Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Electronic Supplementary Information

Nitric oxide-releasing *S*-nitrosated derivatives of chitin and chitosan for biomedical applications

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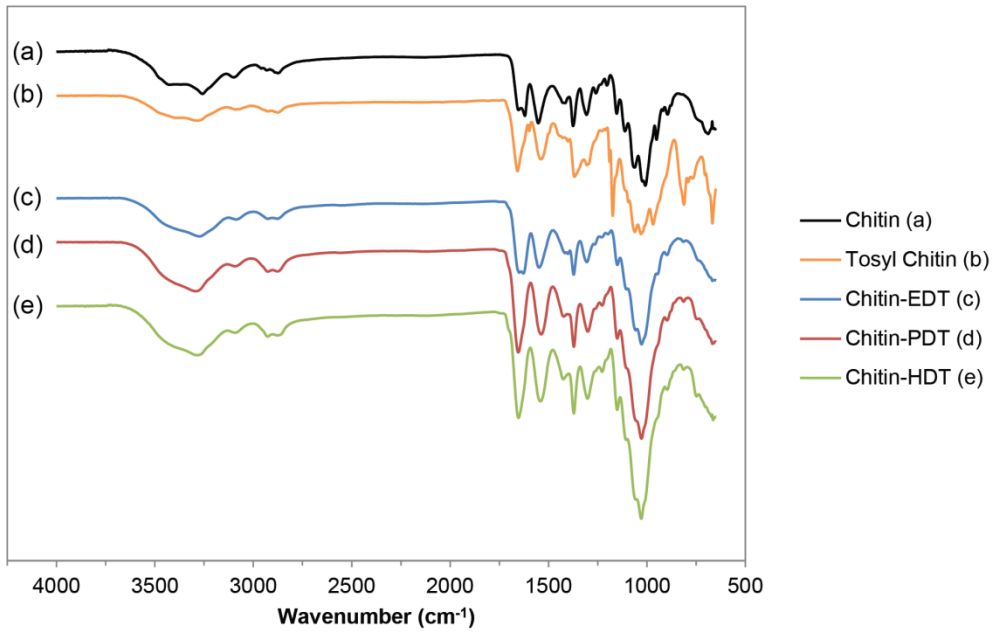

Fig. S1 ATR-IR spectra of thiolated chitin derivatives. See Table S1 for diagnostic peak assignments.

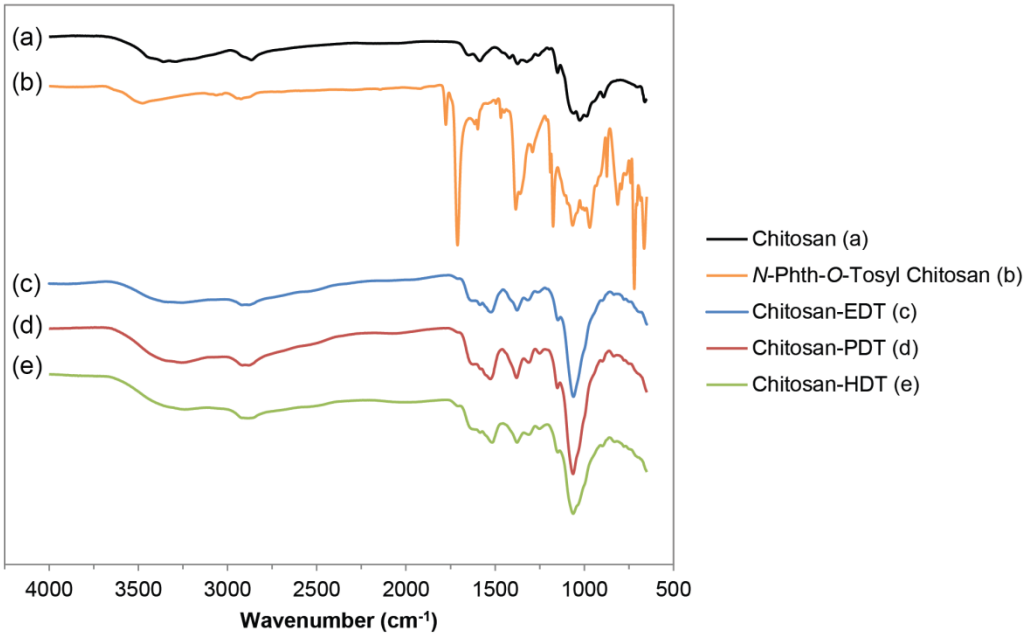

Fig. S2 ATR-IR spectra of thiolated chitosan derivatives. See Table S1 for diagnostic peak assignments.

Material	Diagnostic IR peaks (cm^{-1})											
	Hydroxyl (O-H)[1]	Amine (N-H)[1]	Amide (N-H)[1]	Phthaloyl (C=O)[2]	Phthaloyl (C=O)[2]	Amide I[1]	Aromatic (C-C)[3]	Amide II_1	Tosyl (S=O)[3]	Ether, alcohol (C-O)[1]	Tosyl (aromatic C-H)[3]	Phthaloyl (aromatic C-H)[2]
Chitin	3600 – 3200	-	3259	-	-	1653	-	1552	-	1024	-	-
O-Tosyl Chitin	3600 – 3200	-	3281	-	-	1657	1598	1538	1174	1031	811	-
Chitin-EDT	3600 – 3200	-	3277	-	-	1652	-	1548	-	1027	-	-
Chitin-PDT	3600 – 3200	-	3293	-	-	1653	-	1537	-	1028	-	-
Chitin-HDT	3600 – 3200	-	3280	-	-	1652	-	1541	-	1029	-	-
Chitosan	3600 – 3200	3359 3295	-	-	-	1650	-	1586	-	1062	-	-
N-Phthaloyl-*O*-Tosyl Chitin	3600 – 3200	-	-	1776	1711	-	1614 1597	-	1175	1066	813	720
Chitosan-EDT	3600 – 3200	3334 3258	-	-	-	-	-	-	-	1061	-	-
Chitosan-PDT	3600 – 3200	3334 3260	-	-	-	-	-	-	-	1063	-	-
Chitosan-HDT	3600 – 3200	3320 3242	-	-	-	-	-	-	-	1062	-	-

Table S1 Diagnostic IR peaks for thiolated chitin and chitosan materials. Peaks not used for diagnostic purposes (i.e. alkyl C-H) are not reported here. [1]F. G. Pearson, R. H. Marchessault, C. Y. Liang, *J. Polym. Sci*., 1960, **13**, 101. [2]K. Kurita, H. Ikeda, M. Shimojoh and J. Yang, *Polym. J.*, 2007, **39**, 945. [3]K. Kurita, H. Yoshino, K. Yokota, M. Ando, S. Inoue, S. Ishii and S. Nishimura, *Macromolecules*, 1992, **25**, 3786.

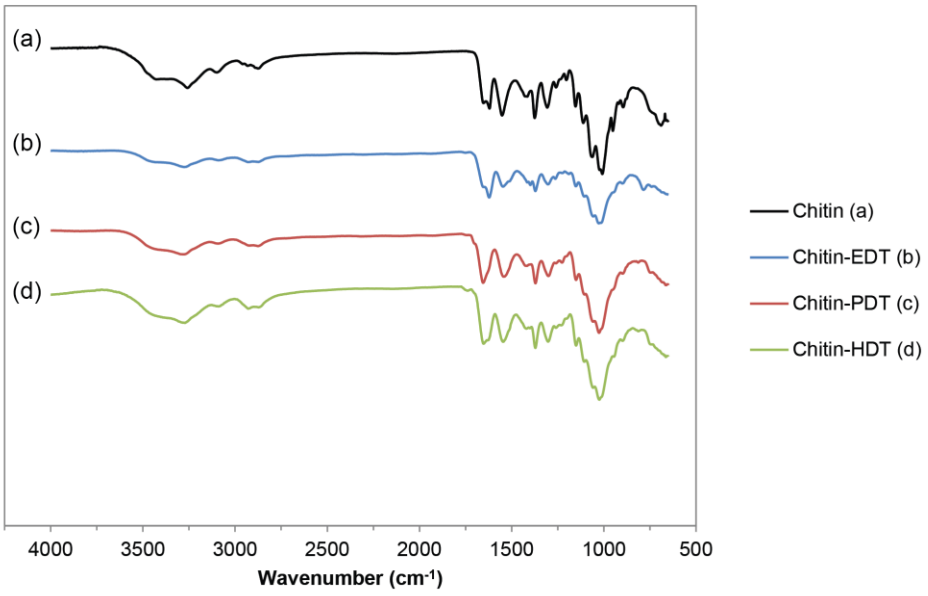

Fig. S3 ATR-IR spectra of *S*-nitrosated chitin derivatives. See Table S2 for diagnostic peak assignments.

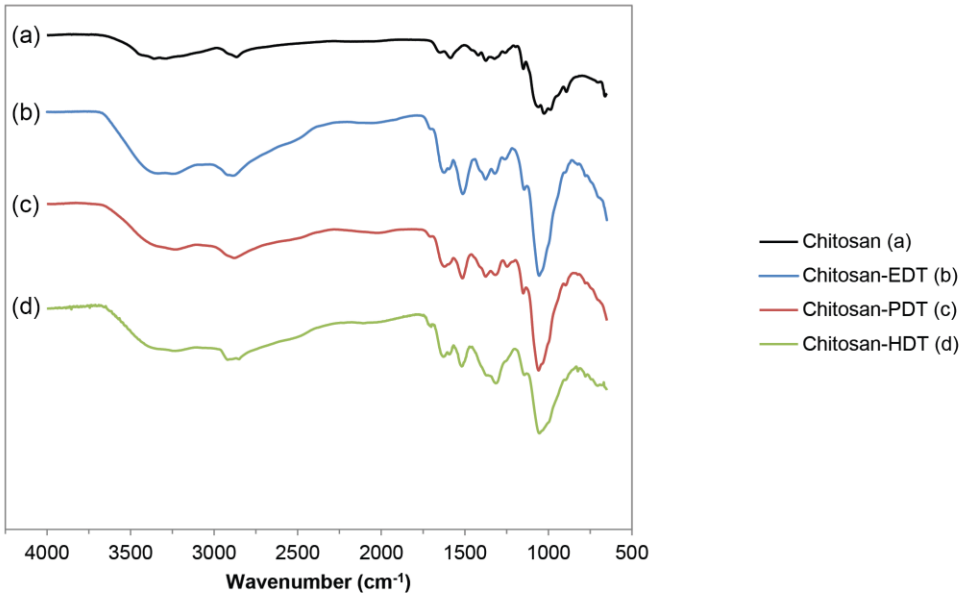

Fig. S4 ATR-IR spectra of *S*-nitrosated chitosan derivatives. See Table S2 for diagnostic peak assignments.

Material	Diagnostic IR peaks (cm^{-1})					
	Hydroxyl (O-H)[1]	Amine (N-H)[1]	Amide (N-H)[1]	Amide I[1]	Amide II_1	Ether, alcohol (C-O)[1]
Chitin	3600 – 3200	-	3259	1653	1552	1024
Chitin-EDT	3600 – 3200	-	3285	1652	1537	1028
Chitin-PDT	3600 – 3200	-	3282	1655	1544	1026
Chitin-HDT	3600 – 3200	-	3272	1652	1546	1024
Chitosan	3600 – 3200	3359 3295	-	1650	1586	1062
Chitosan-EDT	3600 – 3200	3335 3253	-	-	-	1055
Chitosan-PDT	3600 – 3200	3341 3224	-	-	-	1058
Chitosan-HDT	3600 – 3200	3344 3234	-	-	-	1053

Table S2 Diagnostic IR peaks for *S*-nitrosated chitin and chitosan materials. Peaks not used for diagnostic purposes (i.e. alkyl C-H) are not reported here. [1]F. G. Pearson, R. H. Marchessault, C. Y. Liang. *J. Polym. Sci*., 1960, **13**, 101.

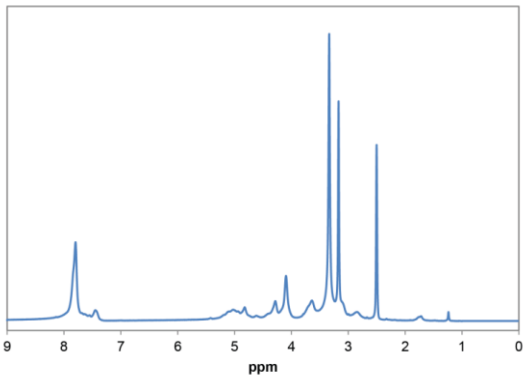

Fig. S5 ^{1}H NMR spectrum of *N*-phthaloyl chitosan.^{1}H NMR δ_H/ppm (400 MHz, DMSO-d_6, Me_4Si) 7.80 (s, *N*-phthaloyl), 7.45 (s, *O*-phthaloyl), 5.4 – 2.6 (m, carbohydrate).

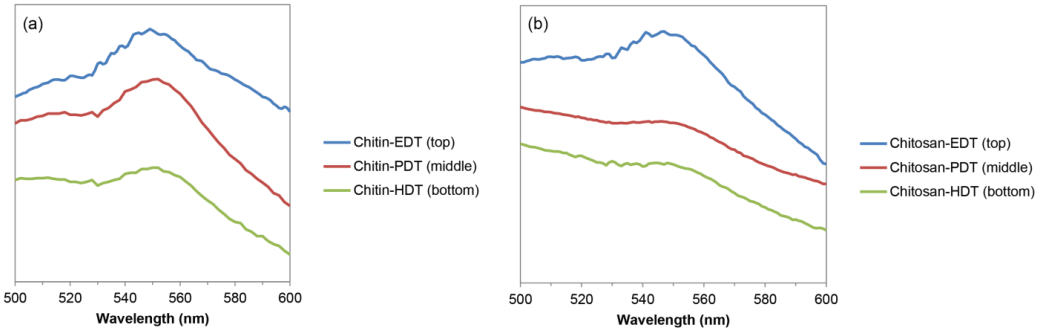

Fig. S6. Diffuse reflectance UV-Vis spectra of *S*-nitrosated chitin and chitosan derivatives depicting the characteristic $n_N \rightarrow \pi^*$ transition of *S*-nitrosothiols. UV-Vis λ_{max}/nm 549 (chitin-EDT), 552 (chitin-PDT), 551 (chitin-HDT), 547 (chitosan-EDT), 546 (chitosan-PDT), and 544 (chitosan-HDT).

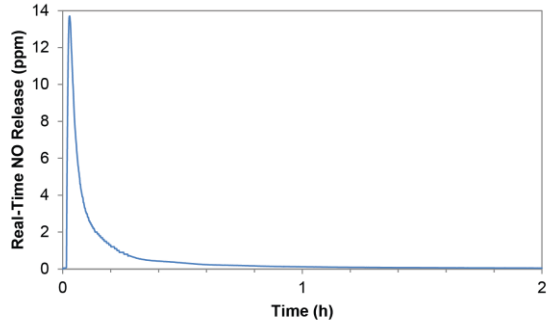

Fig. S7. Representative thermal decomposition of chitosan-EDT. The material was heated to 120 °C under a nitrogen atmosphere and the resulting nitric oxide (NO) emission was measured by chemiluminescence-based detection until returning to baseline. This process caused accelerated decomposition of the S-nitrosothiol, liberating quantifiable NO, and resulted in the concomitant decomposition of the polysaccharide backbone.