Harnessing molecular isomerization in polymer gels for sequential logic encryption and anticounterfeiting

Yu Dong1,2,3†, Yao Ling1,2,3†, Donghui Wang1,2,3, Yang Liu1,2,3, Xiaowei Chen1,2,3, Shiya Zheng1,2,3, Xiaosong Wu1,2,3, Jinghui Shen1,2,3, Shiyu Feng1,2,3, Jianyuan Zhang4*, Weiguo Huang1,2,3*,

Using smart photochromic and luminescent tissues in camouflage/cloaking of natural creatures has inspired efforts to develop synthetic stimuli-responsive materials for data encryption and anticounterfeiting. Although many optical data-encryption materials have been reported, they generally require only one or a simple combination of a few stimuli for decryptions and rarely offer output computability that prevents trial-and-error attacks. Here, we report a series of multiresponsive donor-acceptor Stenhouse adducts (DASAs) with unprecedented switching behavior and controlled reversibility via diamine conformational locking and substrate free-volume engineering and their capability of sequential logic encryption (SLE). Being analogous to the digital circuits, the output of DASA gel–based data-encryption system depends not only on the present input stimulus but also on the sequence of past inputs. Incorrect inputs/sequences generate substantial fake information and lead attackers to the point of no return. This work offers new design concepts for advanced data-encryption materials that operate via SLE, paving the path toward advanced encryptions beyond digital circuit approaches.

INTRODUCTION

Synthetic materials that respond to chemical and physical stimuli have shown great promise in information storage and encryption technologies. Classical examples of encryption applications range from security threads in money bills that glow under ultraviolet (UV) light to hidden watermarks in passports or merchandises. The applied stimuli include light (1–8), heat (9–13), water (14), gas (15), electricity (16, 17), mechanical force (18), magnetism (19, 20), and pH (21), while color changing and luminescence are typically preferred outputs that can be read by naked eyes (22–24). These economical solutions are ideal for anticounterfeit technologies in “one-to-many” encryptions. However, they can still be copied or mimicked because of their simple, one-dimensional (1D) stimuli response (Fig. 1, A and B). For important, high-value applications, “end-to-end encryption” (E2EE) that requires the recipient to input correct information and that disallows multiple attempts in brute-force attacks would bring the security to the next level (25).

Sequential logic encryption (SLE) scheme, which is widely used in the digital circuits for data protection, requires multiple keys to be input in an exact preset sequence rather than a simple combination of multiple keys (1, 6, 8, 10, 26, 27). As a result, the output of SLE depends not only on the present input but also on the sequence of past inputs (Fig. 1C). Upon receiving incorrect keys or input sequences, the SLE system would generate fake information that is deceptive to the attackers. Overall, SLE scheme provides excellent resistance against attacks and a high level of security. Despite the promises, SLE scheme has, so far, been only applied to digital circuits and has not yet been implemented on responsive photochromic and luminescent molecules, probably because its required complexity is beyond the reach of most responsive molecules.

Here, we present a hardware SLE solution based on multi-responsive molecular logic gates. The fundamental designs are based on the responsive behavior of donor-acceptor Stenhouse adducts (DASAs), including the following: (i) We devise a series of multi-responsive DASA molecules featuring photochromic, thermochromic, and hydrochromic characteristics to overcome the drawbacks of traditional light-responsive materials that only respond to one or two stimuli. Therefore, the encryption level and the number of keys (stimuli) or key combinations required for data decryption could be largely enhanced. (ii) We customize the responsive behaviors and reversibility of DASAs via a newly found diamine conformational locking (DACL) and free-volume engineering of the substrate (i.e., covalently attach DASAs into a polymeric gel with a proper free volume). (iii) We compose the data-encryption pattern/system via selecting different DASAs with distinctive responsive behaviors and desired reversibility and construct a specific decryption scheme through carefully arranging the stimulus input sequences. Our designs require not only correct keys but also the correct key sequences for data decryption. Attacks with wrong keys or input sequences would end up with a deceptive output. The built-in irreversibility in the schemes prevents trial-and-error attacks that are often problematic for materials-based encryptions. This work also provides real examples of E2EE deliverables and opens new avenues to multiresponsive materials for E2EE applications.

RESULTS

DASAs are a type of negative photochromic materials first developed by Alaniz’s group in 2014 (28–34). Most established photoswitches such as azobenzenes (35), spiropyrans (36), diarylethenes (37), and other photochromic motifs (38, 39) have their isomerization triggered with high-energy UV light. While upon structural modifications, these can operate under visible light irradiation (40–42). DASAs are inherently triggered with visible light in their basic design, as well as
water, to achieve complete isomerization (30, 33, 34, 43–47). In
general, DASAs contain a “donor” (electron rich) and an “acceptor”
(electron deficient) bridged by a nearly planar triene-enol (Fig. 1,
D to F). Under visible light or water, DASAs convert themselves
from a colored “linear” form into a colorless “cyclic” form. The pro-
cess can be reverted under heat (Fig. 1D) (45). The color of the linear
form is determined by the donor and acceptor structures, as well
as the solvents (31, 32, 48). Currently, at least three generations of
DASAs with distinct donors and acceptors have been developed
(28, 33, 34). However, the reported DASAs generally show reversible
responses toward three stimuli (i.e., light, heat, and water) with
good repeatability, which not only makes their behavior monotonous
and predictable but also raises the risk from repeated brute-force
attacks (49). Hence, they have been rarely applied to advanced
data encryption.

To tailor the switching behavior of DASAs, we have developed
two strategies: (i) DACL, i.e., the alkyl diamines with proper molec-
ular length remarkably facilitate the isomerization of DASAs from
linear to cyclic form and lock the conformation of DASA with
cyclopentenone form via multiple hydrogen bonding (Fig. 2A); and
(ii) substrate free-volume engineering, i.e., the introduction of a gel

network with proper free volume (unoccupied volume) helps to
alleviate (even eliminate) the solid substrate effect that hampers
DASA isomerization. To comprehensively evaluate the above two
strategies, 12 DASAs with three different donors and four different
acceptors are synthesized (see the Supplementary Materials for
details) (28, 33, 34, 44, 50).

DACL effect

The discovery of DACL effect starts with the observation that adding
several microliters of N′-ethylpropane-1,3-diamine into a 3-ml pink
DASA-1 toluene solution caused rapid decoloration even without
light irradiation. Motivated by this phenomenon, we moved forward
to add a small amount of N′-ethylpropane-1,3-diamine into various
DASA solutions (Fig. 2B) and observed a similar trend in all. Even
for DASA-4 with indanedione as the acceptor, whose solution is ex-
tremely stable and well maintains its blue color under prolonged light
irradiation, it also fades quickly upon addition of N′-ethylpropane-
1,3-diamine. The respective lifetimes of four open-formed DASA-1 to
DASA-4 (τ, defined as the time when 90% of the DASAs convert to
the closed form) in the presence of N′-ethylpropane-1,3-diamine are
98, 85, 54, and 718 min, respectively (Fig. 2D and see the Supplementary
Materials for more details). Unexpectedly, these faded solutions did not restore their initial colors after being heated up, which is in contrast to the typically understood DASA behavior. In general, both linear and cyclic forms of DASAs coexist in the solution due to the thermodynamic equilibrium between the open and closed forms, which can be shifted by light irradiation or heat (30, 48, 51). Removing these stimuli would again restore their initial equilibrium states. However, N′-ethylpropane-1,3-diamine breaks the...
association constant of diamine and the closed form of DASA in toluene with an isothermal titration. N-alkylamines, the inability to form multiple hydrogen bonding with the good conformational match between them. For the mono- and di- amines, the triene hydroxyl group of the open form of DASAs is more likely to play the role of hydrogen bonding donor rather than an acceptor. Hence, the open form of DASAs could only weakly interact with diamine (Fig. 2A). Alternatively, the primary amine group on the diamine could also possibly interact with both "O" atoms on the cyclopentenone and on the acceptor unit with two bifurcating hydrogen bonds, leading to a locked conformation of DASA (Fig. 2A).

To verify the above proposed mechanism, we move forward to conduct a series of control experiments with a variety of amine derivatives at identical molar ratios (80:1) to the DASAs, including isopropylamine, diethylamine, N-methylamine, ethylenediamine, aniline, 1,3-diaminopropane, 1,6-hexanediamine, and branched polyethyleneimine (bPEI). As shown in Fig. 2C and E, 1,3-diaminopropane, ethylenediamine, N'-ethylpropane-1,3-diamine, and bPEI exhibit the highest decoloration rate among all amines, with the respective "r" values of 72, 56, 52, and 7.8 min. The highest decoloration rate of bPEI is consistent with the densest diamine groups in the polymer. 1,6-Hexanedi amine takes longer time to fade the DASA solutions, with a "r" value of 171 min, probably due to its conformational mismatch with the closed form of DASAs that weakens its ability to fully lock the closed conformation of DASAs, whereas diethylamine, isopropylamine, aniline, and N-methylamine barely decolor the DASA solutions. These results imply that diamines with two or three carbon atoms (n = 0 and 1 in Fig. 2A) between two nitrogen atoms interact most effectively with the closed form of DASAs due to the good conformational match between them. For the monoamines, the inability to form multiple hydrogen bonding with DASAs notably decreases the decoloration rate. In addition, the large steric hindrance of benzene ring on N-methylamine and aniline limits its interaction with DASAs, and therefore, no decoloration of DASAs was observed. In addition, isothermal titration calorimetry measurements clearly demonstrate a strong interaction between diamine and the closed form of DASA in toluene with an association constant of $K_a = 3.42 \times 10^5$ M$^{-1}$ (Fig. S1), which is an unexpectedly high value considering that the $K_a$ values of some host-guest supramolecular systems with well-defined binding sites and molecular conformations are in the range of $10^4$ M$^{-1}$ (S2, S3).

To exclude decoloration caused by DASA degradation in the presence of diamines, we conducted NMR characterizations for the faded DASA in CDCl$_3$. Figure 2F shows the $^1$H NMR spectra of DASA-1 before and after adding 1,3-diaminopropane. The vanishing of triene protons (peaks a to d) and triene hydroxyl proton [peak e at 12.0 parts per million (ppm)], together with the appearance of cyclopentenone protons (peaks f and g), clearly indicates the isomerization of DASA-1 from the open form to the closed form upon diamine addition (detailed in Materials and Methods). Further mechanistic evidence is provided by the density functional theory (DFT) calculation that reveals that the DASA (closed form)–diamine complex is more stable (10 kcal/mol lower in energy) than the DASA (open form)–diamine complex.

According to the DACL effect, bPEI is introduced and serves as the donor and as a diamine for conformation locking. The resulting Gel-DASA-9 to Gel-DASA-12 with bPEI as the donor behave differently from the other eight DASAs in the solution. As shown in Figs. S2 and S3, DASA-1 to DASA-8 (except DASA-4) readily respond to light irradiation and could be thermally reverted to the open form, representing the typical characteristics of DASAs. In contrast, Gel-DASA-9 to Gel-DASA-12 fade their colors upon light irradiation but fail to recover after being heated up, due to the abundant primary amines on bPEI that lock the closed conformation of DASA-9 to DASA-12 (Fig. S4).

**Substrate free-volume impact on the DASA switching behaviors**

Although most DASAs could readily isomerize in solutions, the construction of advanced data encryption based on the solutions is not practical because of their poor handleability and difficulties in write-in and storing data. Therefore, solid substrates are the highly preferred media for data encryption. However, it is reported that DASAs exhibit poor switching behaviors and incomplete thermal recoveries on solid substrates, particularly for the first-generation DASAs with alkylamine donors (28). This not only limits the diversity of DASA switching behaviors but also generates ambiguous logic outputs (i.e., neither "0" nor "1" could be obtained). To overcome this challenge, we attach DASAs on a quasi-solid substrate, i.e., a polymeric gel with 3D networks (Figs. S5 and S6) and proper free volumes (denoted as “Gel-DASA” in Fig. 3) (54). To balance the final color intensity of the resulting DASA gels and their reversibility of isomerization, we intentionally allow only 2 to 8% secondary amine side chains to couple with the furfural-acceptor adducts while leaving the rest 92 to 98% side chains unreacted (step 2 in Fig. 3A; see the time-dependent NMR in Figs. S7 to S9 for more details). The calculated distance between two neighboring cross-linking points of poly(pentafluorophenyl acrylate) (pPFPA) gel at a given cross-link density (5%) is around 2.6 nm (Fig. 3B), corresponding to a free volume of 17 nm$^3$, which is large enough for the isomerization of most DASAs (~1.3 nm in length in the open form).

Unlike most DASAs on other solid substrates (e.g., filter paper) that barely respond to light (Figs. 3C and 4), Gel-DASAs show distinct photo-responsive behaviors (Fig. 5 and Figs. S10 to S12). Gel-DASA-5, Gel-DASA-6, and Gel-DASA-7 exhibit complete cyclization upon light irradiation and full recovery under heat. Gel-DASA-1 and Gel-DASA-2 also respond to light but with an incomplete cyclization or poor recovery. The emerging light responses of Gel-DASA-1, Gel-DASA-2, and Gel-DASA-5 to Gel-DASA-7 are induced by the presence of free volume in the gel network (Fig. 3B), which facilitates the intramolecular rotation of DASA during isomerization. As for Gel-DASA-9 to Gel-DASA-12, bPEI occupies most of the free volume in the gel network and therefore hampers the isomerization of attached DASAs.
As expected, these Gel-DASAs also behave differently with the corresponding small molecular DASAs on the filter paper in terms of water exposure. It is reported that water facilitates the transformation of triene-ol to cyclic form by reducing the energy barrier between two isomers (45). The resulting colorless DASA·$H_2O$ can return to a colored linear form upon heating (45, 43, 46). All 12 DASAs on the filter paper readily decolor upon water exposure, indicating the formation of water molecule–coordinated DASA·$H_2O$. Heating up to 180°C restores the initial colors of DASA-1, DASA-2, and DASA-5 to DASA-7. For the rest of DASAs, they well retain their colorless status (Fig. 4A and figs. S13 to S15). UV-visible (UV-vis) absorption spectra provide quantitative evidence for their hydrochromic behaviors (Fig. 4, E to G). In contrast, Gel-DASA-3 and Gel-DASA-5 to Gel-DASA-8 lost their hydrochromic behaviors, as evidenced by negligible color change even after long-time water treatment (Fig. 5A and figs. S16 to S18). The possible reason is that the hydrophobic benzene ring of the N-phenylethylenediamine prevents water from diffusing into the gel network, leading to an encapsulating effect to the DASAs, which is verified by the contact angle measurements (fig. S19). Gel-DASA-2 and Gel-DASA-4 not only retain their response to water but also gain the capability of completely recovering upon heating (Fig. 5, A and B). Note that the free volume of Gel-DASA-9 to Gel-DASA-12 could be enlarged upon water exposure because of the high hydrophilicity of bPEI. As a result, the DASA-9 to DASA-12 could readily isomerize to the closed form upon water exposure and then maintain the closed states due to the DACL effect imparted by bPEI chains.

Classification of the responsive behavior of DASAs
As mentioned above, all 12 small molecular DASAs on the filter paper are not photoresponsive but water responsive. They can be classified into two categories based on their reversibility (Table 1). The first category containing DASA-1, DASA-2, and DASA-5 to DASA-7 well recovers when being heated at 180°C. The rest of the DASAs compose the second category, which is completely irreversible after water/moisture treatment. Hence, their responsive behaviors are less diverse and highly predictable. After being attached to the gel and using the DACL effect, they can be classified into six categories (Table 2). The first category consists of Gel-DASA-1, which shows good photochromic and hydrochromic behaviors but poor recoveries. The second category consists of Gel-DASA-2, which shows incomplete photo-response but complete hydrochromic behaviors, although with full recoveries. Gel-DASA-4 in category 3 well responds to water but not light and fully recovers under heat. In category 4, Gel-DASA-5 to Gel-DASA-7 readily switch to cyclic form under light irradiation with full recoveries after being heated. However, they are very stable in water and show no hydrochromic behaviors. In the fifth category, Gel-DASA-3 and Gel-DASA-8 show neither photochromic nor hydrochromic behaviors. In the last category, Gel-DASA-9 to Gel-DASA-12 behave similarly to Gel-DASA-4 but give irreversible change to water/moisture. Therefore, by manipulating the DACL effect, free volume of substrate, steric hindrance, and encapsulating effect, highly diverse and much less predictable DASA responsive behaviors could be achieved, paving the way for constructing highly programmable advanced data-encryption systems.

Digital data encryption
Having successfully tailored the photo-, hydro-, and thermochromic responses of the Gel-DASAs, we move forward to construct an advanced data-encryption system. Here, DASA-4, DASA-5, and DASA-7 to DASA-9 are selected and in situ attached to a pPFPA gel and form a number “8” that consists of Gel-DASA-4, Gel-DASA-5, and Gel-DASA-7 to Gel-DASA-9 as the frames (Fig. 6, A and B, and detailed in the Supplementary Materials). The above Gel-DASAs are selected on the basis of the following considerations: (i) They exhibit either full or no responses to light, water, and heat and thus provide clear logic output 1 or 0. (ii) These Gel-DASAs come from different categories with distinct colors and diverse and even orthogonal photochromic behaviors (e.g., Gel-DASA-4 versus Gel-DASA-5). As a consequence, a number of keys or key sequences are required for decryption, which increases the encryption complexity. Relying on these features, it makes the outputs unpredictable and remarkably enhances the data security level. (iii) The tailored reversibility of the above Gel-DASAs not only further enhances encryption complexity but also enables SLE. That is, the outputs are determined by both inputs and input sequences. Incorrect input sequences would give wrong data and lead the attackers to the point of no return and therefore eliminate the risks associated with trial and error.

As shown in Fig. 6, Gel-DASA-4 and Gel-DASA-9 with excellent hydrochromic behavior locate at the top left and bottom left frame of the number 8, respectively. Gel-DASA-5 and Gel-DASA-7 with a robust photothermal switching behavior compose the bottom and top frame of number 8, respectively. Gel-DASA-8 with neither photochromic nor hydrochromic behaviors forms the rest of the frames. The frames of the resulting number 8 gain distinct colors and...
responsive behaviors. When number 8 is exposed to water, both the top left and bottom left frames decolor because of the hydrochromic behavior of Gel-DASA-4 and Gel-DASA-9, giving rise to a number “3” (routes 1 and 2 in Fig. 6C). After being heated at 80°C, only the top left frame recovers but not the bottom left frame due to the lack of reversibility in Gel-DASA-9, and therefore, a number “9,” rather than the initial number 8, is formed. Subsequent light irradiation decolors both top and bottom frames, leading to a number of “4.”

Fig. 4. Isomerization of DASAs on the filter paper. (A) The photochromic, hydrochromic, and thermochromic behaviors of 12 DASAs on filter paper. The evolution of normalized UV-vis reflection spectra of (B) DASA-1 to DASA-4, (C) DASA-5 to DASA-8, and (D) DASA-9 to DASA-12 upon light irradiation and heating. The evolution of normalized UV-vis reflection spectra of (E) DASA-1 to DASA-4, (F) DASA-5 to DASA-8, and (G) DASA-9 to DASA-12 upon water vapor treatment and heating. White light intensity: 9 mW/cm². Heat temperature: 180°C. Water: water vapor at 25°C.
As a result, an output of “394” is obtained after an input sequence of “water-heat-light” and is defined as the correct output. However, when light irradiation is applied after water exposure (route 2), a number “-1” appears and then turns to number “9” after being heated. As a result, an output of “3-19” is obtained. The above results clearly indicate that a slightly different input sequence would end up with a significant output change. In routes 3 and 4, when input sequences “light-heat-water” and “light-water-heat” are applied, outputs of
Table 1. Classification of the responsive behaviors and reversibility of DASAs on the filter paper. The responsive behavior and thermal reversibility of 12 DASAs on the filter paper.

| Category | DASA on filter paper | Light responsive | Recover Water responsive | Recover |
|----------|----------------------|------------------|--------------------------|---------|
| 1        | 1, 2, 5, 6, and 7    | ×                | ×                         | √       |
| 2        | 3, 4, 8, 9, 10, 11, and 12 | ×                | ×                         | √       |

Table 2. Classification of the responsive behaviors and reversibility of Gel-DASAs. The responsive behavior and thermal reversibility of 12 Gel-DASAs.

| Category | Gel-DASA | Light responsive | Recover Water responsive | Recover |
|----------|----------|------------------|--------------------------|---------|
| 1        | 1        | √                | Partially                | √       |
| 2        | 2        | ×                | ×                         | √       |
| 3        | 4        | ×                | ×                         | ×       |
| 4        | 5, 6, and 7 | √                | ×                         | ×       |
| 5        | 3 and 8  | ×                | ×                         | ×       |
| 6        | 9, 10, 11, and 12 | ×                | ×                         | √       |

“H83” and “H-19” are obtained, respectively. In routes 5 and 6, when an input sequence of “heat-light-water” and “heat-water-light” is applied, an output of “8H-1” and “83-1” is obtained, respectively. These outputs are different from the correct output of “394”. The fact that using three stimuli (keys) with six input sequences leads to five wrong outputs but only one correct output unambiguously demonstrates the substantial output corruptibility of the system and the high level of data security. Note that once the number is treated with water, it is impossible to return it to the initial number 8 because of the irreversible hydrochromic behavior of the bottom left frame made of Gel-DASA-9. As a consequence, the attackers lose the chance to start from the beginning. In addition, the final output of route 1 is a number “4”, which does not appear in any other routes (Fig. 6C), manifesting the uniqueness and high security of the designed data-encryption system. Furthermore, this system is also generalizable for encryption of other numbers (number sequences) via properly selecting the Gel-DASAs for different frames and elaborately designing the decryption sequences.

As a control, a number 8 is also written on a filter paper with the corresponding small molecular DASAs as the frames rather than Gel-DASAs (Fig. S20). In detail, DASA-4 and DASA-9 form the top left and bottom left frames of number 8, respectively. DASA-5 and DASA-7 compose the bottom and top frames of number 8, respectively. DASA-8 forms the rest of the frames. In route 1, treating the number 8 with moisture leads to decoloration of all frames due to their excellent responses to water. Sequential heating fails to fully restore the color of the frames because of their poor irreversibility. The following light irradiation causes no change to the number. Therefore, output “8ØØ” (“Ø” is the symbol for null) is obtained from route 1. Similarly, when “water-light-heat” is applied, output “8ØØ” is observed as well in route 2. In routes 3 and 4, the number 8 shows negligible change after light irradiation due to the inability to respond to light. The sequential heating or water treatment causes no change or completely decolors all frames of number 8. As a result, outputs “8Ø” and “8ØØ” are obtained in routes 3 and 4, respectively. As would be anticipated, outputs “8ØØ” and “8ØØ” are obtained in routes 5 and 6, respectively. These results clearly show that the DASAs on the filter paper are incompetent for data encryption. Furthermore, the DASAs on the filter paper are vulnerable to solvent etching or rinsing (fig. S21 and movie S1). The above results clearly demonstrate the unique advantage of pPFPA gel substrate for highly secure data encryption and protection.

In addition, we have evaluated the possibility of data decryption by applying multiple stimuli simultaneously. Figure S22 shows the evolution of a number 8 after being treated by four different combinations of multiple stimuli, i.e., (i) water–(light + heat), (ii) (water + heat)–light, (iii) (light + water)–heat, and (iv) (water + light + heat). Note that the stimuli in the bracket are applied simultaneously, e.g., in the first case, we treat the number 8 with water first and then with “light + heat” simultaneously. As anticipated, we obtained numbers 9, -1, 9, and 3 in cases 1, 2, 3, and 4, respectively, whereas the true information, i.e., the number 4, does not appear in any cases. This result again emphasizes that the stimuli must be input in a correct sequence for data decryption, manifesting a high security level of the Gel-DASA–based sequential data-encryption system.

Relying on the good transparency of pPFPA gel, we are able to create a 3D data-encryption system by overlaying different pPFPA gels, which further improves the data security and reliability. As shown in fig. S23, the system consists of three-layer pPFPA gels written with different data and different “site-specific” modifications. The first, second, and third layers of pPFPA gel contain a number 8, a letter “A,” and a number “6,” respectively. The ink used for each frame is indicated in fig. S23. The readout, e.g., (8A6 8), consists of two parts: The first part is the output of each individual layer (i.e., 8A6, denoted as “separated readout”), and the second part is the overlayed output (i.e., 8, denoted as “apparent readout”). In route 1, the readout is (8A6 8), (3FF 8), (9PE 8), and (4µL V) after being treated by an input sequence of water-heat-light. The last output of route 1 (i.e., 4µL V) is defined as true information. Note that (i) upon applying stimulus, the data on the different gel platform show different responses, e.g., after water treatment, the top left and bottom left frames of number 8 on the first gel platform disappear; the top right and bottom right frames of letter A on the second gel platform disappear; the bottom and bottom right frames of number 6 on the
third gel platform disappear. Similar differences were also observed upon light irradiation and heat. All these differences indicate that the protection of encryption is improved, and it is difficult to reversely engineer the frame functions. (ii) Although the last apparent readout of route 1 (i.e., \( \mathcal{V} \)) also appears in routes 3 to 5, their corresponding separated readouts (i.e., HH \( \mathcal{V} \) versus 4\( \mathcal{L} \)) differ notably. (iii) The last separated readout of route 1, i.e., 4\( \mathcal{L} \), does not appear in any other routes. (iv) The apparent readout 8 contains three possible separated readouts, i.e., 8A6, 3FF, and 9PE, which greatly complicates the decryption outputs and effectively confuses the attackers. (v) The outputs and output sequence of route 1, i.e., (8A6 8), (3FF 8), (9PE 8), and (4\( \mathcal{L} \) \( \mathcal{V} \)), are substantially different from all other five routes. All these features, rendered by the three overlayed pPFPA gels, remarkably improve the data security and reliability.

Besides the digital numbers, text encryption (fig. S24) and more complicated quick response (QR) code encryption (fig. S25), which can carry a much larger amount of information and enable smart readout via a mobile phone scanning, could also be achieved by these Gel-DASAs. Note that most reported data-encrypted QR codes are static and only require UV light to activate the pattern. The QR code developed here is dynamic and visible under natural light, which not only facilitates the scanning but also greatly enhances the security level of encrypted data. The results clearly demonstrate the good generalizability of Gel-DASA–based SLE.

pPFPA gel also has good shape reprogramming property and shape-memory behavior. As shown in Fig. 7 (A and B) and movie S2, the soft pPFPA gel can be reprogramed to a coiled shape when being heated to 40°C, which is well maintained even after being cooled.
DOWN TO ROOM TEMPERATURE. REHEATING THE GEL WOULD RECOVER ITS FLAT
SHAPE. AS A RESULT, THE DATA ARE PHYSICALLY HIDDEN AND PROTECTED BY
THE CURLED GEL, ELIMINATING THE RISK ASSOCIATED WITH SURFACE SCRATCH
AND INTENTIONAL ABRASION FROM ATTACKERS. TO DECRYPT THE DATA, A
HEATING STEP IS REQUIRED TO FLATTEN THE GEL. THEREFORE, THE SHAPE
MORPHING OF pPFPA PROVIDES AN ADDITIONAL LEVEL OF DATA SECURITY. MOWEVE,
THE DASAS ARE COVALENTLY ATTACHED TO THE GEL, RENDERING GOOD
STABILITY TO THE DATA. RINSING THE DATA WITH COMMON ORGANIC SOLVENTS
HARLY ERASES THE DATA (FIG. S21 AND MOVIE S3), UNLIKE DATA PRINTED
ON PAPER THAT CAN BE EASILY REMOVED. THE pPFPA GEL IS HIGHLY TRANS-
SPARENT AND SOFT AND CAN BE EASILY ATTACHED TO A VARIETY OF SUBSTRATES
INCLUDING FINGERS, CERAMICS, GLASSES, PLASTICS, FOAMS, AND METALS WITH
NO NEED OF GLUE (FIG. 7, C TO J). THEREFORE, IT CAN BE POTENTIALLY USED
AS SMART LABELS. LAST, ALL THESE DASAS HAVE SIMILAR MOLECULAR STRUCTURES
AND A RELATIVELY LOW LOADING (2 TO 8%) IN THE GEL. AS A RESULT, THE CHEMICAL
STRUCTURES AND ELEMENTAL COMPOSITIONS OF THE DIFFERENT FRAMES OF NUMBER 8 ARE VERY SIMILAR, WHICH REDUCES THE RISK ASSOCIATED WITH DATA DECRYPTING AND COUNTERFEITING VIA SOPHISTICATED INSTRUMENTAL ANALYSIS (E.G., ELEMENTAL ANALYSIS, FOURIER TRANSFORM INFRARED,
AND OTHERS).

DISCUSSION
In summary, we have successfully harnessed the photo-, hydro-, and
thermochromic behaviors of DASAs by manipulating the DACL
effect, free volume of substrate, steric hindrance, and encapsulating
effect. The resulting Gel-DASAs exhibit tailored responses to light
and heat and well-controlled thermal reversibility, making their
photochromic behaviors much less predictable, more diverse, and
highly programmable for constructing advanced data-encryption
systems. Relying on the above features, we have achieved an SLE
system based on smart responsive materials. The system requires
multiple stimuli (i.e., light, water, and heat) to be input in a preset
sequence rather than a simple combination of three stimuli. Upon
receiving incorrect stimulus or input sequences, the system would
generate fake information that is deceptive to the attackers and does
not allow a reversal. By virtue of the above merits, this Gel-DASA–
based data-encryption system exhibits good resistance against attacks
and ensures a high level of data security. However, we notice that the
frame function of number 8 (or other data) could possibly be
reversely engineered if the attackers get six identical copies of the
gel platform. To overcome this issue, we have built a 3D data-
encryption system by overlaying three different pPFPA gel platforms
with different data and different site-specific modifications, which
helps to further improve the data security and reliability. In addition,
the pPFPA gel has good shape morphing and shape-memory
properties, offering the chance to reprogram its shape at elevated
temperatures and enhancing the security level to the encrypted data.
Moreover, the DASAs are covalently attached to the gel substrates,
ensuring high stability against solvent etching. The pPFPA gels are
highly flexible and capable of conforming to a variety of substrates,
demonstrating its applicability as smart labels. This work opens a
new door for developing responsive materials for advanced EZEE via
the SLE scheme that was generally only applied to electrical circuits.

MATERIALS AND METHODS
Quantification of color from images
We used software Adobe Photoshop to quantify the color change of
DASAs. Specifically, the chromatic values \(L^*a^*b^*\) in the Inter-
national Commission on Illumination guidelines were chosen as a
measure of color change, where \(L^*\) stands for lightness, \(a^*\) for color
opponent red/green, and \(b^*\) for color opponent yellow/blue. The
difference between two colors can be represented by \(\Delta E^*\). The larger
the \(\Delta E^*\) value, the greater the color difference. \(\Delta E^*\) can be calculated by the following equation

\[
\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}
\]

In the experiment, the sample color at different time points was
compared with the original sample color, and thus a series of \(\Delta E^*\)
were obtained.

NMR characterization of DASAs before and after
diamine treatment
In detail, 0.5 mg of DASA-1 solid and 500 μl of chloroform-d were
put into an NMR tube, and the \(^1\)H NMR signal of DASA-1 was
recorded. Then, 1,3-diaminopropane (80 times in molar ratio) was
added into the NMR tube. After the solution color faded out, the \(^1\)H
NMR signal of DASA-1 was recorded again.

DFT calculations
All DFT calculations were carried out with the Gaussian16 package
(55) in SMD solvent model (56). Geometry optimizations and
vibration frequencies were studied by DFT at M06-2X (57)/maug-cc-pVdz (58) level. The binding energy of DASA-1 and 1,3-diaminopropane was calculated at M06-2X/maug-cc-pVTZ level using the counterpoise correction to solve the basis set superposition error (59).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.add1980.

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