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Metastable 9-fluorenone: Blue-shifted fluorescence, single-crystal-to-single-crystal reactivity, and evaluation as a multi-modal fingerprint visualization treatment

Grace E. Florence,^[a] Katy A. Bruce,^[a] Helena J. Shepherd,^[a] and William J. Gee*^[a]

Dedication ((optional))

Abstract: A metastable form of 9-fluorenone (MS9F) has been characterized using Raman spectroscopy, fluorimetry, and X-ray diffraction techniques. MS9F emits blue fluorescence ($\lambda_{\text{max}} = 495$ nm) upon 365 nm irradiation and undergoes a single-crystal-to-single-crystal (SCSC) transformation to reach the ground state form (GS9F) over ca 30 minutes, whereupon it emits the expected green fluorescence. A structure-property relationship for this fluorescent behavior has been posited. MS9F and GS9F were applied as a means of visualizing latent fingerprints on a non-porous surface. This approach identified three different modes of fluorescent fingerprint visualization using 9-fluorenone.

Latent fingerprints (*i.e.* fingerprints) constitute important forensic evidence. Fingerprint residues contain an emulsion of polar (*e.g.* amino acids) and nonpolar (*e.g.* lipids) dermal components. Of these, the nonpolar fraction is more resistant to environmental degradation, and thus persists longer on surfaces than the polar fraction.^[1] For this reason, new visualization methods that target the nonpolar components of fingerprints provide great interest to the forensic community. Our previous work has shown that sublimation can be harnessed to direct luminescent chemical reagents, *e.g.* lanthanide complexes, into the lipid fraction of fingerprints to aid visualization.^[2] This work aims to complement the established fingerprint visualization technique vacuum metal deposition (VMD), which is known for its high sensitivity and applicability across a wide range of surfaces.^[3] VMD could be improved by developing inherently luminescent fingerprint coatings, as presently this is achieved by applying additional treatments, such as fluorescent staining with Basic Yellow 40.^[4] Additional steps such as this complicate and lengthen the VMD process, and risk damaging the fragile fingerprint evidence.

While effective, the luminescent rare earth method to visualize fingerprints is not as cost-effective as other strategies.^[1,2] By comparison, many small organic fluorophores are inexpensive, and offer a wide diversity of emission profiles spanning the visible spectrum. 9-Fluorenone is one such small organic fluorophore, and it forms the basis of many luminescent molecular devices and materials. This is exemplified by fluorenone scaffolds found in light emitting diodes,^[5] charge-transfer compounds,^[6] copolymers,^[7] devices for studying protein-ligand interactions,^[8] and organic solar cells.^[9] 9-Fluorenone has enabled fundamental study of fluorescent

processes such as quenching,^[10] population of excited states,^[11] two-photon absorption processes,^[12] and theoretical modelling studies in both the gas- and solution-phase.^[13] Given the importance of the 9-fluorenone motif to emissive materials,^[14] this discovery of a new polymorph provides new insights from a proposed structure-property relationship, potentially guiding the design of new materials.

The fluorescent behavior of the archetypal species, 9-fluorenone, has been extensively studied in solution.^[15] In this medium the fluorescent emission is highly susceptible to perturbation by both solvent polarity and temperature.^[13,15] This is exemplified by shifting of the emission maximum from ca 500 nm for the nonpolar aprotic hexane, to 570 nm in the polar protic solvent methanol owing to the influence of hydrogen bonding.^[13] This wavelength range is ideal for forensic applications because it spans the optimal detection range of the human eye.^[16] The physical properties of 9-fluorenone are similarly interesting, with a sublimation vapor pressure of 0.0121 Pa and an enthalpy of sublimation of 88.5 ± 3.7 kJ mol⁻¹ at 300 K,^[17] and suggest that sublimation represents a viable vector of delivery into a latent fingerprint.

Given the well-documented physical properties of 9-fluorenone, and an established protocol for delivery of volatile species into fingerprint residues,^[2] work began by applying fluorenone using this prior protocol. Uptake of 9-fluorenone into the fingerprint was apparent even without optimizing the heating and vacuum conditions (Fig. 1, Details of the fingerprint study and subsequent visualization conditions listed in ESI). Unexpectedly, two distinct luminescent species were clearly visible. These correspond to the expected green-emitting ground-state 9-fluorenone (GS9F), and a previously unreported metastable blue-emitting form (MS9F). Past characterization of solid-state 9-fluorenone has been limited to a poorly-resolved absorption spectrum with a maximum at ca $\lambda = 395$ nm, and an emission maximum at $\lambda = 510$ nm.^[18] To the best of our knowledge, no metastable forms of 9-fluorenone have been reported to date. Given the ubiquity of 9-fluorenone and its derivatives in fluorescent materials, coupled with the promise of forensic science

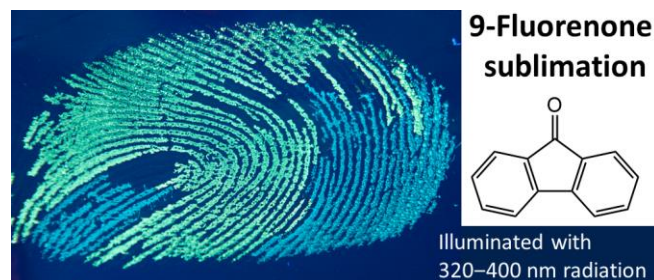


Figure 1. The unexpected observation of two luminescent 9-fluorenone species after unoptimized chemical treatment of a latent fingerprint. GS9F emits green fluorescence, whereas MS9F produces a blue-shifted emission.

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applications, the new metastable form identified in this work offers important insights. A structure-property relationship rationalizing the differences in emission properties is proposed below, and a study exploring delivery of either GS9F, or MS9F, into fingerprint residues is reported. The differences in emission spectra between the two polymorphs enables the possibility of multi-modal visualization of fingerprints using a specific desired fluorescent form.

Large quantities of metastable MS9F were sourced during this study by dropping molten 9-fluorenone onto aluminum foil whereupon rapid crystallization occurs. Screening the resultant MS9F and GS9F forms was performed using a UV light source ($\lambda = 365$ nm) and manually sorting the products according to color of the fluorescent emission, with approximately half the material typically adopting the metastable form. Bulk purity of MS9F was confirmed using powder X-ray crystallography (ESI, Fig. S2), with the measured diffraction pattern matching the features predicted from single crystal measurements performed on the metastable species. Analysis of both species by thermogravimetric analysis showed that MS9F has a depressed melting point onset of 72.8 °C relative to GS9F at 84.4 °C. Continued heating resulted in slow onset of mass loss for both species from *ca* 100 °C as 9-fluorenone volatilizes (ESI, Fig. S3, S4).

Solid-state fluorimetry was used to characterize and compare the excitation and emission characteristics of MS9F and GS9F. The ground state form, GS9F (Fig. 2, green trace), has a broad emission profile spanning 450–700 nm when irradiated at 365 nm. The maxima is located at 515 nm, corresponding to the expected green color. These emission characteristics are blue-shifted for MS9F (Fig. 2, blue trace), with an emission maximum located at 495 nm, and an emission profile spanning from 430–650 nm.

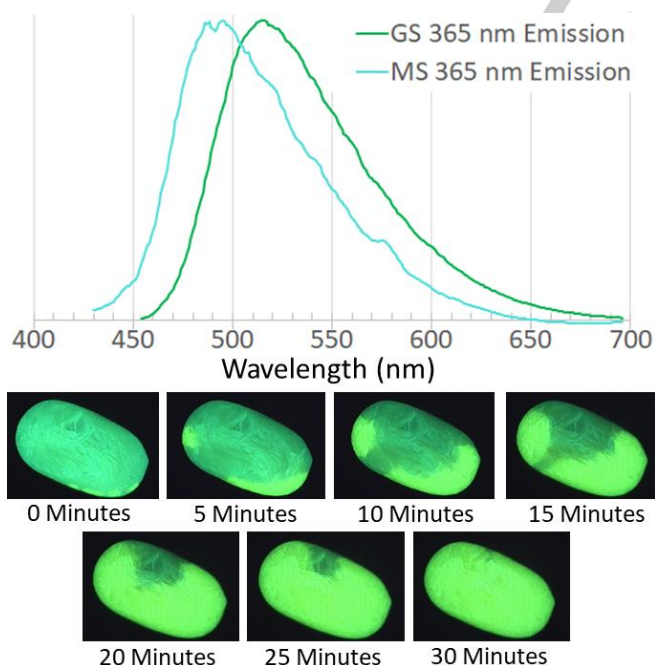


Figure 2. Top: A comparison of the emission profile for both MS9F (blue trace) and GS9F (green trace) when irradiated at 365 nm in the solid-state. Bottom: The SCSC transformation of MS9F to GS9F occurring over 30 minutes with an image taken every 5 minutes.

Single crystals of MS9F that were suitable for X-ray diffraction studies were grown by slow-cooling of 9-fluorenone dissolved in hot mineral oil. Full details of synthetic procedures and an expanded crystallographic discussion are available as ESI. The diffraction pattern of MS9F contains first-order satellite peaks corresponding to an incommensurate modulation of the crystal structure, as described in more detail in the supplementary information. Full analysis of the incommensurate modulation is beyond the scope of the present communication and consequently the structure was refined only against the main Bragg reflections. The result is a model displaying whole molecule disorder, with two possible orientations of the molecule that are approximately coplanar, related by an inversion center, each with 50% occupancy. While it is possible to compare overall crystal packing motifs between MS9F and GS9F it is important to note that no conclusions as to the long-range order of specific intermolecular interactions can be drawn from this model.

In order to compare the differences in structure and resultant fluorescent properties it is necessary to briefly revisit the known GS9F structure.^[21] The asymmetric unit of GS9F contains two crystallographically distinct molecules, which form a dimer through π - π stacking interactions, as shown in the green box in Figure 3, with interplanar distances between the rings between 3.50 and 3.65 Å. The molecules are oriented such that the keto groups are aligned parallel. There are no further significant supramolecular interactions between adjacent molecules in GS9F. By contrast, in MS9F, it is possible for molecules to be oriented such that their keto groups are aligned antiparallel, as shown in the blue box in Figure 3. Intermolecular ketone distances of 3.088(X) Å for C(1)⋯O(1') and O(1)⋯C(1') imply the formation of bond dipole-dipole interactions occurring between adjacent opposing keto groups. This difference in ketone environment may well be responsible for the observed differences in the emission spectra of the two compounds.

The ability of dipole-dipole interactions to direct crystal structure has been debated,^[19] however functional groups with strong dipole moments, such as nitriles (3.6 D) or ketones (2.9 D), are known to influence the orientation of neighboring molecules when in close proximity (<3.6 Å).^[20] Despite the planar aromatic nature of 9-fluorenone, no π - π stacking interactions were evident in the metastable MS9F structure. Weak C-H⋯O hydrogen bonding has been found to meaningfully contribute to stabilization of specific crystal forms under certain conditions,^[22] however such interactions do not appear to influence the solid-state structures of either MS9F or GS9F, given that the donor-acceptor distances are >3.4 Å, and owing to non-optimal directionality of the hydrogen donor atoms.

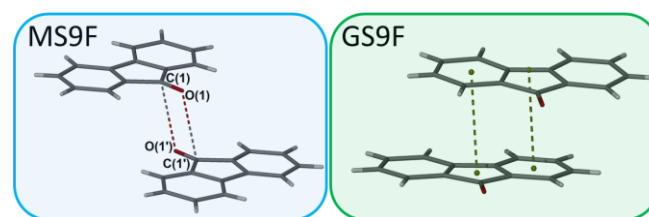


Figure 3. Blue box: The solid-state structure of MS9F. The proposed ordering force, bond dipole-dipole interactions, occurs between antiparallel keto groups. Green box: The solid-state structure of GS9F.^[21] Here the dominant ordering force is π - π stacking interactions between aromatic rings of 9-fluorenone.

spectrum revealed matching features. Similarly, no additional peaks were evident in either fingerprint spectrum. This confirms the identity of crystalline GS9F and MS9F as the emissive species present within the fingerprints after treatment. Both fingerprint spectra exhibited greater fluorescence and a more undulating baseline than the reference samples, which likely derive from fingerprint sebum or other biological residues.^[28]

The most significant peak differences in the Raman spectra derived from the fingerprint samples containing either GS9F or MS9F corresponded to unique lattice and ketone environments (Fig. 5). There is a peak in the low energy phonon region for GS9F that appears at 85 cm⁻¹, while in MS9F a peak is found at 102 cm⁻¹. This is indicative of a significant change in the long-range translational symmetry between the two crystal structures. The ketone stretching mode shifts from 1712 cm⁻¹ for GS9F to 1719 cm⁻¹ for MS9F, and can be attributed to a change in chemical environments at the ketone upon transition between the polymorphic forms. Both findings are supported by the observations made in the X-ray diffraction study discussed above.

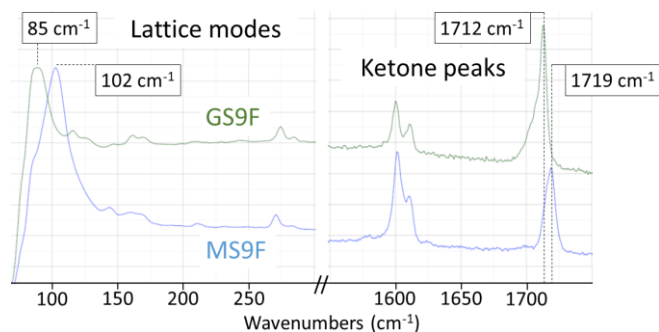


Figure 5. The unique lattice and ketone environments observed for GS9F (green upper trace) and MS9F (blue lower trace) present within fingerprint samples placed on aluminum foil when analyzed by Raman spectroscopy.

The sum of these results showcase a new metastable form of 9-fluorenone, its physical properties, and its ability to contribute to the visualization of fingerprints. Single-crystal X-ray diffraction methods provide a structural comparison of the metastable and ground-state forms, enabling a plausible structure-property relationship linking the chemical environment of the keto group within the crystalline lattice to the Stokes shift of the fluorescent emissions. The metastable form was found to convert over the space of 30 minutes to the ground-state form by a single-crystal-to-single-crystal transformation, in which molecules of 9-fluorenone must rotate significantly. Finally, the ability to selectively impart either form into fingerprint residues to allow their fluorescent visualization was achieved. This work shows that the metastable form, the ground-state form, and a non-crystalline form could all be infused into fingerprints, each providing a unique fluorescent emissive profile. These preliminary findings show promise for multimodal imaging of fingerprints using a single chemical reagent, however further work is needed to validate this method in a forensic context. Limitations of the current work include that only a single surface type was investigated, that the fingerprints were not aged beyond 24 hours, and that only a relatively small pool of fingerprints / donors were evaluated (See ESI for full study details). A thorough overview of the factors needing consideration

when undertaking fingerprint research was recently published by the International Fingerprint Research Group.^[29] These guidelines provide detailed assessment criteria for evaluating the results of pilot studies such as this.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Fluorescence • Forensics • Fingerprint • Fluorenone • Raman spectroscopy

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Layout 2:

COMMUNICATION

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**Metastable 9-fluorenone: Blue-shifted
fluorescence, single-crystal-to-single-
crystal reactivity, and evaluation as a
multi-modal fingerprint visualization
treatment**

The unexpected discovery of two unique emissive forms of 9-fluorenone after using it to treat latent fingerprints has resulted in the characterisation of a new metastable polymorph. This species exhibits single-crystal-to-single-crystal reactivity, blue-shifted fluorescent emission, and potential forensic applications. A structure-property relationship has been posited comparing the ground and metastable forms to promote understanding.

