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Supplementary information for:

Enhanced anti-counterfeiting measures for additive manufacturing: coupling lanthanide nanomaterial chemical signatures with blockchain technology

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General materials and instrumental methods. Natural poly(lactic) acid pellets were obtained from Push Plastic (Springdale, AR, USA). $Eu(NO_3)_3{\cdot}5H_2O$ (99.9%) and $Tb(NO_3)_3{\cdot}5H_2O$ (99.9%) were supplied from Sigma-Aldrich. D-Aspartic Acid (>98%) was purchased from TCI America. Deionized water with a resistance of 18.2 MΩ was used during nanomaterial syntheses. All other materials were obtained from commercial sources at reagent grade or better and were used as received. Bath sonication was performed with a Branson 2510. Fluorescence spectra were obtained on powder samples and on sections of filaments placed in wells of a black plate using a Tecan Safire instrument. TGA experiments were performed using a Netzsch TG 209 F3 in Al_2O_3 pans. Samples (typically 15-20 mg) were held at 40 °C for 20 min before heating to 800 °C at a ramp rate of 4°C min^{-1} in an air atmosphere. TEM was performed on a Tecnai G2 F20 (FEI Corporation) operating at 200 kV. Helium ion microscopy (HeIM) was performed using a Zeiss Helium Ion Orion Plus. Full details on the use of a smartphone (Apple IPhone 5s) for acquiring fluorescence images and the subsequent image processing steps using Fiji software for measuring color differences are provided on page S5.

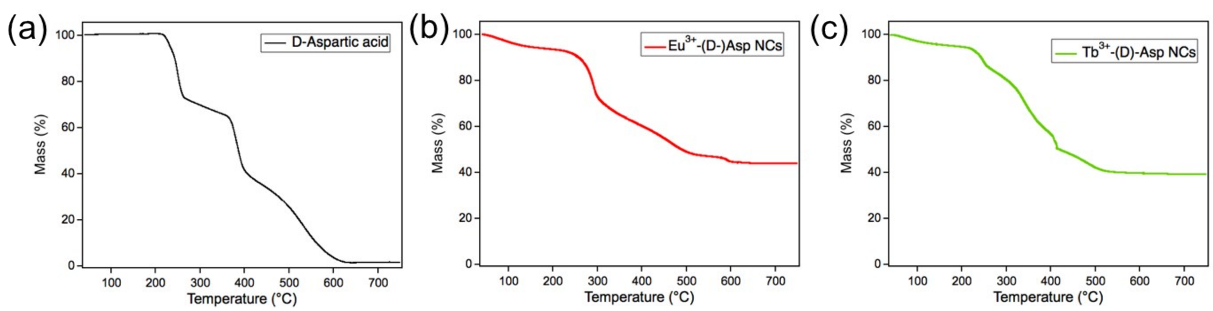

Figure S1: TGA data of pure (a) D-Aspartic acid, (b) Eu^{3+}-(D)-Asp NCs, and (c) Tb^{3+}-(D)-Asp NCs. Note, no mass is lost (apart from adsorbed H_2O <150 °C) until after 215 °C. All data was recorded in an air atmosphere with a heating rate of 4 °C min^{-1}.

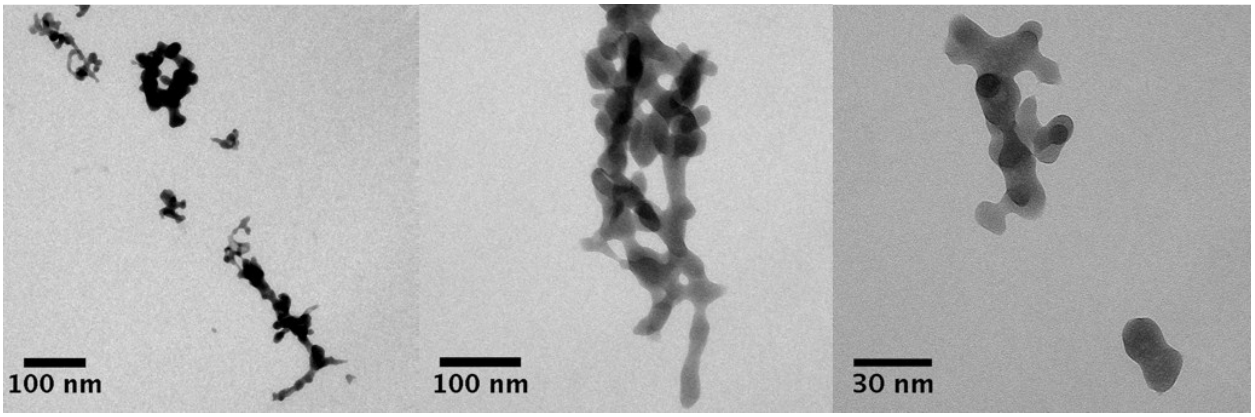

Figure S2: TEM images of Eu^{3+}-(D)-Asp NCs.

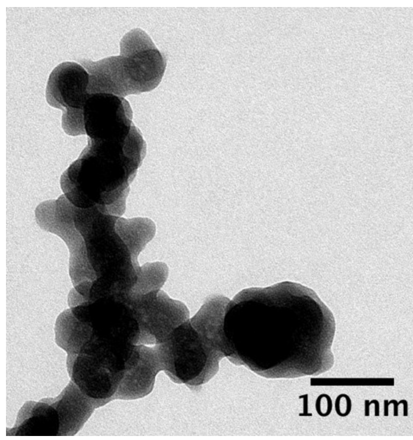

Figure S3: TEM image of Tb^{3+}-(D)-Asp NCs.

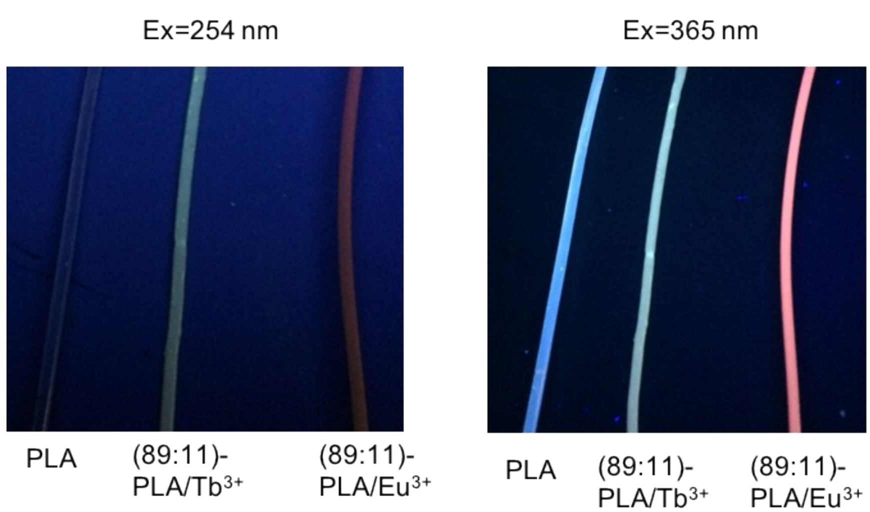

Figure S4: Photographs of pure PLA and PLA/Ln^{3+} filaments with UV light.

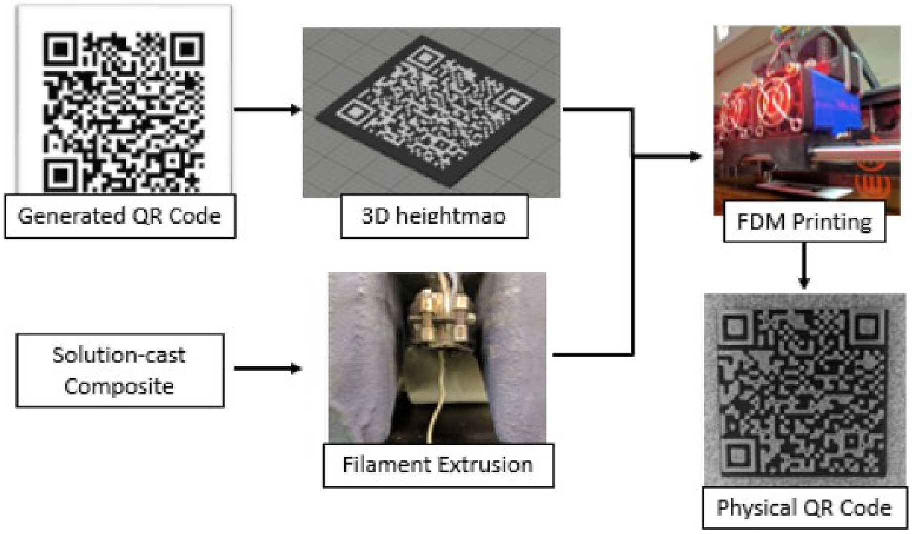

Figure S5: The process to generate QR codes by FDM 3D printing.

Quantification of QR code fluorescent color signature data when excited by UV light using a smartphone and Fiji software

3D-printed (89:11)-PLA/Ln^{3+}-(D)-Asp on PLA parts and a dispersed continuous thin layer of pure Ln^{3+}-(D)-Asp powder (the same Ln^{3+} species as was present in the QR code) were arranged adjacent to each other on a flat surface. The orientation of the QR code relative to the reference powder was determined not to have any effect on the outcome of color quantification. The part and reference materials were then illuminated in the dark at a height of approximately 10 cm using a 4 W UV hand lamp equipped with both 254 nm (for Ln = Tb^{3+}) and 365 nm (for Ln = Eu^{3+}) emission wavelengths. Images of the resulting fluorescence emission color were recorded through a camera application (Manual) on a standard Apple IPhone 5s smartphone by positioning the camera parallel to the UV light source at approximately the same height. As indicated in the main text, the camera's basic image acquisition conditions were kept constant. A shutter speed of 1/15 sec, ISO setting of 750, and a color temperature of 5000 K were fixed for all images acquired.

The images at a size of 3264 x 2448 pixels were then processed, after transferring to a computer, using the Fiji package for ImageJ software to calculate the color difference (ΔE) of three selected areas of the QR code (fiducials) relative to the reference powder. The smartphone records the color information in sRGB format. A Fiji software plugin "Color Transformer 2"[1] was used to convert the recorded images from the sRGB to Lab color space (CIELAB). After conversion, the L* (lightness) and a*, b* (color components) were separated into separate channels resulting in an image stack. Fiducial areas (typically 7000-10000 sq. pixels) were drawn arbitrarily using the *rectangle* tool in Fiji within each of the three orientation squares of the QR code. The average values over the fiducial areas for each channel (L*, a*, b*) were obtained using the measure tool (analyze → measure) in Fiji. Similarly, an area was drawn in the reference material and the average channel values were obtained. Figure S6 illustrates this process and the resulting average values for each channel for a Tb^{3+}-based QR code (a) and for a Eu^{3+}-based QR code (b).

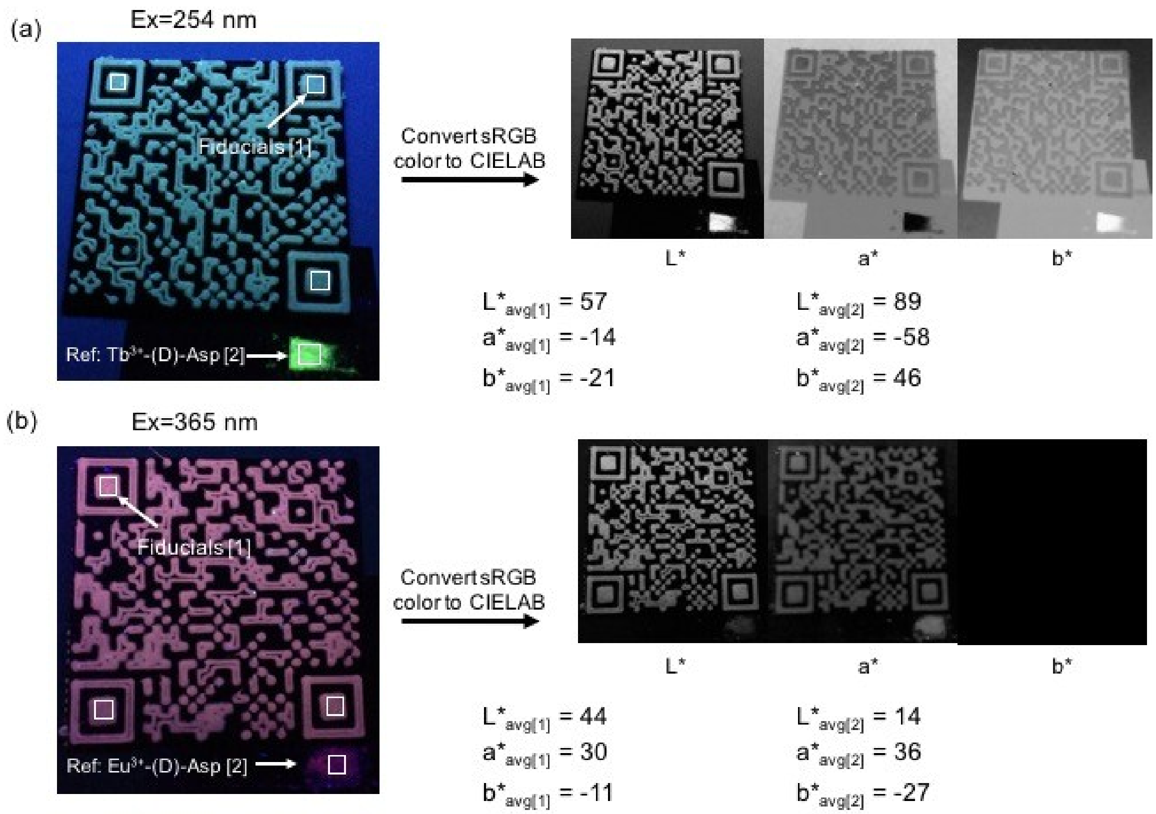

Figure S6

The ΔE values obtained in this study were specifically the ΔE_{76} value, in reference to the distance formula derived after the development of the CIELAB color space by the International Commission on Illumination (CIE) in 1976.[2] The ΔE value was obtained from the following equation,[3] where "1" represented the average channel values across the QR code fiducial areas and "2" represented the average values across the reference area:

Using (L_1^*, a_1^*, b_1^*) and (L_2^*, a_2^*, b_2^*), two colors in L*a*b*:

$$\Delta E_{ab}^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

For the example image in Figure S6a, ΔE = 87 and for the image in Figure S6b, ΔE = 34.

Further details on the specific data included in the virtual part or digital twin related to QR code composed of (89:11)-PLA/Tb^{3+} and PLA

Transactions

1. *Printing conditions used to produce (89:11)-PLA/Tb^{3+} and PLA part*
   a. Describes FDM printer setup conditions for part
      i. $T_{extruder1}$ = 200 °C; $T_{extruder2}$ = 200 °C; $T_{printer\ bed}$ = 60 °C; $Thickness_{layer}$ = 0.2 mm; $Diameter_{nozzle1}$ = 0.4 mm; $Diameter_{nozzle2}$ = 0.4 mm.
      ii. Ethereum Transaction TxHash = "0x67524f782ef53ab1bc8accd4d731db60ce4a9b669629ad830072ea605898fa78" https://etherscan.io/tx/0x67524f782ef53ab1bc8accd4d731db60ce4a9b669629ad830072ea605898fa78

2. *QR-code G-code for a selected area*
   a. Computer-aided design file (.stl) translates 3D part information into directions for the FDM printer by slicing into "G-code". A line of G-code (for the area in yellow on the part below in Figure SX) is listed in 2.i.
      i. G1 X-16.413 Y16.413 Z1.600 F2400 A108.78067

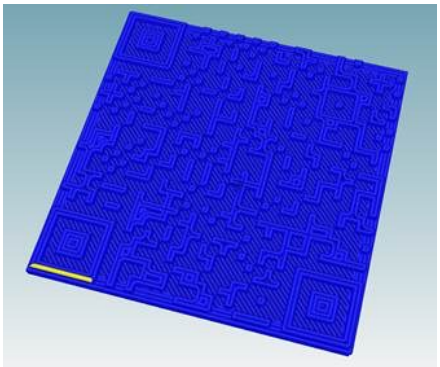

Figure S7: 3-D heightmap .stl file for parts containing QR codes.

      ii. Ethereum Transaction TxHash = "0xc6c68cf7f7416bdc1465fe6d115d3f8dd377b0be4384c0e227826db7f5236562" https://etherscan.io/tx/0xc6c68cf7f7416bdc1465fe6d115d3f8dd377b0be4384c0e227826db7f5236562

3. *Tb^{3+}-Asp fluorescence of QR code fiducials (ΔE to reference) at ex. = 254 nm.*
   a. Average fluorescence emission of QR code fiducial areas relative to reference Tb^{3+}-Asp powder recorded in the same photo. Color data obtained from a smartphone was quantified after conversion of sRGB values to LAB color. The average ΔE value for this transaction was given a 3σ tolerance:
      i. LAB deltaE = 87.6 +/- 7.2
      ii. Ethereum Transaction TxHash = "0x72e676e10953f7b4e777e71525348bfbb8aceb29c0b6f12adf5a7545f60add8f"

https://etherscan.io/tx/0x72e676e10953f7b4e777e71525348bfbb8aceb29c0b6f12adf5a7545f60add8f

One way compression to reduce cost and/or privatize data of uploaded information onto the blockchain

One way compression creates data that is a fingerprint of the original data. The fingerprint data is uploaded onto the blockchain but it is difficult if not impossible to reverse the original "DNA" information from the fingerprint. End users who have access to the parts can acquire the original "DNA" by testing and compare the data with the blockchain fingerprint. For example, LAB ΔE data of 87.6 +/- 7.2 after one way compression with a MD5 hash algorithm becomes: 7bf169259f38ad81349528c1339532fd instead of the hexadecimal 38372e36202b2f2d20372e3220. While the MD5 data uploaded to the blockchain is accessible by anyone, it is not useful unless one possesses the part that can generate the original LAB deltaE data. One way compression in concept may allow for privatized data to be uploaded onto a public blockchain ledger that can then be used to verify parts.

Chain of custody of PNNL 3D printed part #1

An example set of transactions and the format for them is shown below:

<prefix><header>colon<data format>colon<public key of recipient>

(1) 1st Transaction TxHash for chain of custody, transfer of custody to new user; 0x077dfb792ada0ee2cbd6c4b90d1bde2de5e20ad80d3d958e5e2f6ad13aba22cf; Input data = <prefix><PNNL 3D printed part #1, transfer of custody to owner of attached public key>:<hex>:<d5f95a34233b68efa212092af5b54d2a8bc6fd53>

(2) 2nd Transaction TxHash for chain of custody, confirmation of receipt by new user; 0xf011f9f989e0c7f7654455813d0bbad4ef91671b48afed91a349f8a7c221131f; Input data = <prefix><PNNL 3D printed part #, received PNNL 3D printed part #1 from address this transaction is directed to>

One important point of verification for chain of custody is the time stamp associated with the transactions. The receipt of part transactions (2nd Transaction TxHash) originated from the recipient's public key after the transfer was initiated by the original owner. Subsequent trusted data from the part can be associated with the recipient's public key for transactions after the 2nd Transaction's time stamp. Figure S8 visually summarizes the transactions involved with a change in the chain of custody.

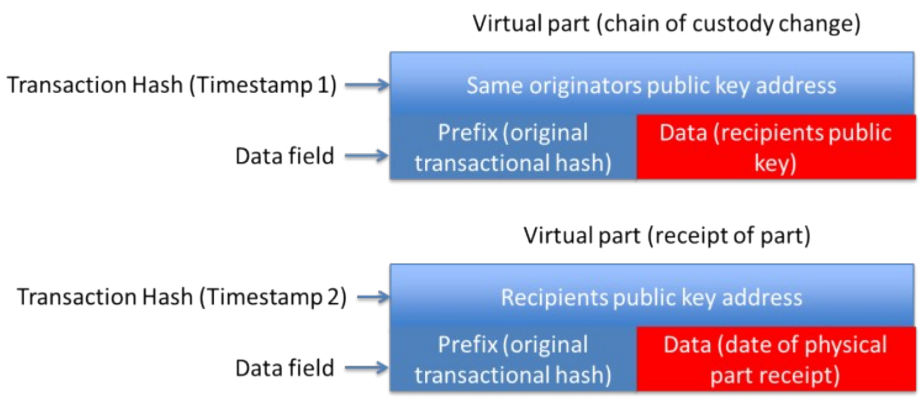

Figure S8: Blockchain transactions involved in chain of custody**.**

Supplementary information references

1. http://www.russellcottrell.com/photo/colorTransformer2.htm
2. McLaren, K. XIII—The Development of the CIE 1976 (L* a* b*) Uniform Colour Space and Colour-difference Formula. *J. Soc. Dyers Colour* **1976**, *92*, 338-341.
3. https://en.wikipedia.org/wiki/Color_difference