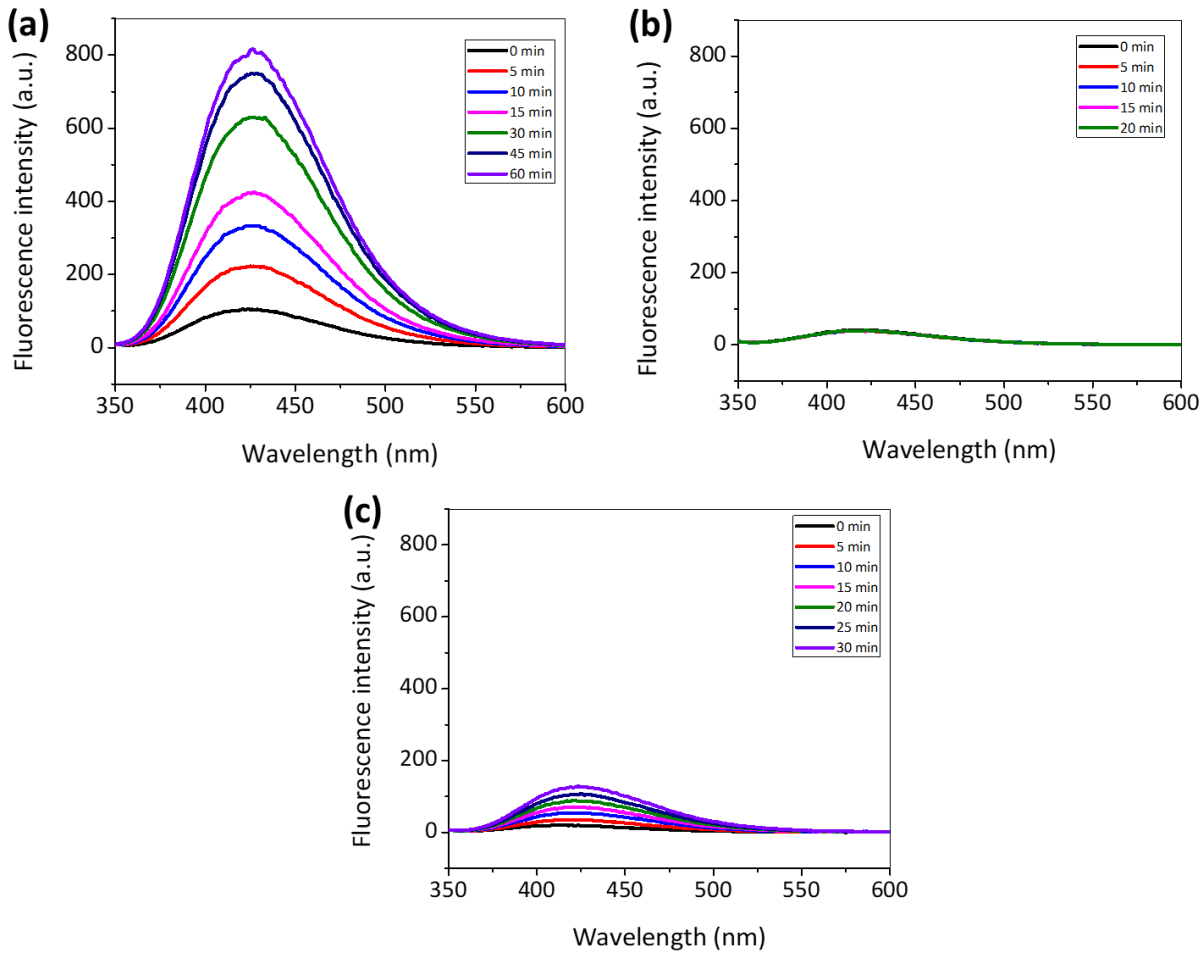

Figure S13. Fluorescence intensity (a) in presence of 50 µL HRP, 100 µL HVA and 50 µL H_2O_2 in 2300 µL PBS without PNIPAM@MnO_2NPs; (b) 10 µL PNIPAM@MnO_2NPs in presence of 50 µL HRP and 100 µL HVA and 2340 µL PBS without H_2O_2; (c) 10 µL PNIPAM@MnO_2NPs in presence of 50 µL HVA and 50 µL H_2O_2 in 2390 µL PBS without HRP at 37°C in PBS (λ_{Ex} = 312 nm).

As reference experiments, the fluorescence intensity of the non-fluorescent HVA dye in PBS was measured in time in the absence of PNIPAM@MnO_2NPs, H_2O_2, and HRP respectively (Figures S13a-c) was measured. It is evident from comparing the three spectra that H_2O_2 is essential for fluorescence enhancement and, thus, formation of the HVA dimer, as there is no increase in fluorescence without H_2O_2. In the absence of either the NPs or HRP the fluorescence increased in time. However, without HRP, the fluorescence intensity increase was 5 times lower than without the presence of PNIPAM@MnO_2NPs indicating the importance of HRP to catalyse the HVA dimerization.

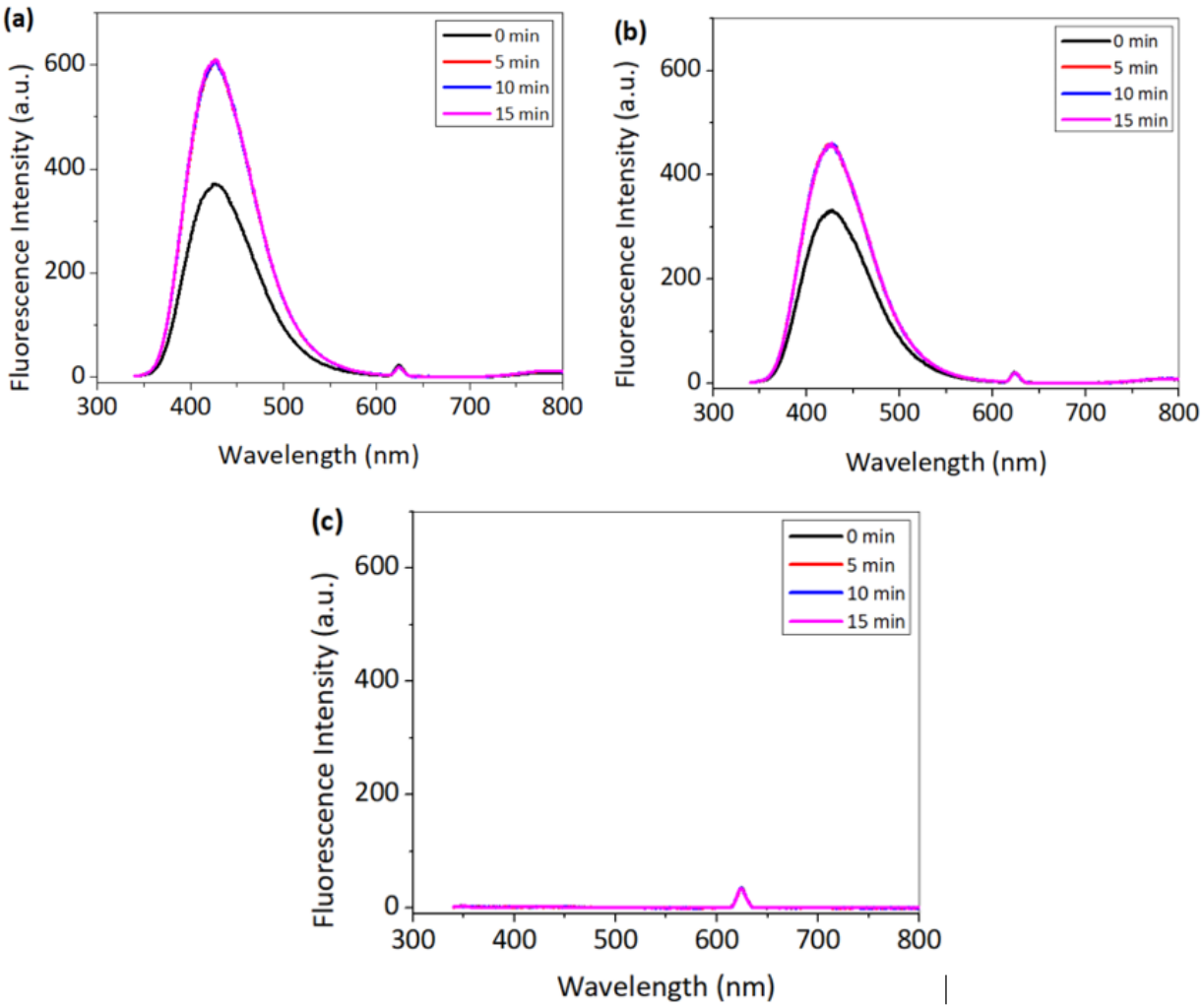

Figure S14. Fluorescence intensity in presence of (a) 50 µL HRP solution, 100 µL HVA, 2300 µL PBS and 50 µL H_2O_2 (b) 50 µL HRP solution, 100 µL HVA, 2325 µL PBS and 25 µL H_2O_2 and (c) 50 µL HRP solution, 100 µL HVA, 2350 µL PBS and 0 µL H_2O_2 at 37 °C ($\lambda_{Ex.}$ = 312 nm).

To confirm the importance of H_2O_2 for oxidization of HVA in presence of HRP, two experiments were performed. In one experiment, 50 µL HRP solution, 100 µL HVA, 2300 µL PBS and 50 µL H_2O_2 were added in cuvette and measurement was done at 37 °C. As anticipated, a clear fluorescent signal is visible around 420 nm due to dimer formation. After 5 min the intensity reaches its maximum and no further change occurs after 10 or 15 min (at 0 min H_2O_2 was already present which is why a fluorescent signal is already noticeable) (Figure S14a). A decrease in $\lambda_{em,max}$ of 149 a.u. was observed by changing the H_2O_2 concentration from 50 mM to 25 mM (Figure S14b). In contrast when the same experiment was done without adding H_2O_2 no fluorescence signal is observable (Figure S14c). These results indicate that HRP can only oxidize HVA when H_2O_2 is present.