

Supplementary Information

Dansyl fluorophore functionalised hierarchically structured mesoporous silica nanoparticles as novel latent fingerprint development agents

Lais F.A.M. Oliveira^a, Lais V.A.T. da Silva^a, Artur F. Sonsin^a, Meclycia S. Alves^a, Cristiane V. Costa^a, Jeane C.S. Melo^a, Nicholas Ross^b, Paul T. Wady^c, Thomas Zinn^c, Ticiano G. do Nascimento^a, Eduardo J.S. Fonseca^a, Alexandro M.L. de Assis^{a,d,e}, A. Robert Hillman^{b,*}, Adriana S. Ribeiro^{a,*}

* Corresponding author: A. Robert Hillman, *e-mail*: arh7@leicester.ac.uk; Adriana S. Ribeiro, *e-mail*: aribeiro@qui.ufal.br

^a Federal University of Alagoas, Campus A. C. Simões, 57072-970, Maceió-AL, Brazil

^b Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

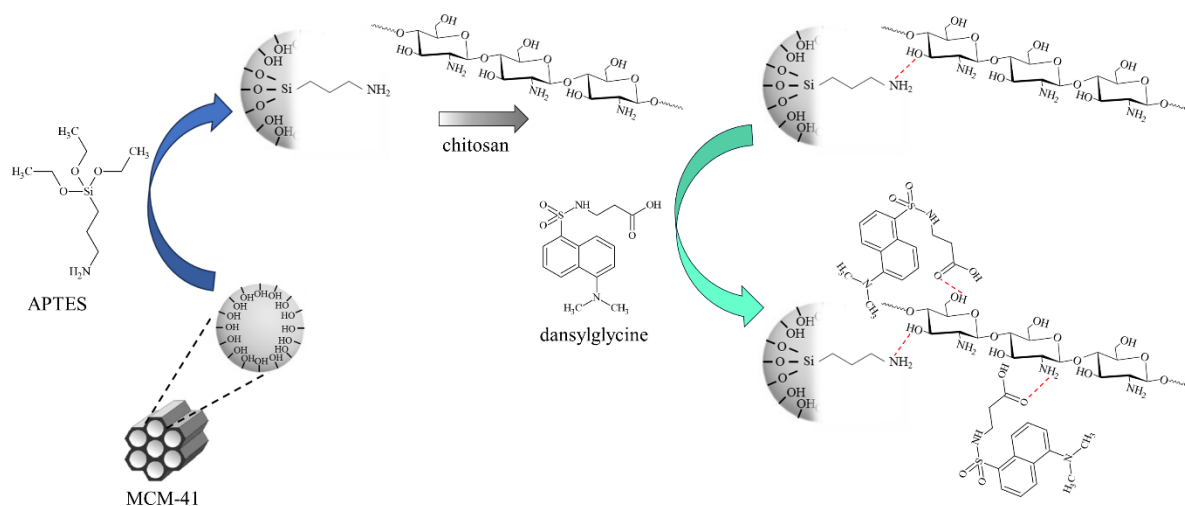
^c Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, UK

^d Technical and Scientific Section of Alagoas, Federal Police, 57025-080, Maceió-AL, Brazil

^e National Institute of Criminalistics, Federal Police, 70610-902, Brasília-DF, Brazil

Silica nanoparticles¹, polymer dots² and conjugated polymer nanoparticles³ have been reported as fluorescent nanomaterials useful for latent fingerprint development. Nevertheless, preparation of these materials involves several synthetic steps, for example a cross-linking reaction induced by UV irradiation.² In one case, they were applied in the less convenient form of a dispersion instead of a nanopowder³ and tested on only one substrate (adhesive tape).

Synthesis, characterization and application of MCM-based nanoparticles as delivery vehicles for the dansylglycine fluorophore is motivated by the restricted efficacy of previously studied materials (exemplified by electrospun PCL/dansylglycine nanofibers; see ref. 4) to chemically and physically simplistic surfaces, such as metal. In the specific case of the electrospun nanofibers, the requirement for laboratory facilities (to generate and handle the reagent) is also a practical impediment. MCM-41@chitosan@dansylglycine nanoparticles present better interaction with the fingerprint residues. As a result, they are more effective for visualization of latent fingerprints on a wider range of substrates (glass, plastic, bullet cartridge cases, polymer banknotes), on aged samples and on complex substrates with spatially varying topography, composition and color. Additionally, the application of nanoparticles (as a powder) enables development of latent fingerprints at the crime scene, without laboratory facilities.



Scheme S1. Schematic representation of the MCM-41 surface modification with APTES, chitosan and dansylglycine showing the possible reactions/interactions on the silica surface.

In the representation of Scheme S1, we note the possibility of either covalent bond formation (ester and amide chemistry) or hydrogen bond formation. The former is more likely in protic media, and the latter in aprotic media. In the aprotic solvent used here (CHCl_3), hydrogen bond formation is the more likely. FTIR spectra (see Figure 1) are more consistent with this latter possibility. Based on this evidence, the silanol groups on the MCM-41 surface react with APTES: -OH groups on the silica surface are largely replaced by -NH₂ groups.^{5,6} The -NH₂ and -OH groups from chitosan interact with APTES by formation of hydrogen bonds. Considering the chitosan deacetylation degree of 85%, carboxyl groups (15%) may also form hydrogen bonds with the APTES functionalities (-NH₂ or unreacted -OH). This scenario is consistent with previous studies⁷ indicating hydrogen bond interactions between dansylglycine (carboxylic acid) molecules and chitosan polymer chains.

References:

- [1] S. Zhang, R. Liu, Q. Cui, Y. Yang, Q. Cao, W. Xu, L. Li, *ACS Appl. Mater. Interfaces* 2017, **9**, 50, 44134.
- [2] H. Chen, K. Chang, X. Men, K. Sun, X. Fang, C. Ma, Y. Zhao, S. Yin, W. Qin, C. Wu, *ACS Appl. Mater. Interfaces* 2015, **7**, 26, 14477.

- [3] H. Chen, R.-l. Ma, Y. Chen, L.-J. Fan, *ACS Appl. Mater. Interfaces* 2017, **9**, 5, 4908.
- [4] E.G. Mazzini Júnior, J.D.A. Cantalice, A.M.L. de Assis, J.D. de Freitas, L.M.M. Costa, A.S. Ribeiro, *J. Appl. Polym. Sci.*, 2020, **137**, 49804.
- [5] R. Ojani, J. -B Raouf, S. Fathi, *J. Solid State Electrochem.* 2009, 13, 837.
- [6] Z. Shakeran, M. Keyhanfar, J. Varshosaz, D.S. Sutherland, *Mater. Sci. Eng. C* 2021, **118**, 111526.
- [7] A.P.P. Praxedes, A.J.C. da Silva, R.C. da Silva, R.P.A. Lima, J. Tonholo, A.S. Ribeiro, I.N. de Oliveira, *J. Coll. Interf. Sci.*, 2012, 376, 255.

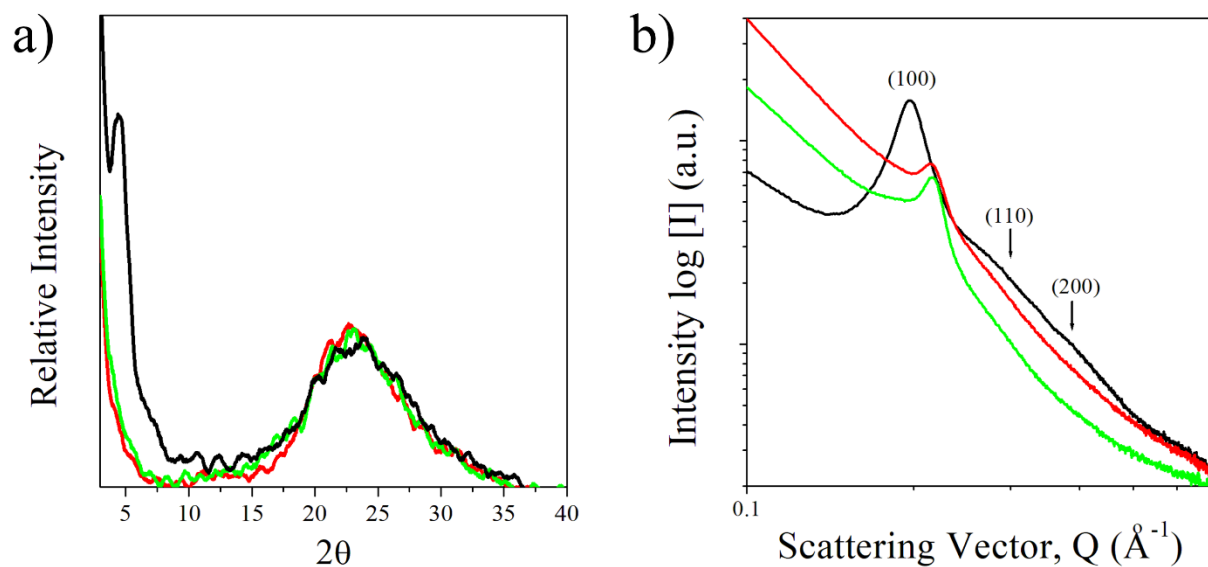


Figure S1. a) Powder X-ray Diffraction (PXRD) and b) SAXS patterns of MCM-41 (—), MCM-41@Ch (—) and MCM-41@Ch@DnsGly (—).

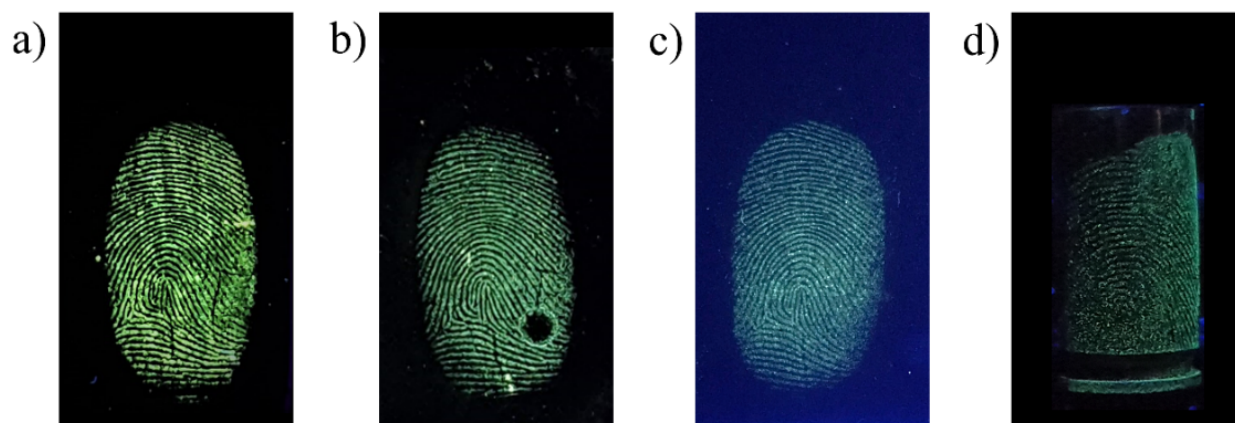


Figure S2. Representative images of developed fingerprints by applying MCM-41@Ch@DnsGly NPs on a) stainless steel, b) glass, c) plastic and d) unfired cartridge case on 30 days old samples.

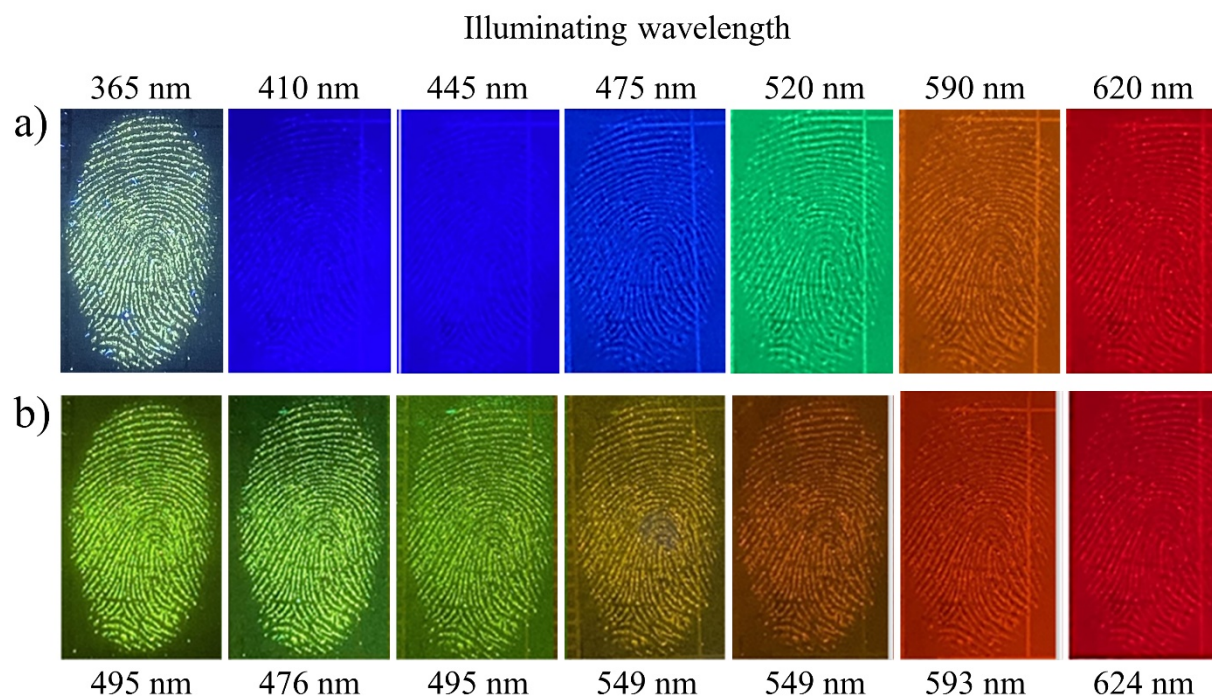


Figure S3. Fingerprint developed with MCM-41@Ch@DnsGly illuminated with all available wavelengths a) viewed with no filter and b) viewed with chosen ‘best’ viewing filter noted below.

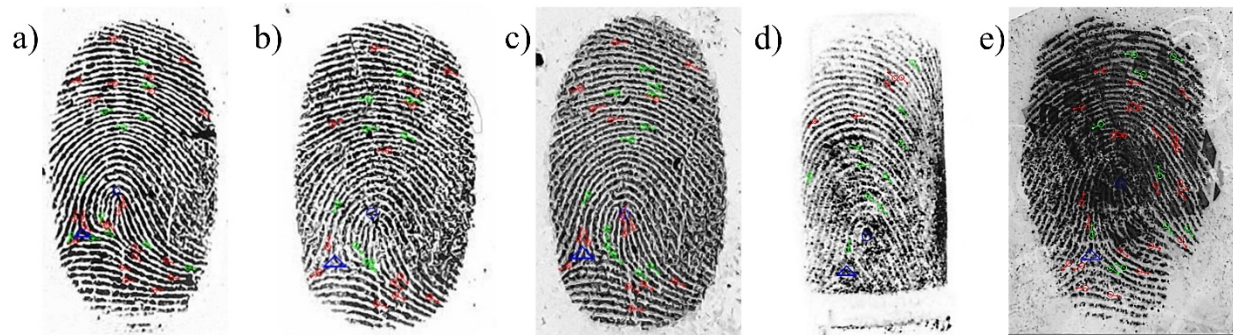


Figure S4. Representative images of developed latent fingerprints on a) stainless steel, b) glass, c) plastic, d) cartridge case and e) banknote with level 1, 2 and 3 details identified: ridge ending (red), bifurcation (green), delta (blue triangle) and core (blue circle), showing 38, 24, 30, 14 and 37 minutiae, respectively.

Table S1. UK Home Office grading for the samples investigated according to the surface and aging.

Surface	Grade (% of samples)				
	1 day	7 days	15 days	30 days	Total
Stainless steel	4 (100%)	4 (100%)	4 (50%)	4 (50%)	4 (75%)
			3 (50%)	3 (50%)	3 (25 %)
Glass	4 (100%)	4 (100%)	4 (100%)	4 (50%)	4 (87.5%)
				3 (50%)	3 (12.5%)
Plastic	4 (100%)	4 (100%)	4 (75%)	4 (50%)	4 (81.3 %)
			3 (25%)	3 (50%)	3 (18.7%)

Cartridge	4 (50%)	4 (25 %)	4 (75 %)	3 (50 %)	4 (38.9 %)
case	3 (17%	3 (75 %)	3 (25 %)	2 (50 %)	3 (38.9 %)
	2 (33%)				2 (22.2%)
	4 (93.8%)	4 (81.3%)	4 (75%)	4 (37.5%)	4 (69.7%)
Total	3 (6.2%)	3 (18.7%)	3 (25%)	3 (50%)	3 (24.2%)
				2(12.5%)	2 (6.1%)