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High Photoluminescent Metal—Organic Frameworks as Optical Markers for the Identification of Gunshot Residues

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Ⓢ *Supporting Information*

ABSTRACT: Gunshot residue (GSR) are solid particles produced when a firearm is discharged, and its detection is important evidence in forensic investigations. Currently, scanning electron microscopy coupled to energy dispersive spectroscopy (SEM-EDS) is the standard technique adopted for the analysis and identification of GSR; however, this methodology is inefficient for lead-free ammunition. Herein, we report the inclusion of high photoluminescent metal—organic frameworks in ammunition to allow for the visual detection of GSR. The tests indicated that marked GSR is easily visible in proportions above 5.0 wt %. A total of 1 g of marker suffices to tag 100 0.38 mm bullets or 62 0.40 mm bullets.
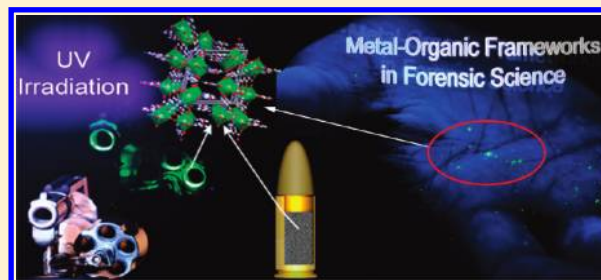
Gunshot residue (GSR) consists of solid particles produced when a firearm is discharged, and its detection provides very important evidence in forensic investigations.[1,2] GSR is used to estimate the distance at which a bullet is shot, recognize bullet holes, and provide important information to pinpoint suspects, deny or confirm an alibi, differentiate between homicide and suicide, etc.[3] This is possible because some of the discharged residue remains on the gun and is also normally deposited on the perpetrator's hands, clothes, hair, and body.[4-6]

Since the early 20th century, several methodologies have been proposed to identify GSR. Initially, colorimetric methods were employed to identify barium, lead, and nitrites through chemical reactions with sodium rhodizonate and *para*-sulfanilic acid (Griess reagent).[7] Although these methods involve fairly simple procedures, their results cannot be considered conclusive since they produce a high percentage of false-negatives due to their low sensitivity and high instability of the chemical species (nitrites). Moreover, colorimetric methods do not indicate whether the analytes originate from environmental or occupational contamination or from a weapon discharge.[8]

The 1960s and 1970s saw the introduction of neutron activation analysis (NAA) and flameless atomic absorption spectroscopy (FAAS), which served to determine barium, lead, and antimony, respectively. Although these methodologies allow for the determination of small amounts of metallic elements, the problem of identifying the origin of particles remains. Moreover, both these techniques require very specific instrumentation, and their results may be compromised by organic molecules.[9] The introduction of scanning electron microscopy coupled to energy dispersive spectroscopy (SEM-EDS) provided more reliable criteria for the identification of GSR. When a shot is fired, the residue is subjected to extreme conditions of pressure and temperature, causing the particles to assume a spheroidal shape.[10] The morphology and peculiar chemical composition of the residue enables one to distinguish between GSR and residue of environmental or occupational origin.[11] Therefore, SEM-EDS was adopted as a standard procedure for the analysis and identification of GSR.[2,8,12,13] Spheroidal particles consisting of lead—antimony—barium are undoubtedly considered GSR, while antimony—barium, barium—lead, and antimony—lead should be assumed to be indicative of GSR.[14]

Recently, a new type of lead-free ammunition was introduced on the market, aiming to reduce the impact on human health caused by lead-rich airborne pollution. Investigations with shooting instructors have revealed the incidence of high blood lead levels, near to the limit of 60 μg lead/100 g of whole blood established by the National Institute for Occupational Safety and Health (NIOSH).[15] Lead has shown a toxic effect on tissue and interferes with enzymes and proteins affecting the nervous system.[16] Although, the environmental and health advantages of this clean or green type of ammunitions, SEM-EDS methodology becomes ineffective because it is impossible to identify the characteristic metals.[17] Martiny et al. stated that the absence of a specific chemical taggant makes it very difficult to identify lead-free GSR particles, since none of the detected elements can be considered unique or characteristic of firearm handling for purposes of identification.[17]

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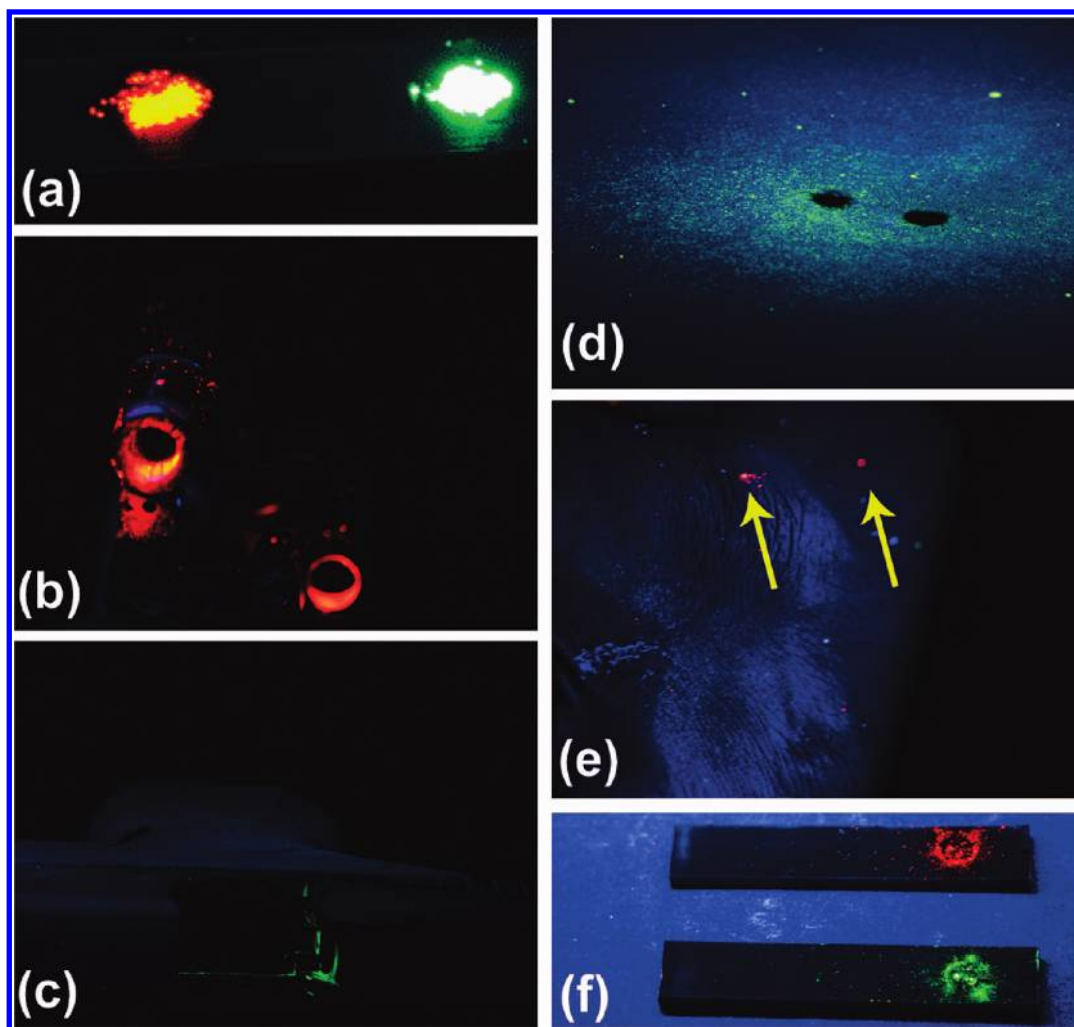dx.doi.org/10.1021/ac200680a | *Anal. Chem.* 2011, 83, 4720–4723

Figure 1. Images of the R- and G-Markers under UV lamp exposition: (a) R-Marker and G-Marker as-prepared; (b) R-Marker on 0.38 gun after shot; (c) G-Marker on the 0.40 gun pistol after shot; (d) G-Marker on the target surface; (e) R-Marker on the shooter's hand (R-Marker residues are indicated by yellow arrows); (f) lead-free ammunition primers' residues containing R- and G-Markers.

The above-described scenario justifies the need for the development of a low-cost, fast, and powerful method for identifying GSR. In this perspective, our group recently proposed the inclusion of high photoluminescent markers in ammunition to allow for the visual detection of GSR.[18] It should be noted that this practical approach simplifies investigative routines considerably, enabling the identification of GSR directly at a crime scene using only an ultraviolet lamp. In addition, these markers are composed of a unique chemical composition not commonly found in the environment or in occupational tasks.

The materials proposed in this work are based on a class of crystalline materials that in the last 15 years has attracted wide attention of scientific community. Metal−organic frameworks (MOFs), also known as coordination polymers, are promising for development of the markers due to high thermal and chemical stability.[19] In terms of optical properties, lanthanide−organic frameworks (LOFs) have great potential to be efficiently used as highly photoluminescent markers, since these compounds may act as light-conversion molecular devices (LCMDs).[20]

To the best of our knowledge, only two studies have dealt with luminescent recognition of GSR. These works report the detection of lead and antimony emissions (at 385 and 660 nm,

respectively) at cryogenic temperatures under Xe lamp excitation.[21,22] However, these methodologies are evidently unsuitable for lead-free ammunition.

The markers described in this work are based in two isostructural 2D MOFs previously reported,[23,24] $_∞[Ln(DPA)-(HDPA)]$, where H_2DPA is pyridine 2,6-dicarboxylic acid and $Ln = Eu^{3+}$ and Tb^{3+} ions. It is important to note that Eu^{3+} and Tb^{3+} materials were designed as R-Marker and G-Marker, respectively. Crystallographic structure, powder patterns, and the final Rietveld plot for the materials are in the Supporting Information. Obviously, we have tested several other luminescent materials, such as ceramic, metal oxides, glasses, and organic compounds; however, lanthanide-containing MOFs presented here have shown the best results. It can be justified by the efficient antenna effect by DPA ligands and high emission of Ln^{3+} ion corroborated by lack of solvent molecules directly coordinated to the metal center. Figure 1 shows the R-Marker and G-Marker as prepared and after shooting on the target surface, on the firearms, and on the shooter's hand after firing, all subjected to irradiation under an UV lamp.

The materials are highly photoluminescent, and their optical properties remain unaltered after a bullet is fired. The marked
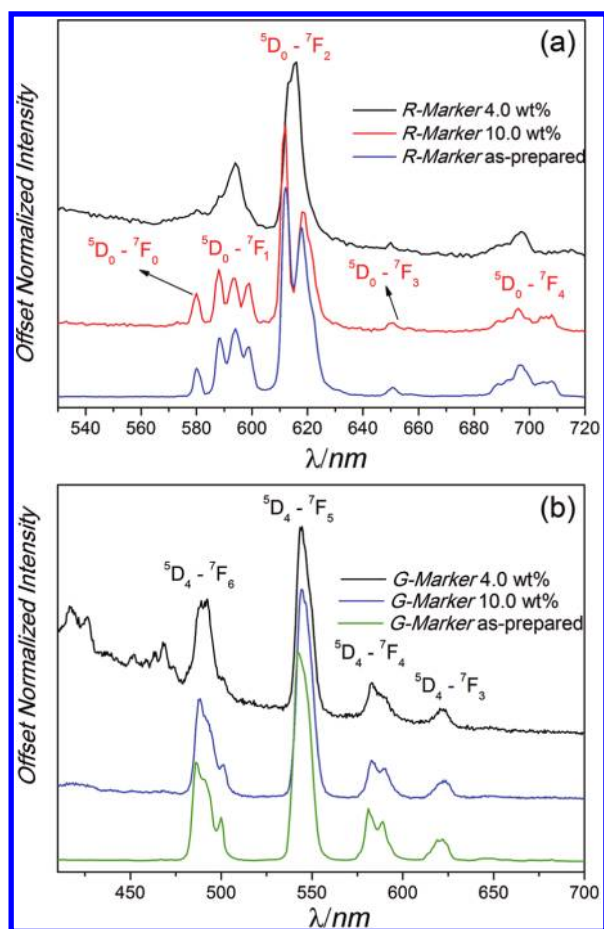
Figure 2. Emission spectra of the markers as-prepared and marker-tagged primer after discharging: (a) R-Marker and (b) G-Marker.
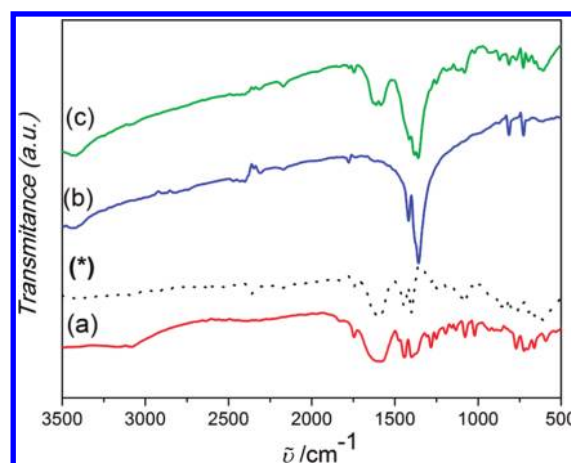

Figure 3. Infrared spectra of (a) G-Marker, (b) pure ignited primer, and (c) ignited primer containing 10 wt % of G-Marker. (∗) The dotted line represents the subtraction of lines (c) and (b), highlighting the marker IR absorption feature.
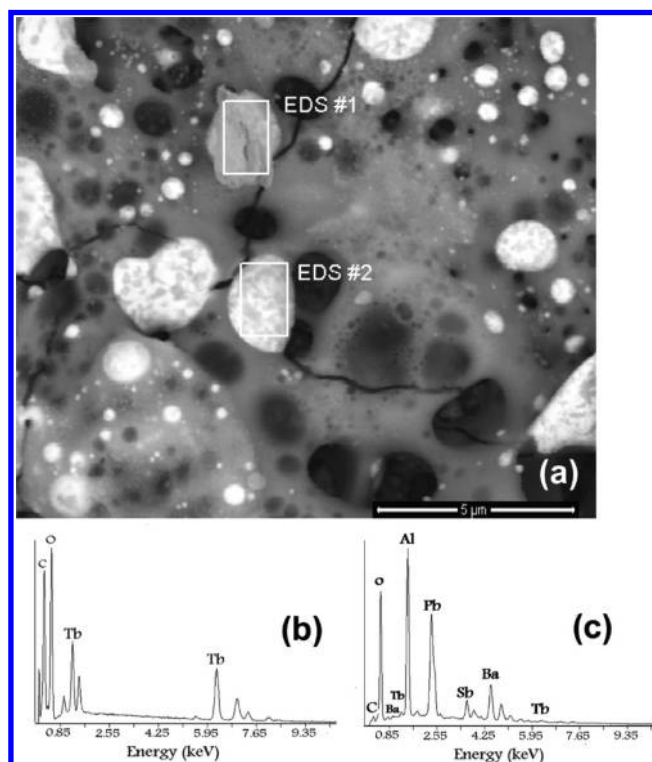

Figure 4. (a) SEM images of marked GSR deposited on the target and (b) EDS spectra of G-Marker particle (EDS no. 1) and (c) traditional GSR particle (EDS no. 2).

GSR was identified visually on the shooter's hand and clothes, on the gun, and on the target surface, as depicted in Figure 1. The samples collected from the target surface remained luminescent for more than 30 months, even when stored in a damp environment. These results clearly attest the efficacy and simplicity of the method, confirming the significant characteristics of the markers, i.e., (i) thermal stability, resistance to the high firing temperatures and remaining chemically stable after long periods of time; (ii) chemical inertia, nonreactive with gunpowder, primer, or the metallic parts of a gun; (iii) high luminescence.

The tests indicated that marked GSR is easily visible in proportions above 5.0 wt %. At lower concentrations of markers, GSR particles are difficult to identify visually, but the methodology proposed here is not compromised and homogenization should allow this value to be reduced. The emission spectra of R-Marker and G-Marker (Figure 2) acquired at room temperature by respective excitations at maxima absorption of the organic matrixes, 291 and 294 nm, display the typical red and green emissions associated with Eu^{3+} $^5D_0 \rightarrow {}^7F_J$ and Tb^{3+} $^5D_4 \rightarrow {}^7F_J$ transitions. After the shots, the characteristic transitions of Eu^{3+} and Tb^{3+} ions were found to be similar to those of the pure markers, suggesting that the markers' structures had not undergone any significant change. It should be noted that Eu^{3+} transitions, in particular, are affected by the chemical environment of the first coordination sphere.[25−27] Therefore, the relative intensity and splitting of the respective transitions serve to

confirm the robustness of the markers, since they resist the extreme conditions that prevail when the bullet is fired.

FT-IR spectra of the pure G-Marker, the pure ignited primer, and the ignited primer containing 10.0 wt % of G-Marker are shown in Figure 3.

The FT-IR spectrum of ignited primer containing G-Marker, shown in Figure 3c, corresponds to ignited primer plus pure G-Marker spectra. Subtraction of the FT-IR spectrum of the primer containing 10.0 wt % of G-Marker from the FT-IR spectrum

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of the pure primer with the resulting spectrum of the pure marker. Moreover, as the figure indicates, the primer spectrum showed no major change, suggesting the absence of a chemical interaction between the primer and the marker. Therefore, the hypothesis of chemical inertness of the markers is proved, since the marker's and the primer's structure are unaltered.

The SEM image (Figure 4) indicates that some of the conventional marked GSR has a spheroidal morphology which is typical of residue from conventional ammunition. In addition, the EDS spectra confirm the presence of Pb, Sb, Ba, and Tb in the composition.

These results demonstrate that the SEM-EDS methodology can be used to confirm visual and spectroscopic observations. In the case of lead-free ammunition, the rare earth ions in markers can be undoubtedly used as a chemical tag to recognize GSR. Allied to minor changes in the composition of these markers, SEM-EDS may be regarded as a versatile alternative for identifying the ammunition manufacturer and/or weapon caliber and to distinguish between civilian, military, and law enforcement ammunition.

The markers developed in this study are inexpensive (ranging from U.S. $2.00 to 5.00 per gram in laboratory conditions). One gram of marker suffices to tag approximately 100 0.38 mm bullets or 62 0.40 mm bullets. Another advantage is that in general lanthanides ions and their compounds have shown lower toxicity in comparison to those of lead;[28,29] however, a detailed investigation is necessary to determine the real toxicity degree of the marked GSR produced.

■ ASSOCIATED CONTENT

⑤ Supporting Information. Experimental procedures, crystallographic structure, X-ray powder patterns with final Rietveld fits, and handguns, shooter body parts, primers, and target images under UV irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

■ REFERENCES

(1) Basu, S. J. Forensic Sci. **1982**, 27, 72–91.
(2) Dalby, O.; Butler, D.; Birkett, J. W. J. Forensic Sci. **2010**, 55, 924–943.
(3) Rendle, D. F. Chem. Soc. Rev. **2005**, 34, 1021–1030.
(4) LaGoo, L.; Schaeffer, L. S.; Szymanski, D. W.; Smith, R. W. J. Forensic Sci. **2010**, 55, 624–632.
(5) Rijnders, M. R.; Stamouli, A.; Bolck, A. J. Forensic Sci. **2010**, 55, 616–623.
(6) Zeichner, A. Anal. Bioanal. Chem. **2003**, 376, 1178–1191.
(7) Romolo, F. S.; Margot, P. Forensic Sci. Int. **2001**, 119, 195–211.
(8) Garofano, L.; Capra, M.; Ferrari, F.; Bizzaro, G. P.; Di Tullio, D.; Dell'Olio, M.; Ghitti, A. Forensic Sci. Int. **1999**, 103, 1–21.
(9) dos Reis, E. L. T.; Sarkis, J. E. S.; Rodrigues, C.; Neto, O. N.; Vieg, S. Quim. Nova **2004**, 27, 409–413.
(10) Di Maio, V. J. M. In Gunshot Wounds: Practical Aspects of Firearms, Ballistics, and Forensic Techniques, 2nd ed.; CRC Press LLC: New York, 1999.
(11) Wright, D. M.; Trimpe, M. A. Forensic Sci. Commun. **2006**, 8.
(12) Meng, H. H.; Caddy, B. J. Forensic Sci. **1997**, 42, 553–570.
(13) White, R. S.; Owens, A. D. J. Forensic Sci. **1987**, 32, 1595–1603.
(14) ASTM. Standart E1588-10e1, Standard Guide for Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-ray Spectrometry, 2008, DOI: 10.1520/E1588-10E01, www.astm.org.
(15) NIOSH. Reducing Exposure to Lead and Noise at Indoor Firing Ranges; U.S. Department of Health and Human Services (DHHS), National Institute Occupational Safety and Health (NIOSH), 2010, 113, www.cdc.gov/niosh/docs/wp-solutions/2010-113/pdfs/2010-113.pdf.
(16) Anttila, A.; Heikkila, P.; Nykyri, E.; Kauppinen, T.; Pukkala, E.; Hernberg, S.; Hemminki, K. J. Occup. Environ. Med. **1996**, 38, 131–136.
(17) Martiny, A.; Campos, A. P. C.; Sader, M. S.; Pinto, M. A. L. Forensic Sci. Int. **2008**, 177, E9–E17.
(18) Weber, I. T.; Melo, A. J. G.; Alves Júnior, S.; Lucena, M. A. M.; Rodrigues, M. O. BR Patent WO/2010/105326, 2010.
(19) Eddaoudi, M.; Li, H.; Yaghi, O. M. J. Am. Chem. Soc. **2000**, 122, 1391–1397.
(20) Rodrigues, M. O.; Paz, F. A.; Freire, R. O.; de Sa, G. F.; Galembeck, A.; Montenegro, M. C.; Araujo, A. N.; Alves, S. J. Phys. Chem. B **2009**, 113, 12181–12188.
(21) Jones, P. F.; Nesbitt, R. S. J. Forensic Sci. **1975**, 20, 231–42.
(22) Nesbitt, R. S.; Wessel, J. E.; Wolten, G. M.; Jones, P. F. J. Forensic Sci. **1977**, 22, 288–303.
(23) Fernandes, A.; Jaud, J.; Dexpert-Ghys, J.; Brouca-Cabarrecq, C. Polyhedron **2001**, 20, 2385–2391.
(24) Rodrigues, M. O.; Brito-Silva, A. M.; Alves, S.; De Simone, C. A.; Araujo, A. A. S.; de Carvalho, P. H. V.; Santos, S. C. G.; Aragao, K. A. S.; Freire, R. O.; Mesquita, M. E. Quim. Nova **2009**, 32, 286–291.
(25) Rodrigues, M. O.; da Costa, N. B.; de Simone, C. A.; Araújo, A. A. S.; Brito-Silva, A. M.; Paz, F. A. A.; de Mesquita, M. E.; Júnior, S. A.; Freire, R. O. J. Phys. Chem. B **2008**, 112, 4204–4212.
(26) dos Santos, E. R.; Freire, R. O.; da Costa, N. B.; Paz, F. A. A.; de Simone, C. A.; Júnior, S. A.; Araújo, A. A. S.; Nunes, L. A. n. O.; de Mesquita, M. E.; Rodrigues, M. O. J. Phys. Chem. A **2010**, 114, 7928–7936.
(27) Binnemans, K. Chem. Rev. **2009**, 109, 4283–4374.
(28) Hirano, S.; Suzuki, K. T. Environ. Health Perspect. **1996**, 104, 85–95.
(29) Yanagida, H.; Yamasaki, A.; Yanagisawa, Y. Environ. Sci. Technol. **2004**, 39, 371–376.