Supporting Information for:

Redox-responsive release of active payloads from depolymerized nanoparticles

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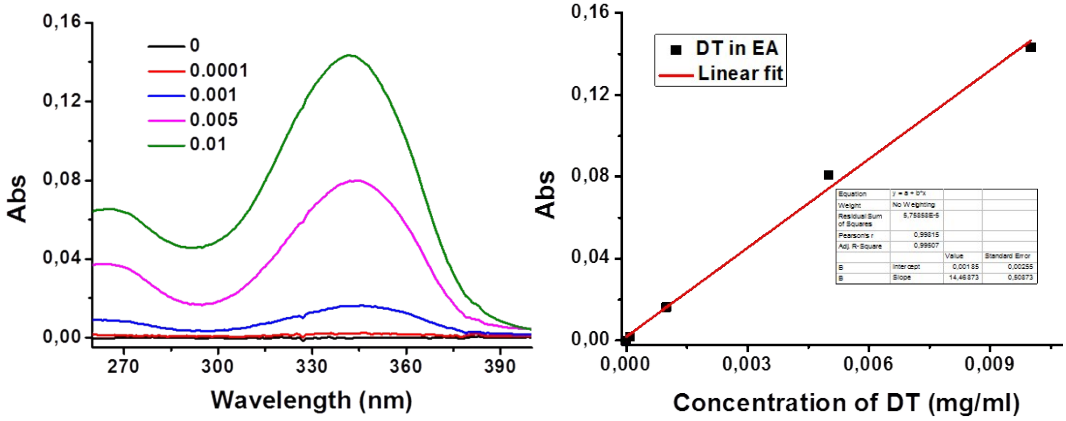


(a) (b)

Fig. S1 a) UV-vis spectra of DMcT dissolved in EA with varied concentration of DMcT. b) Calibration curve of DMcT in EA.

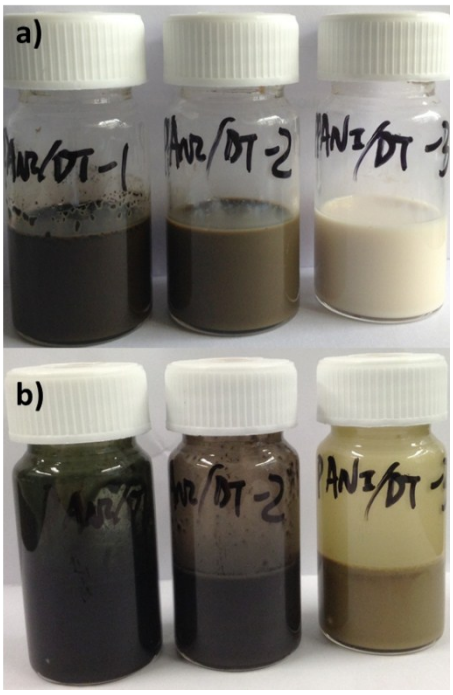
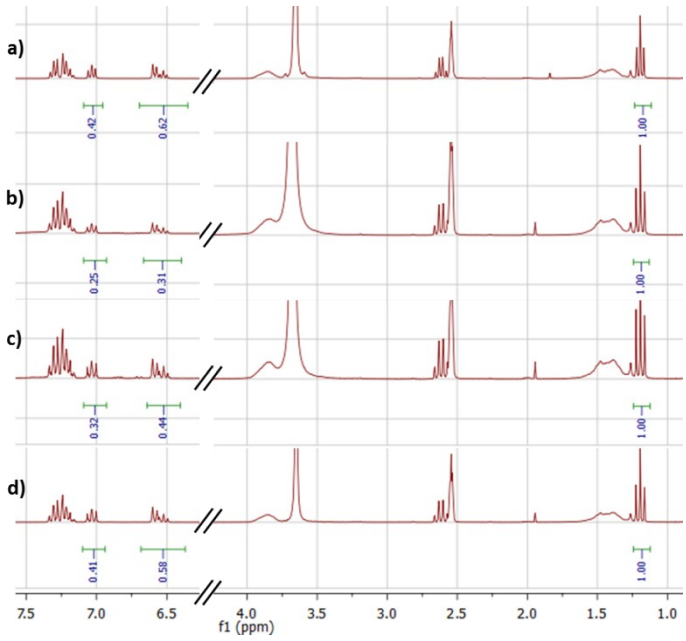


Fig. S2 Digital photos of PANI/PDMcT-1, 2 and 3 (from left to right) dispersions after addition of initiator(s) for (a) 5 min and (b) after 1 week. The initial color of all the three dispersions is milky white.



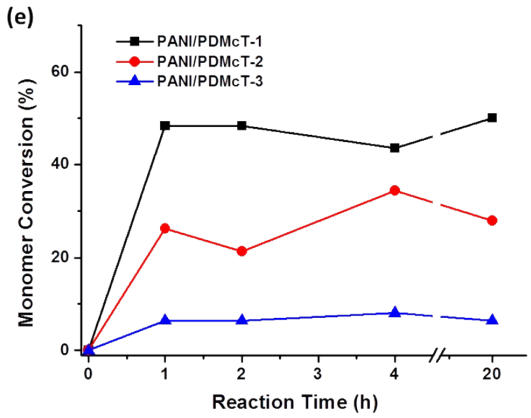


Fig. S3 ^{1}H NMR spectra of PANI/PDMcT miniemulsion dispersion: (a) before polymerization and sample (b) PANI/PDMcT-1, (c) PANI/PDMcT-2, and (c) PANI/PDMcT-3 after reaction for 20 h. (d) Monomer conversion of ANI for the three samples as time increased.

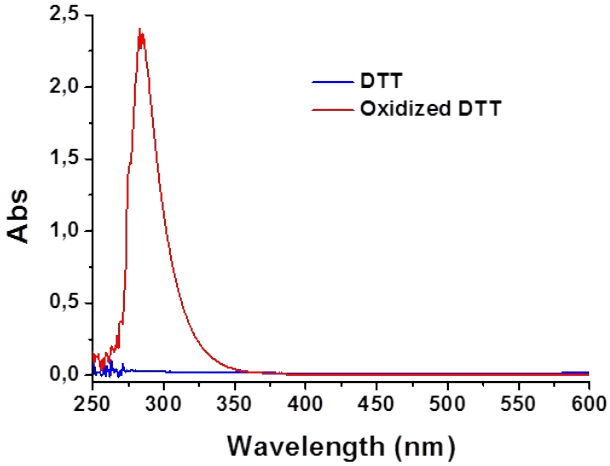


Fig. S4 UV-vis spectra of DTT and oxidized DTT by H_2O_2

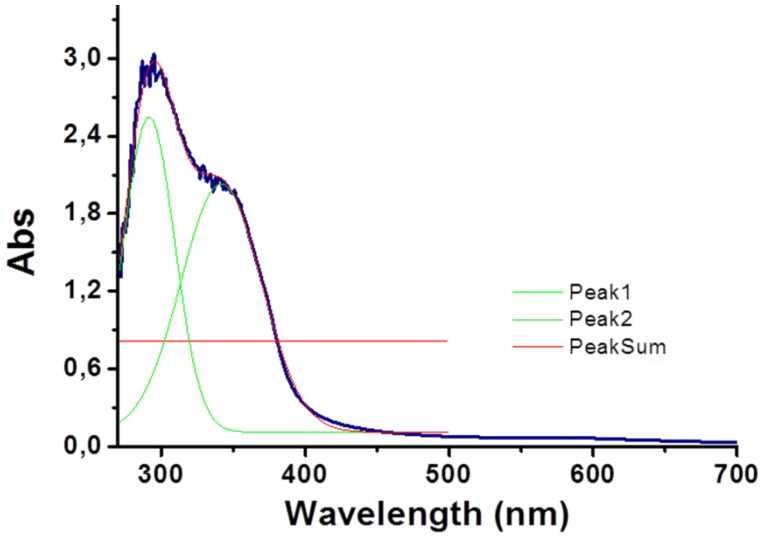


Fig. S5 Peak fitting and splitting of the UV-vis spectrum. The two peaks were assigned to cyclo-DTT and released DMcT, respectively. The spectrum from one of the released point of PANI/PDMcT-2 was taken as an example.

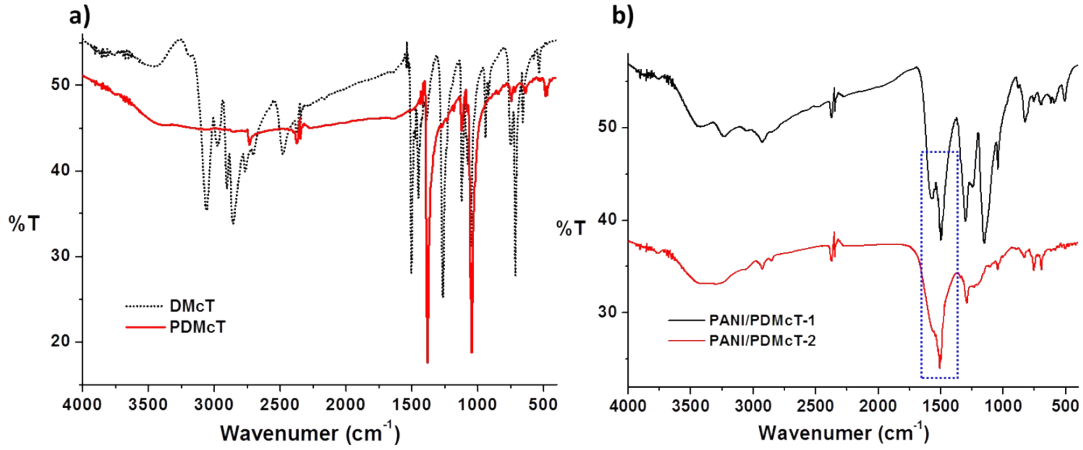


Fig. S6 FT-IR spectra of DMcT, PDMcT, PANI/PDMcT-1 and PANI/PDMcT-2 after purification.

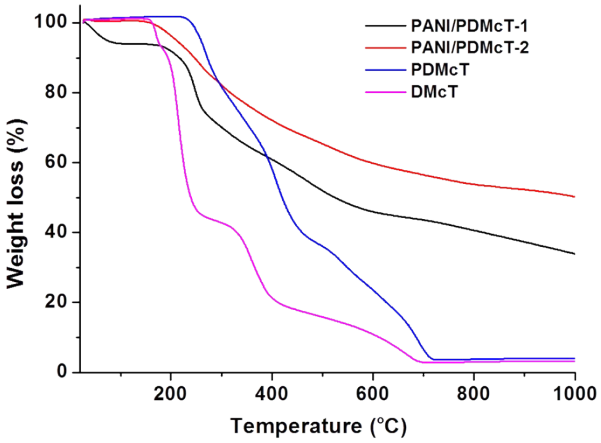


Fig. S7 TGA spectra of DMcT, PDMcT, PANI/PDMcT-1 and PANI/PDMcT-2 after purification.

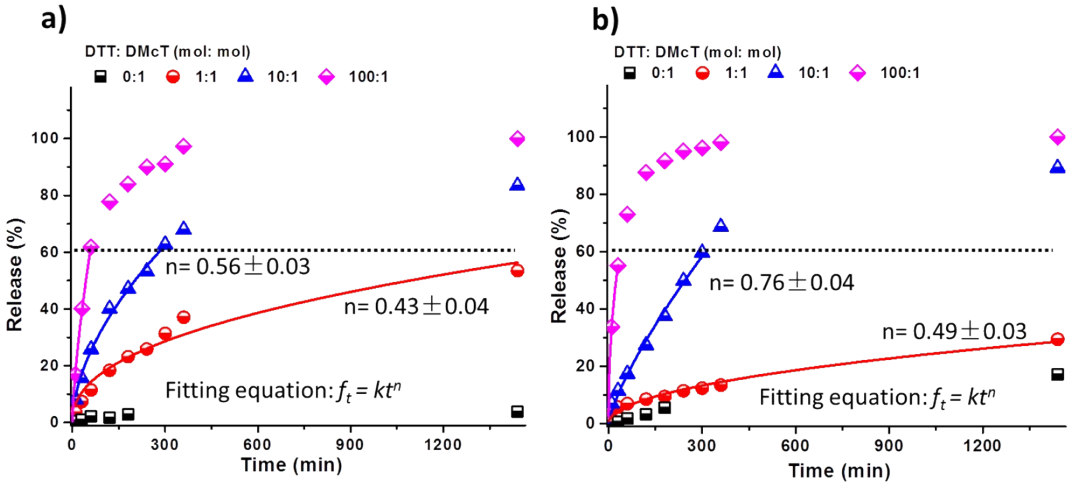


Fig. S8 Fitting profiles of release for a) PANI/PDMcT-1 and b) PANI/PDMcT-2 using the Korsemeyer-Peppas model. Only the portion of the release profile where f < 60% was fitted.

Considering that the triggered release of DMcT from PANI/PDMcT system involves both the degradation of PDMcT and diffusion of DMcT, the Korsemeyer-Peppas model [1, 2]:

$$f_t = k\,t^n$$

is expected to be more applicable to fit the release profiles with f the experimentally measured %cumulative drug release, k the kinetic constant incorporating structural and geometric characteristic of material, n the diffusion exponent characteristic of release mechanism, and t the time of release. It should be noted that, to evaluate the release data by the above model, the portion of the release profile where f <60% was only valid to use [1, 3].

As shown in Fig. S8, the release profiles were fitted with the Korsemeyer-Peppas model below f <60% using software of Origin Pro 9.1. The diffusion exponent n was calculated to be 0.43 ± 0.04 and 0.56 ± 0.03 for PANI/PDMcT-1, and 0.49 ± 0.03 and 0.76 ± 0.04 for PANI/PDMcT-2 at the condition when DTT: DMcT= 1:1 and 10:1 was applied respectively. Diffusion exponent $0.43<n<0.85$ was found for all the release at the above mentioned conditions, indicating that the release mechanism is an anomalous non-Fickian transport involving both the Fickian diffusion and the polymer degradation procedure. [4] That means, when reducing agent with the molar ratio of DTT: DMcT= 1:1 or 10:1 was applied to the PANI/PDMcT nanoparticles, the degradation of PDMcT was initiated and then the diffusion of degraded product DMcT started. During the time when the release process was examined, the two events, *i.e.* the degradation of polymers and diffusion of payloads, took place at the same time scale.

Note that for both samples PANI/PDMcT-1 and 2, when reducing agent with molar ratio of DTT: DMcT = 100:1 was used, the release is not fitted by the Korsemeyer-Peppas model considering that an obvious burst release of payloads is observed and the initial three release points already reached 60% of cumulative release. The Korsemeyer-Peppas model is then supposed not to be very appropriate to fit the release profiles. Instead, the release of DMcT is more a Fickian diffusion, a fist order $t^{1/2}$-time dependent model [4, 5] and driven by the concentration gradient of DMcT, even though the PANI/PDMcT system must first experience the degradation of PDMcT and then the diffusion of DMcT. This release behavior with a burst release of more than 80% of cumulative release in the initial 2 h implies that the degradation of PDMcT and relaxation (reduction) of PANI matrix was very fast when excess amount of reducing agent was applied. Rapid diffusion of DMcT was therefore observed in the presence of an extra assistance of the outer release medium, *i.e.* EA, a very good solvent for DMcT.

To sum up, the release kinetics of DMcT from the PANI/PDMcT system in the current work are influenced by several factors including the relaxation of PANI, degradation of PDMcT and the diffusion of DMcT. It is a complicated case and cannot be well fitted by only one release model, further and deeper understanding of its release mechanism using a more complex model may be expected.

References

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[2] P. Costa, J. M. S. Lobo, *Eur. J. Pharm. Sci*., 2001, **13**, 123-133.

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