

# Polydiacetylene Sensor Arrays as Multimodal Tamper Indicators

Stephanie White, Clayton Curtis, Heidi Smartt, Cody Corbin\*  
Sandia National Laboratories, Albuquerque, NM, United States

## ABSTRACT

Sandia National Laboratories (SNL) is developing a sensing suite of polydiacetylene (PDA) materials for tamper indication. PDAs represent a unique class of polymeric materials that provide drastic visible color changes when exposed to an assortment of different stimuli. Generally, tamper-indicating technologies have only incrementally improved over decades, while adversaries continually advance in their methods to defeat these technologies. Therefore, the tamper-indicating technology toolbox should also continually advance. Current sensing technologies primarily (but not exclusively) rely on visual examination of tamper-indicating devices (TIDs) to detect mechanical changes in the TID; however, visual inspection may not always be useful at detecting changes that result from other methods of attack. The PDA sensing suite described here can visibly change color not only when a TID is attacked via mechanical means, but also when chemical, electrical, and thermal means are used to attack. The multi-functional properties of PDAs offer a noteworthy benefit for detecting a variety of adversarial means of attack, thus increasing the level of difficulty and resources adversaries would need to defeat a TID.

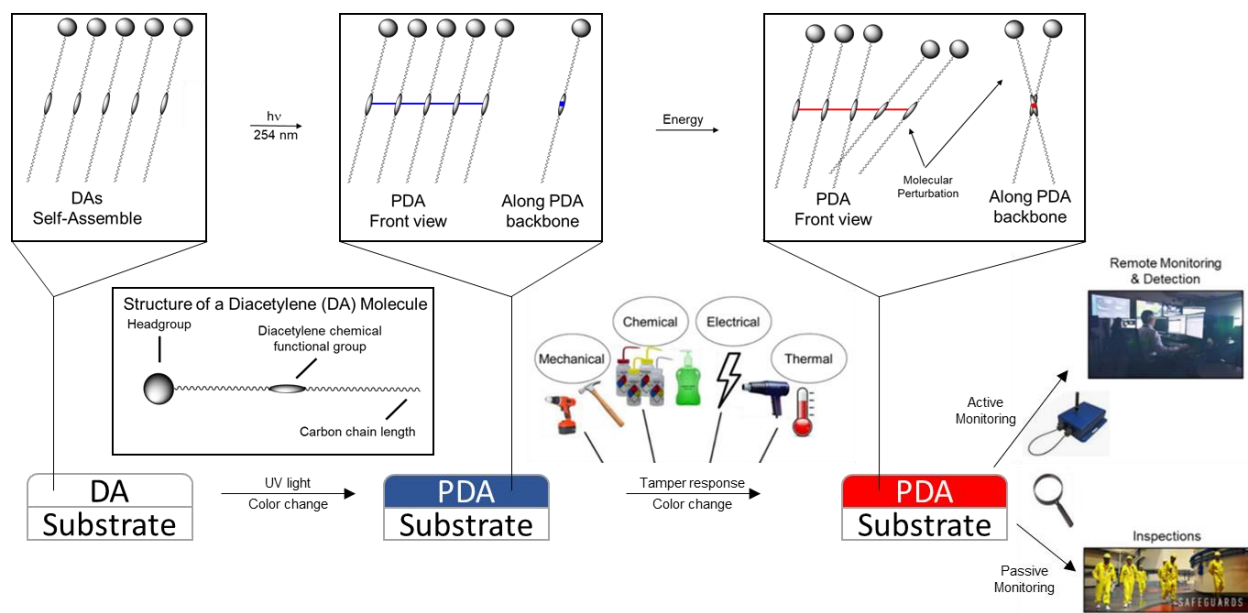
## INTRODUCTION

Treaty verification regimes rely on tamper-indicating technologies to maintain continuity of knowledge in between inspections. These technologies must indicate that tamper into equipment enclosures, material containers, or other items of interest has occurred, and indicate evidence of attempted repair. Current tamper-indicating enclosures (TIEs) [1] used by the International Atomic Energy Agency (IAEA) are designed a) to be verified using external electronic equipment, b) as active self-monitoring enclosures, or c) as a passive material for visual inspection. Searching subjectively for penetrations on anodized aluminum is a passive method [2], conductive traces or materials that cause cryptographic keys to be set to default if penetration is detected are actively self-monitored [3], and an eddy current measurement for locating repairs on metal is an example of an external verification technique requiring characterization equipment in the field [4]. These methods, in general, have three disadvantages: 1) verification can be subjective or require visual observation of difficult-to-access locations (e.g., the bottom of a large cabinet), 2) external equipment may be required (adding burden to inspectors), and 3) they primarily reveal mechanical-based attacks. The capability to detect a wider variety of attack vectors would be beneficial on multiple fronts, including lowering the adversary capability toolbox and gaining data for developing more secure tamper-indicating devices for the future.

We are aiming to develop a novel and unique sensing concept based on the visual color change of polydiacetylene materials that will indicate tamper and respond uniquely to indicate multiple attack methods, including thermal, mechanical, chemical, and electrical attack vectors. These materials benefit treaty verification regimes as well as other applications that require sensing phenomena or efficient and accurate indication of tampering. Our goal is to develop a novel tamper-sensing material system that 1) colorimetrically responds to a plethora of different attack methods that may be used to defeat TIDs, 2) provides quantitative information on the specific attack method used, and 3) is easily processed into packaging-related materials for ease of incorporation into future design builds.

Diacetylenes (DAs) are a unique class of molecules that have a set of carbon-carbon triple bonds ( $C\equiv C$ ) present in the middle of the molecule [5-6]. These typically colorless molecules self-assemble when applied to a substrate due to energetically favored intermolecular forces. Upon exposure to a 254 nm UV light source, the electrons in the triple bonds rearrange, chemically bonding neighboring molecules together to form a blue polydiacetylene (PDA). The vibrant blue color is due to the conjugated newly formed bonds present at the cross-linking sites down the polymer backbone. PDAs have the ability to change their visible blue reflectance to red with the input of a variety of energy-based stimuli including thermal [7-9], mechanical [9,10], electrical [6,11], or chemical [6,12-13]. The physical mechanism behind this color change is a molecular perturbation down the polymer backbone (**Figure 1**). Some of the now bonded-together DAs physically shift with respect to the rest of the polymer, and this shift disrupts the conjugated bond length mentioned earlier which produces the color change [10].

The color change seen in these materials has some dependency with the molecular structure of the DAs. The DAs are similar to lipids in that they contain a polar chemical headgroup of some kind (sometimes on each end) and a C-H-based chain as the tail and/or middle group (**Figure 1**). Though these structural arrangements are what cause the materials to self-align as mentioned earlier, the intramolecular interactions between the headgroups once in PDA form and the carbon chain length cause stabilization/destabilization effects. Upon stimuli addition, the PDA can show 1) no color change (fully stabilized through headgroup chemical interactions), 2) reversible blue-to-red shift (some favored headgroup interactions), and 3) permanent color shift to red (disfavored headgroup interactions). Item 3 is the target phenomena for this project as it can be used for both passive (visible color change) and active (externally monitoring or alert) sensing.



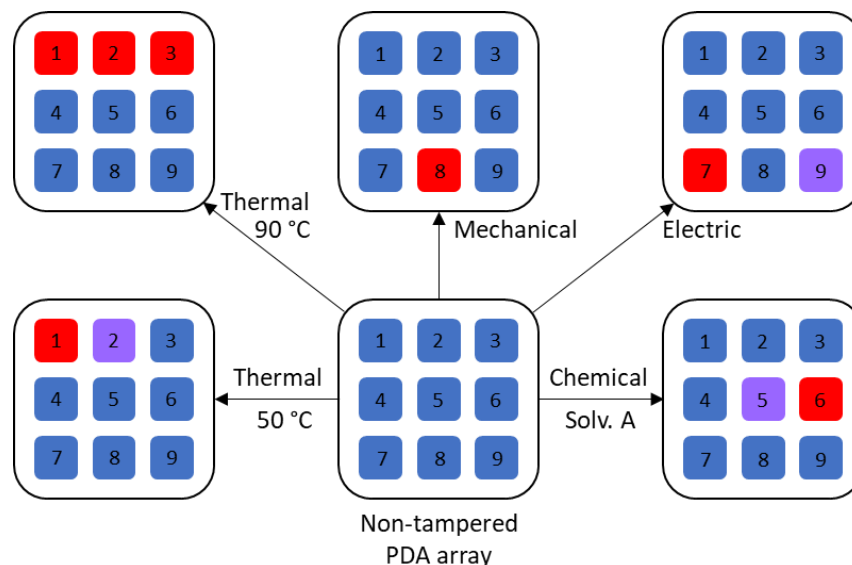
**Figure 1. Generic structure of a diacetylene (DA) molecule (middle left); molecular view of the conversion of self-assembled DAs to polydiacetylenes (PDAs) (top left), which coincides with a visual color change from colorless to blue; molecular view of the kinking of PDA chains upon stimulus (top right), which coincides with a visual color change from blue to red. Overall concept, goal, and representative use-case for utilization of PDAs as tamper-indicating materials (bottom); the response can be evaluated by inspectors passively (right bottom) or actively monitored with appropriate engineering and equipment (right middle).**

Furthermore, PDA materials can be processed easily into devices, which is advantageous for our envisioned application. There are a multitude of methods proven to incorporate DAs into useful materials and then cross-linking them in situ. Some of these methods include mold casting, electrospinning, electrophoretic deposition, and simple inkjet printing [6]. We suspect the variety of methods available will aid future design work in later stages of this project. The focus of this report is the initial synthesis and characterization efforts of DA and PDA materials that we believe can be utilized in designing a tamper indicating suite capable of identifying attack as well as attack vector.

## SYNTHESIS OF DA MONOMERS

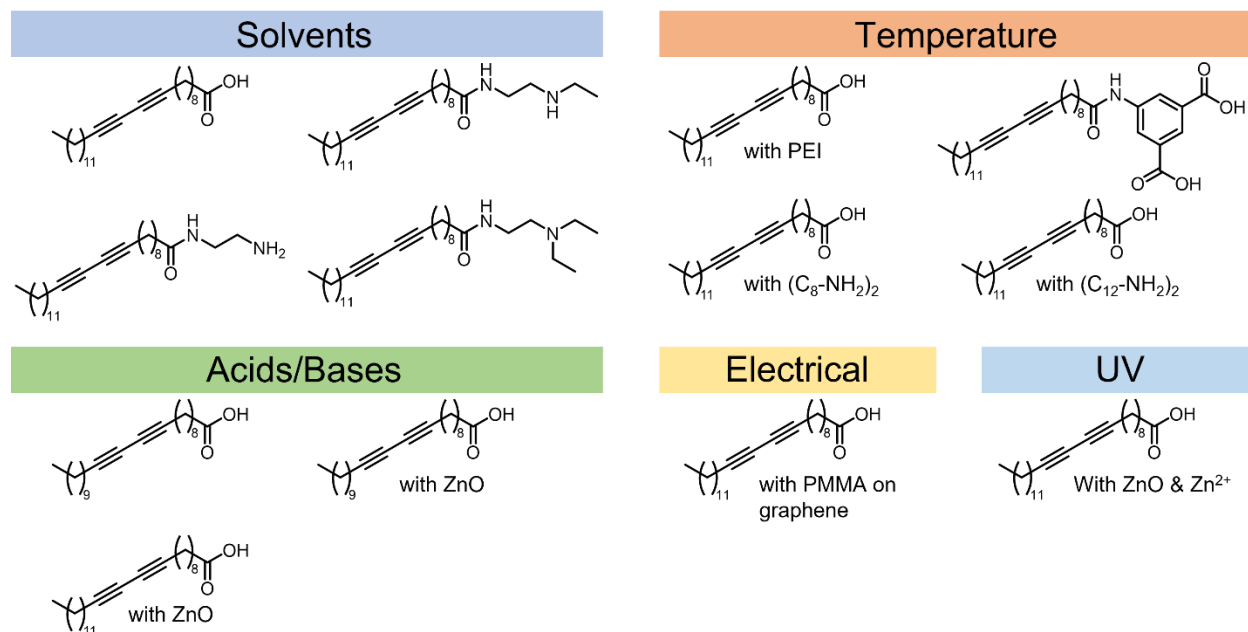
A subset of polydiacetylene compounds were selected as synthetic targets for this project from a review of relevant literature. The aim was for the selected set of PDAs to include those that have been shown to respond to any of a diverse group of potential attack vectors including thermal, chemical, electrical, mechanical, and sonic environmental changes; ideally, the combination of all selected PDAs would give a unique response to any given attack vector such that the means of attack would be identifiable (**Figure 2**). Approximately 20 different PDA compounds have been identified as a starting point for synthesis and analysis (**Figure 3**); if these 20 PDAs do not provide

unique responses to the variety of attack modes tested, we can expand this group to include other, perhaps more uniquely responsive, PDAs.



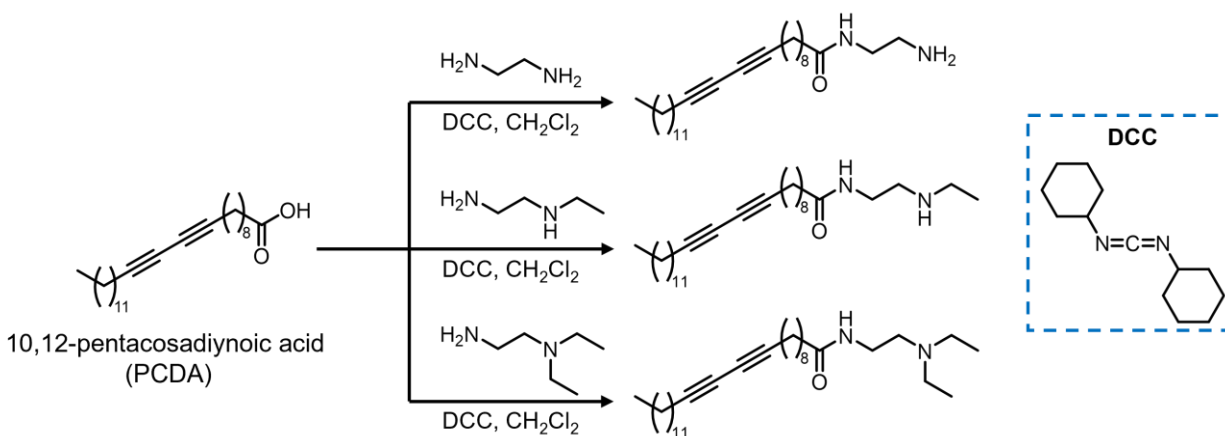
**Figure 2. A simplified representation of a PDA sensing array containing nine different PDA compounds (bottom, middle); with PDAs that are each uniquely responsive to a given attack vector, the extent of color change from all nine PDA compounds (in combination) would be unique and allow identification of the attack type.**

Several of the PDAs selected were based on commercially available DA monomers, so these compounds were used for preliminary testing. In many cases, the as-received DA monomer was first purified by simple filtration to remove any incidentally polymerized material. The remaining selected PDAs will be synthesized in house according to literature procedures.



**Figure 3. Selected synthetic targets of monomeric DAs organized by stimuli response reported in literature.**

The initial synthetic studies have been performed utilizing the DA 10,12-pentacosadiynoic acid (PCDA) (**Figure 4**). This DA molecule features a polar carboxylic acid headgroup and is a convenient precursor for two reasons: 1) it is commercially available and can be purchased and used with only minor purification *via* filtration and 2) the carboxylic acid functional group can be easily modified through literature synthetic procedures to create DA monomers with different headgroups, each producing different responses to external stimuli. Our initial modifications to PCDA introduced polar headgroups featuring aliphatic diamines (**Figure 4**); these were synthesized by following an adapted literature procedure in which PCDA was treated with *N,N'*-dicyclohexylcarbodiimide (DCC) as a coupling agent to activate the carboxylic acid group, followed by treatment with the desired diamine molecule to yield the final modified DA [14]. These amine-modified DAs have been reported in the literature and are known to exhibit sensitive irreversible colorimetric response to multiple solvents of varying polarity. Although each of these three DAs are similar in structure, they differ in the amount of carbon in their headgroups, and as such will present subtle differences in intramolecular interactions (i.e., hydrogen bonding ability) which will in turn affect their colorimetric response to different stimuli.



**Figure 4. Synthetic scheme for the modification of PCDA to introduce three diamine polar headgroups.**

Future modifications will target the incorporation of PCDA into nanocomposites with zinc oxide (ZnO) and Zn<sup>2+</sup> cations. These nanocomposites are known to exhibit colorimetric response to different levels of pH stimuli, as well as UV light exposure [15,16]. Further incorporation of PCDA with either polymeric polyethylenimine (PEI) or long alkyl diamines will be pursued in order to examine response to thermal stimuli [17]. The incorporation into these polymeric substrates will also be attempted with our in-house synthesized DAs in an effort to further tune the colorimetric response to various stimuli.

## UV POLYMERIZATION TO PDAS

Solutions in acetone were prepared from each DA monomer; these solutions were then drop-casted by pipette onto unlined notecards. Each notecard was prepared with three individual drops of the solution in order to allow for replicate measurements of each sample card. Notecards were then exposed to UV light in a crosslinking chamber with a 254 nm light source, allowing for polymerization of the given DA monomer to the corresponding PDA. Initially, studies were conducted to determine the optimal time of UV exposure, as the color of the blue PDA darkens with increasing time of UV exposure. After this, the same amount of time was used for the polymerization of all DA monomers to PDAs such that the resulting initial “non-tampered” sample spots would be a moderate hue of blue.

## QUANTITATIVE ANALYSIS OF PDAS

Quantitative colorimetric analysis was conducted both for the initial “non-tampered” blue PDA spots (to determine the variability in RGB values among “identical” non-tampered PDA samples), as well as for samples exposed to various potential attack vectors (to quantify the extent of color change from blue to red). This analysis consists of three parts: 1) scanning of the notecard coupons using a commercial digital scanner, 2) identification of the RGB values for each PDA sample spot in each notecard coupon using the eyedropper tool in Adobe Photoshop software, and 3) processing of the before-and-after-stimulus RGB values for each sample spot and attempts to correlate the observed RGB changes with the stimulus responsible for the color change. The first two steps are somewhat straightforward, whereas the third step is more of a challenge analytically. Adobe Photoshop was used for quantitative colorimetric analysis due to its ability to identify RGB values as an average over a given sampling size – we used 101x101 pixels – which we believe is important to minimize variability that could otherwise be caused by the specific pixels clicked by the eyedropper tool within a given PDA sample spot.

In general, for each PDA spot (3 per notecard coupon), the initial RGB values of the blue PDA spot (after UV exposure) and the final RGB values of the PDA spot (after the exposure to an environmental stimulus) were used to calculate a value(s) representing the extent of change in color. This can be done for each RGB individually (i.e.,  $\Delta R = |R_f - R_i|$ ,  $\Delta G = |G_f - G_i|$ , and  $\Delta B = |B_f - B_i|$ ), or, the three RGB values can be treated as (for example) XYZ values in a Cartesian coordinate system, where the equation for the distance between two points (i.e., two XYZ sets) can be used to calculate a difference in two colors (i.e., two RGB sets). The first of these systems ( $\Delta R$ ,  $\Delta G$ , and  $\Delta B$ ) was used for producing bar chart displays where the change in R, G, and B values are each individually represented, whereas the second of these systems ( $\Delta(\text{RGB})$ ) was used to treat each color change as a single value (i.e., for plotting color change values against a meaningful x-axis such as polarity or temperature).

As with most quantitative analyses, it is worth noting the extent of variation among samples. RGB analysis was conducted for 69 different spots of PCDA on 23 different notecard coupons, each exposed to UV light for the same amount of time, all without stimuli testing. For each set of R, G, and B values compiled from these 69 “before stimulus” spots, the standard deviation was less than 3% of the average value, which is modest compared to commonplace analytical techniques. This variability could be caused by variability in the testing procedure (i.e., from the Adobe Photoshop eyedropper tool), or variability in the samples (i.e., different PDA spots could actually be slightly differing shades of blue, perhaps due to different volumes of the drop or different spreading/drying of the drop on the notecard).

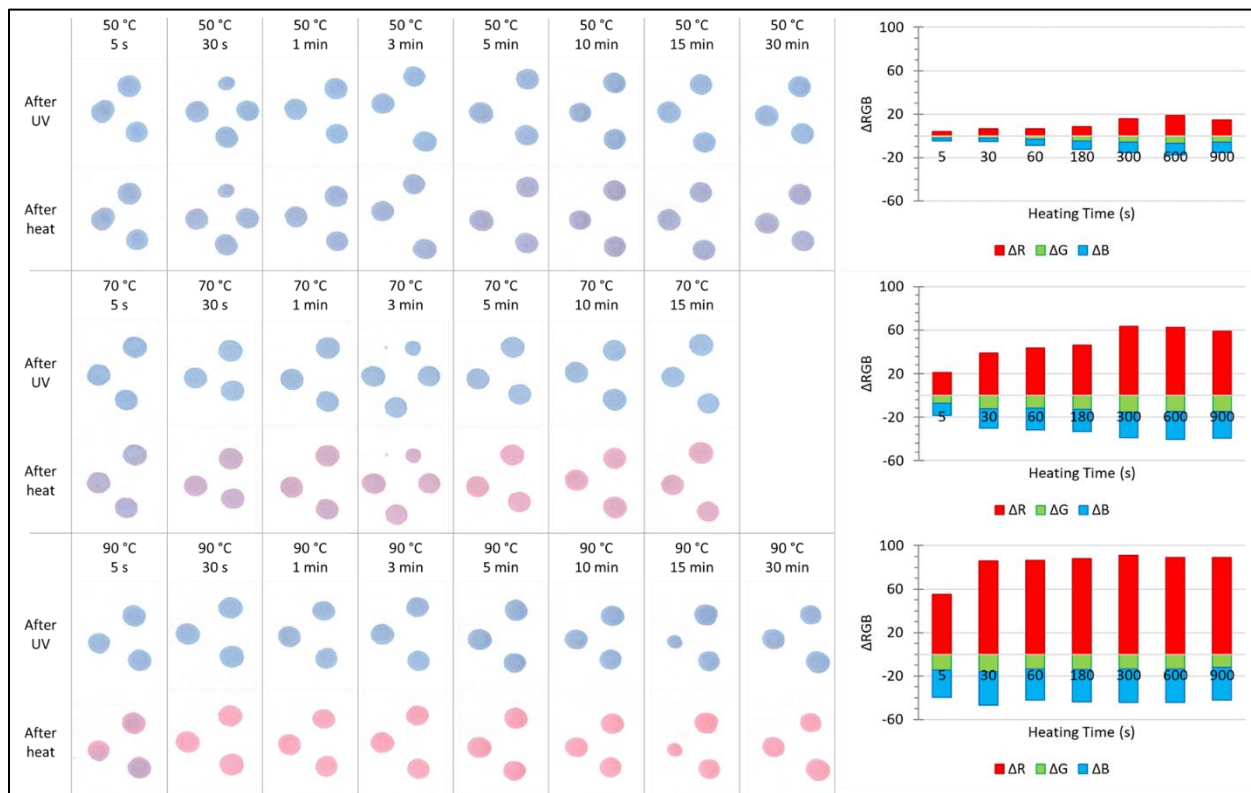
## STIMULI TESTING AND ANALYSIS

Stimuli testing has been conducted on two of the selected target PDA compounds which had commercially available DA monomers. PCDA has been tested for its response to three different temperatures, 15 different chemical solvents, four different concentrations of aqueous HCl (acidic solutions of varying pH), and four different concentrations of aqueous KOH (basic solutions of varying pH); tricosadiynoic acid (TCDA) has been tested for its response to three different temperatures. These stimuli tests will also be performed with the other selected PDA compounds after their synthesis is completed, and work is currently ongoing for testing of other stimulus vectors such as exposure of PDA samples to electric and sonic stimuli.

Notecard coupons were prepared as described above, with three drop-casted spots of DA solution per notecard; UV exposure of the notecards resulted in polymerization to the corresponding PDA, seen visually as three blue spots on each notecard. During stimulus testing, the blue spots can transition in color anywhere along the color spectrum from blue to red; depending on the stimulus, there can be no extent of color change (i.e., retaining the same initial blue color), any degree of moderate color change (i.e., resembling a shade of purple), or a severe extent of color change (i.e., formation of a stark red). As described above, the analysis of the samples, both before and after their exposure to stimulus, was conducted quantitatively using RGB values. This allows the extent of color change caused by the stimulus to be quantified numerically and graphed.

For thermal testing, samples were placed inside a convection oven that was held at a set temperature, then removed from the oven after a given amount of time. Samples were heated individually to avoid issues of temperature fluxuations with opening and closing of the oven door for samples with longer heat times. Three different temperatures were tested – 50, 70, and 90 °C – over eight different time points ranging from 5 s to 30 min. Both the scanned images and the RGB graphs obtained from temperature testing with PCDA demonstrate that the extent of transition from blue to red is more significant for higher temperatures (**Figure 5**); 30 min at 50 °C produces only a very minimal color change to a periwinkle blue, whereas 30 min at 90 °C produces a much more noticeable color change from blue to red. It can also be seen that at sufficiently low

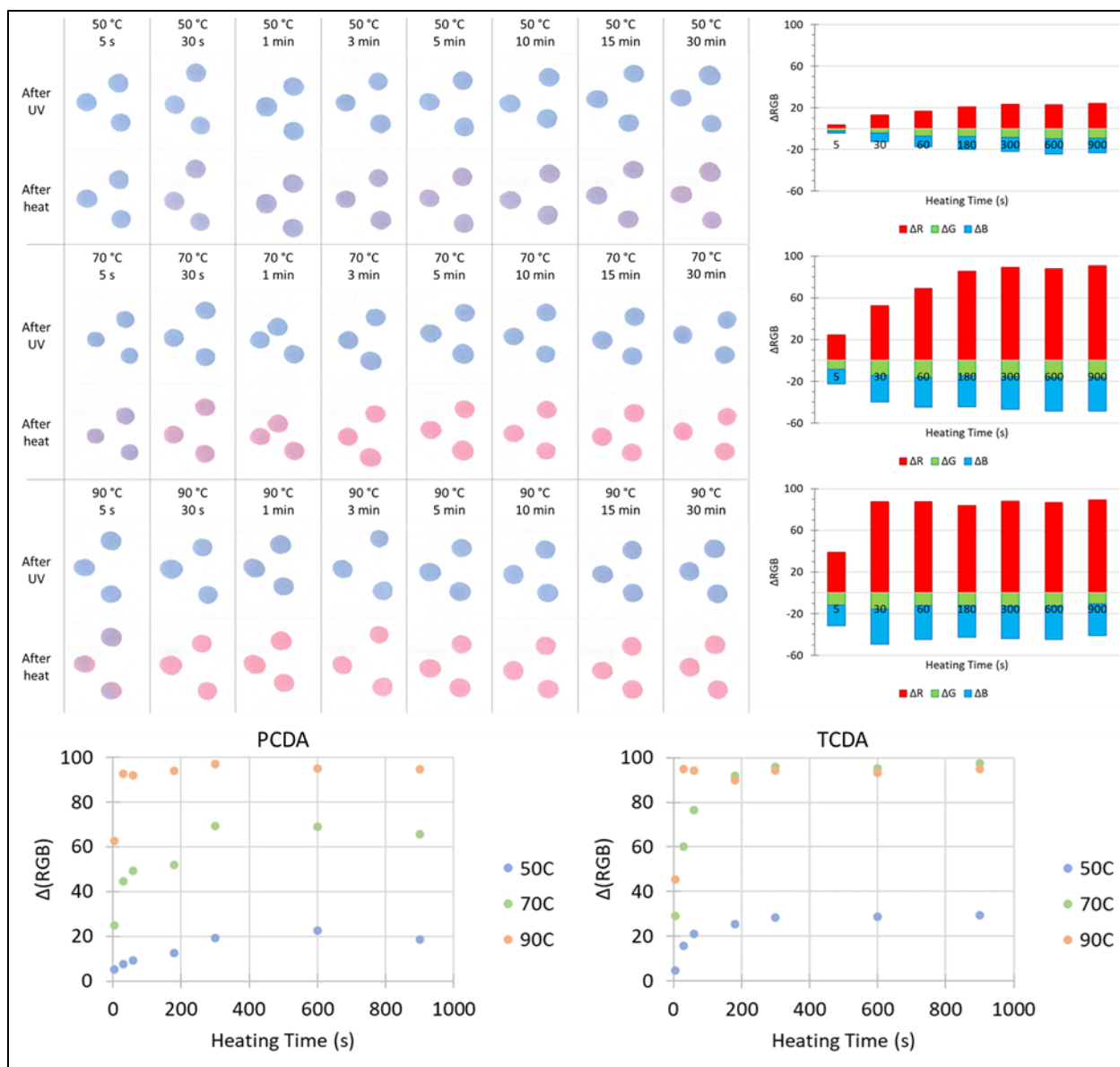
temperatures, color change is minimal regardless of heating time, and at sufficiently high temperatures, color change is drastic even at short heating times, whereas at an intermediate temperature, the extent of color change from blue to red is largely time dependent.



**Figure 5. Exposure of PCDA samples to three different temperatures over eight different time points for thermal stimuli testing. Scanned images of notecard coupons (left), and bar charts of  $\Delta R$ ,  $\Delta G$ , and  $\Delta B$  for before-and-after-stimulus pairs for each sample (right).**

The same procedure was conducted with TCDA, with similar results (**Figure 6, top**). Although it is difficult to discern a difference in thermal responses between PCDA and TCDA from the scanned images and RGB graphs, it is easier to identify a difference in behaviors based on (RGB) plots (**Figure 6, bottom**).

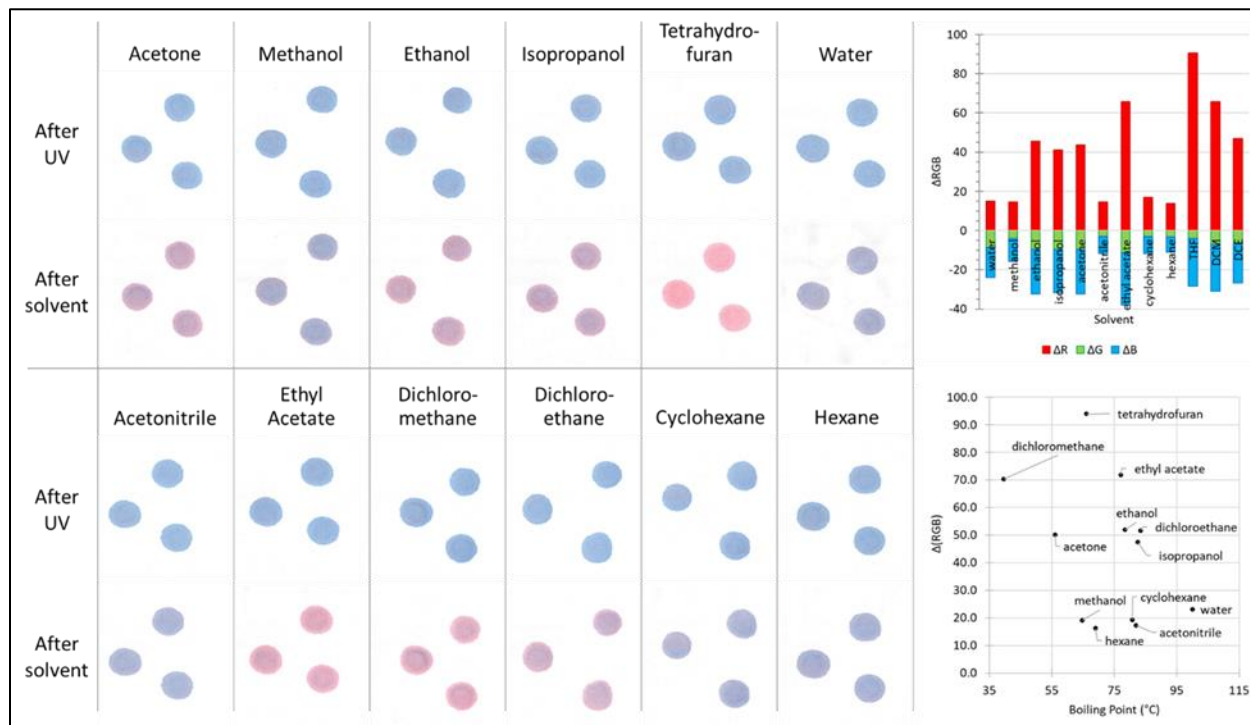




**Figure 6. Exposure of TCDA samples to three different temperatures over eight different time points for thermal stimuli testing. Scanned images of notecard coupons (top left), and bar charts of  $\Delta R$ ,  $\Delta G$ , and  $\Delta B$  for before-and-after-stimulus pairs for each sample (top right); plots  $\Delta RGB$  values versus heating time for PCDA (bottom left) and for TCDA (bottom right).**

For chemical testing studies, samples were submerged within a solution of each solvent for 1 min, then removed and allowed to air-dry before scanning. These solvents were selected with the aim to include those of a range of functional groups properties: water, alcohols (methanol, ethanol, isopropanol), organic solvents with varying polarities (acetone, acetonitrile, cyclohexane, hexane, tetrahydrofuran), and halogenated solvents (dichloromethane, dichloroethane). The results of these tests with PCDA (**Figure 7**) indicate that it responds uniquely to each of these solvents, even among pairs of solvents with similar molecular weights, boiling points, or polarities. This indicates

the sensing sensitivity of this method and the mechanism of intermolecular interactions that are specific to molecular structure.



**Figure 7. Exposure of PCDA samples to a range of solvents for chemical stimuli testing. Scanned images of notecard coupons (left), bar chart of  $\Delta R$ ,  $\Delta G$ , and  $\Delta B$  for before-and-after-stimulus pairs for each sample (right top), and plot of  $\Delta RGB$  values versus boiling points (right bottom).**

## SUMMARY AND NEXT STEPS

We are aiming to significantly improve the ability to sense a suite of tamper attack methods through the utilization of PDA materials. Using the academic literature, we have identified a set of synthetic DA targets that uniquely transition from blue to red upon a tamper event, where each DA has a specific  $\Delta RGB$  response. These are currently in preparation, but in parallel, analysis has been performed on the starting material 10,12-pentacosadiynoic acid (PCDA) under various conditions. These conditions will be replicated with the synthesized PDAs in an array format once created, and the  $\Delta RGB$  quantified to ensure that tamper events can be uniquely identified. Future work in this project will include environmental responses to PDAs to mitigate false positive scenarios and improving material design through integration of robust materials such as epoxy and polyurethane.

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## ACKNOWLEDGEMENTS

The authors would like to acknowledge and thank the U.S. National Nuclear Security Administration (NNSA) Office of Defense Nuclear Nonproliferation R&D Safeguards portfolio for funding and supporting this research.

Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. SAND2023-[number](#).