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Damage-Reporting Carbon Fiber Epoxy Composites

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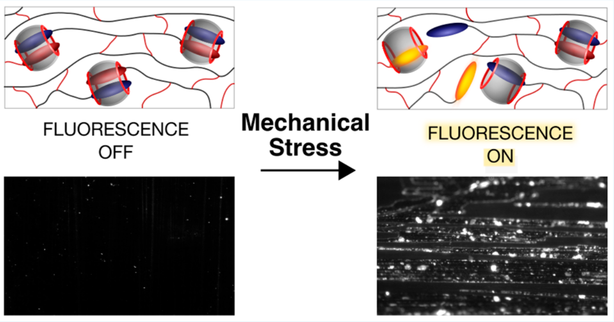
Supporting Information

ABSTRACT: The ability to detect early damage is of great significance in load bearing composite materials used for high performance applications. Microdamages if left unchecked can grow under subsequent stress, leading to catastrophic structural failure. The sensing of early stage damage via nondestructive methods is therefore critically important for the safe use of these materials. Herein a supramolecular approach to self-diagnosis of early stage damage in a carbon fiber epoxy composite material, via the incorporation of a CB[8] based ternary complex as an additive is reported. The complex comprising a fluorescent probe and a quencher encapsulated by the CB[8] is introduced into the epoxy resin of the composite as a supramolecular cross-linking agent, whose stress-induced dissociation results in the turn on of fluorescence of the probe. In this way, detection of irreversible mechanical strain and fatigue at an early stage is attainable, enabling the assessment of microdamage in the material.



KEYWORDS: *damage reporting composites, carbon fiber epoxy resin composites, CB[8] ternary complexes, fluorescence, strain and fatigue detection*

INTRODUCTION

Carbon fiber reinforced composites have emerged as the material of choice in all applications where their unique combination of lightness and high mechanical strength is essential. Relevant examples are airplanes and electrical vehicles, for which long cruising range requires lightweight composites. Since carbon fiber reinforced composites are used mainly as structural components, it is critical to recognize any damage at a very early stage to avoid catastrophic failure. Sites of microscopic damage can act as concentrators of stress resulting in the extension of damage under load. The detection of early stage damage via nondestructive testing methods could substantially increase safety of these materials as well as their service lifetime. Nondestructive testing (NDT) of composites is presently based on X-ray tomography, ultrasound, thermography, or spectroscopic methods.[1−3] In this context, the preparation of self-diagnostic composites that autonomously sense and signal damage and fatigue is of great relevance for all applications where structural integrity is highly desired.

Current approaches toward self-reporting polymers are mainly focused on the introduction of mechanochromic molecules, excimer-forming dyes or microcapsules. So far, most of these studies have focused on the use of mechanochromic plastics, wherein dye-containing polymers change their color upon mechanical stress.[4−6] For this, the chromophoric unit, also called the mechanophore, must be appropriately positioned within a polymer chain to experience mechanical perturbation in a controlled manner and must possess mechanically labile bonds that change through isomerization or precise bond scission events thus producing distinct optical variations. Mechanoresponsive materials have been realized by directly linking dyes into the polymer chains of elastomeric or on glassy cross-linked polymers. In both cases, the mechanical stress is transduced into the electrocyclic reversible ring opening of the covalently linked dye into the open chromophoric form.[7−11] Other systems are based on physical effects such as aggregation or separation-induced emission,[12] alteration of the band gap by physical deformation of single-walled carbon nanotubes (SWCNTs),[13] or the force-induced change in photoluminescence of organometallic complexes.[14] More recently, a different damage-reporting strategy has been introduced, using aggregation-induced emission of fluorophores confined in core−shell microcapsules.[10,15] The mechanical damage causes microcapsule rupture, release of the fluorophore, and consequent fluorescent emission. This approach allows the detection of scratches and microscopic cracks in stiff polymeric matrices.

The use of mechanophores for microdamage detection in structural composites is limited by the brittleness of the

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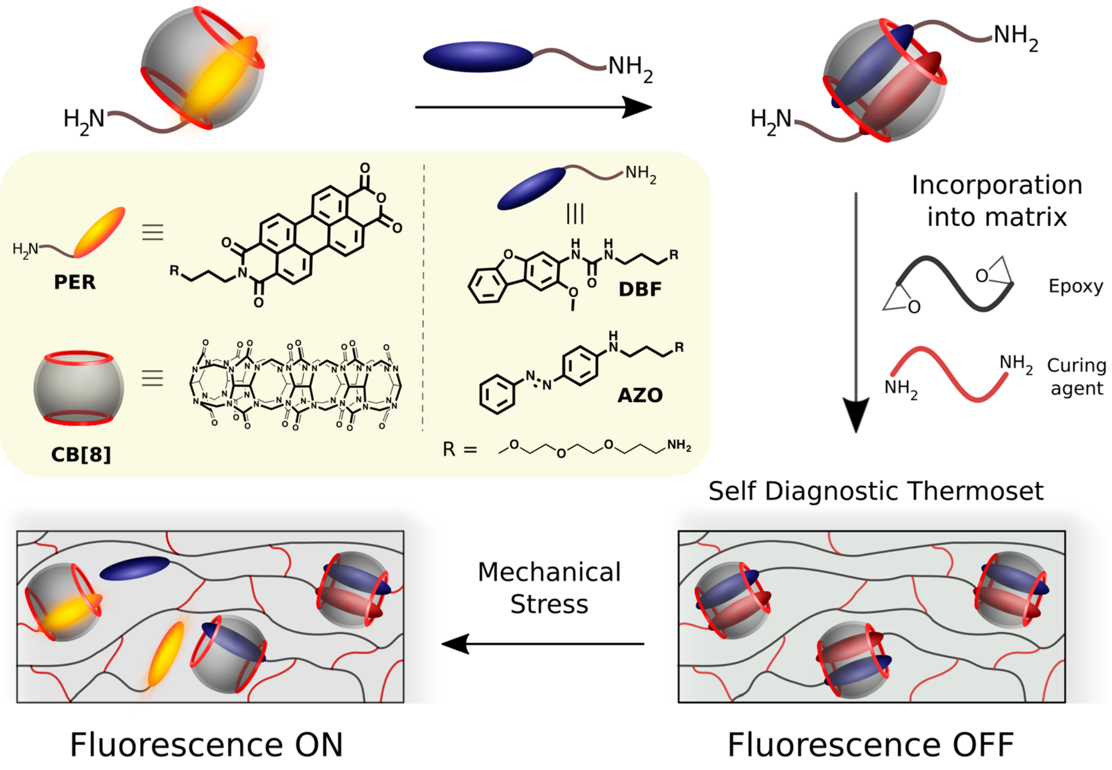


Figure 1. Schematic representation of the working principle and components of the damage reporting carbon fiber-epoxy resin composites.

material, which hampers the transfer of the applied force to the reporting unit.[2] Ideally, a reporting strategy for the detection of initial strain is desired to anticipate sudden fragile ruptures in composites. Supramolecular mechanophores are promising candidates for highly sensitive damage reporting systems, since they are held together by tunable weak interactions. So far, supramolecular mechanoluminophores have been introduced in elastomers in the form of host−guest complexes and rotaxanes. The use of cavitands as hosts and *N*-methylpyridinium derivatives as guests has been recently proposed by our group as reporting agents for strain detection in silicon elastomers.[16] The supramolecular cross-linking complex provides fluorescence response upon dissociation induced by stress well before the formation of cracks. Additionally, Sagara and Weder used the molecular shuttle function of rotaxanes to mechanically activate reversible turn-on fluorescence in elastomeric polyurethanes under stress.[17]

Translation of these studies to obtain self-diagnostic composites has been limited.[18] Visualization of interfacial damage in a silk epoxy composite has been achieved by linking the mechanopore to both the fiber and matrix.[19] The use of a biomimetic approach to self-reporting glass[20] and carbon fiber[21] reinforced composites have been reported recently by Bruns and co-workers. The common feature in the two reports is the use of a fluorescent protein immobilized on the fiber surface as a mechanophore to report delamination and fiber fracture. Oxidation and activation of carbon fiber fabric are required for protein immobilization.

Our approach aims at implementing self-diagnostic properties into carbon fiber epoxy composites using supramolecular mechanoluminophores, transducing the localized stress in the material into a detectable fluorescence signal. The challenge is to produce a fluorescence signal directly linked to the stress-driven local breaking of the weak bonds in host−guest complexes, leading to the visualization of emerging mechanical strain in the polymer matrix of the composite. Since crack nucleation often occurs at the surface of structural elements, its detection by optical measurements will allow a full exploitation of the diagnostic characteristic of the proposed materials.

■ EXPERIMENTAL SECTION

Synthesis. Synthetic schemes and procedures are reported in the Supporting Information (Schemes S1 and S2)

Preparation of Loaded Curing Agent (LCA) Containing PER-AZO-CB[8]. Stock solutions of **PER-CB**[8] at [c] = 65 μM and **AZO** at [c] = 5 mM were prepared in Millipore water. To 20 mL of **PER-CB**[8] stock solution, 26 mL of **AZO** stock solution was added, with the ratio of components in solution **CB**[8]:**PER**:**AZO** = 1:1:100. This solution is added to 300 g of the hardener **W152LR**. The obtained emulsion was placed in the oven at 100 °C and homogenized until the water was completely removed to give **LCA** loaded with **PER-AZO-CB**[8]. The loaded sample was removed from the oven and cooled to room temperature. The component containing the **PER-AZO-CB**[8] is subsequently used for curing the epoxy resin.

Preparation of LCA Containing PER-DBF-CB[8]. A 20 mL solution of **PER CB**[8] stock solution, was used to dissolve 6 mg of **DBF** with the ratio of components in solution **CB**[8]:**PER**:**DBF**= 1:1:10. The solution was used to prepare the loaded curing agent using the above procedure.

Preparation of Carbon Fiber Reinforced Composites. The preparation of the composites and the specimens was done via vacuum infusion and is described in detail in the Supporting Information.

Mechanical Testing. Samples were tested in accordance with American Society for Testing and Materials (ASTM) standards.

Tensile Testing under ASTM D3039. Specimens were subjected to uniaxial tensile testing using MTS Insight Electromechanical Testing Systems 150 kN, with 250 kN hydraulic grips at 2 mm/min (grip pressure: 100 bar) following the ASTM D3039 method (Figure S7). This test method is designed to produce tensile property data for material specifications, research and development, quality assurance, and structural design and analysis. The method determines the in-plane tensile properties of polymer matrix composite materials reinforced by high-modulus and high-strength fibers.

Compression Testing under ASTM D3410. Specimens were subjected to compression testing using MTS Insight Electromechanical Testing Systems 150 kN, with 250 kN hydraulic grips at 2 mm/min (Grip pressure: 100 bar) following the ASTM D3410 method (Figure S7). This test method determines the in-plane compressive properties of polymer matrix composite materials reinforced by high-modulus and high-strength fibers.

Fatigue Testing under ASTM D3479. Tensile fatigue specimens were cut to size according to ASTM D3479 (length 150 mm; width 25 mm). The mechanical tests were performed using MTS Landmark 100 kN. The untested specimen showed no significant fluorescence when viewed under a fluorescence microscope. The specimen was consecutively subjected to 1000 and 10 000 cycles of 60% of UTS with a frequency of 10 Hz. A low stiffness drop was observed. The specimen was then subject to 100 000 cycles under the same conditions. A 40% of stiffness drop was observed after 100 000 cycles.

Fluorescence Imaging Measurements. Fluorescence measurements were performed with a Nikon Eclipse Ti inverted microscope, equipped with an Intensylight Epifluorescence Mercury illuminator and a FITC fluorescence cube ($\lambda_{ex} = 480 \pm 30$ nm, $\lambda_{em} = 535 \pm 45$ nm). Images were acquired by an Andor Clara high sensitivity 16bit camera. A 10× objective was used. Fluorescence images reported in Figures 3−4 have size 936 × 936 μm^2. Images in Figure 5 are 1253 × 936 μm^2. Exposure time was set at 0.5 s; to allow image comparison, their intensity scale was fixed within a 700−7000 count range, chosen to improve readability. Image processing was done using Micro-Manager 1.4.22.

■ RESULTS AND DISCUSSION

Design of Self-Diagnostic Matrix and Reporting Host Guest Complex. The implementation requires the introduction of a tiny amount of nonemissive host−guest complexes in the polymer matrix as supramolecular cross-links,[22] which break apart upon mechanical stress in the strained zone leading to localized fluorescence emission (Figure 1). The host chosen is **CB**[**8**], since it has the unique ability to form heteroternary complexes of high stability in polar environments, therefore suitable to be embedded in polar epoxy resin matrices. Moreover, it offers the possibility to select guest pairs capable of complete quenching when associated in the cavity and strong emission in the epoxy matrix transmission window. Recurring to fluorescence emission in epoxy resins imposes several constrains on the candidate guests. First of all, both the fluorophore and the quencher must be indefinitely stable in the in the final epoxy matrix and under cutting conditions. The absorbance and fluorescence emission of the fluorophore needs to be compatible with the transparency window of the used matrix. Commercial epoxy resins, based on bisphenol A, are transparent only above 400 nm. Highly fluorescent perylene monoimide (**PER**) has all these properties, with absorption maxima above 400 nm, making it an ideal candidate for the fluorescent probe (Figure S1). Furthermore, perylene monoimides and bisimides have detectable fluorescence even at micromolar concentrations upon encapsulation by **CB**[**8**].[23,24] The quencher guests must be able to bind to **CB**[**8**] and effectively quench the perylene fluorescence in the ternary complex (Figures S2−S4). Two candidate quencher guests have been singled out for the purpose according to literature. Azobenzene (**AZO**) and dibenzofuran (**DBF**) derivatives form ternary complexes with perylene imides within **CB**[**8**], quenching its fluorescence upon complexation.[25] Both fluorophore and quencher guests must be equipped with an amino terminated side chain to participate in the covalent cross-linking of the epoxy resin once added to the curing agent (Figure 1). In this way the two guests are covalently attached to the epoxy resin and therefore affected by the strain in the matrix. Amino terminated 4,7,10-trioxa-tridecane connectors were chosen for all guests with the dual purpose of increasing water solubility, necessary for ternary complex formation in water, and conformational flexibility to permit their curing in the matrix. **PER** was synthesized based on a literature procedure from the perylene tetracarboxylic dianhydride (Scheme S1), where the monopotassium salt of the dianhydride was reacted with a diamine glycol to give **PER**.[26] The syntheses of **AZO** and **DBF** quenchers were adapted from literature procedures to insert terminal amino groups (Scheme S1).[25,27,28] **CB**[**8**] was prepared and purified according to a standard procedure.[29]

Incorporation of Reporting Complex into the Composite. Commercial Elan-tech **EC 157.1/W152 LR** (provider Elantas Europe srl), a two-component epoxy system, was used as the primary test matrix. It is a standard formulation for the preparation of carbon fiber composites via vacuum infusion and it has the advantage of room temperature curing with post curing in a moderate 50−60 °C range. The proposed approach involves the insertion of the reporting system as a complex in the precursor before polymerization. The ternary complexes are prepared in water using a 100-fold excess of quencher **AZO** and a 10-fold excess of **DBF**, to ensure the quantitative formation of the ternary complexes. The introduction of each ternary complex to the matrix was done in a step by step process as shown in Figure 2a. The hardener **W152 LR** was first added to an aqueous solution of the complex to give a complex concentration of 4.3×10^{-6} mol kg^{-1}, corresponding to 0.02 wt % in the curing agent. The water was subsequently removed from the emulsion by heating at 100 °C with constant agitation to ensure homogeneity.

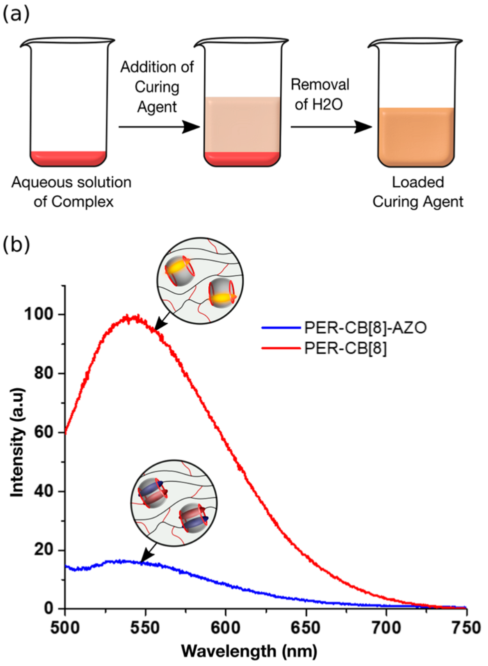


Figure 2. (a) Schematic representation of the incorporation of the complex into curing agent. (b) Emission spectra at $\lambda_{ex} = 480$ nm of **PER-CB**[**8**] (1:1) and **PER-AZO-CB**[**8**] (1:100:1) complexes in the polymer matrix.

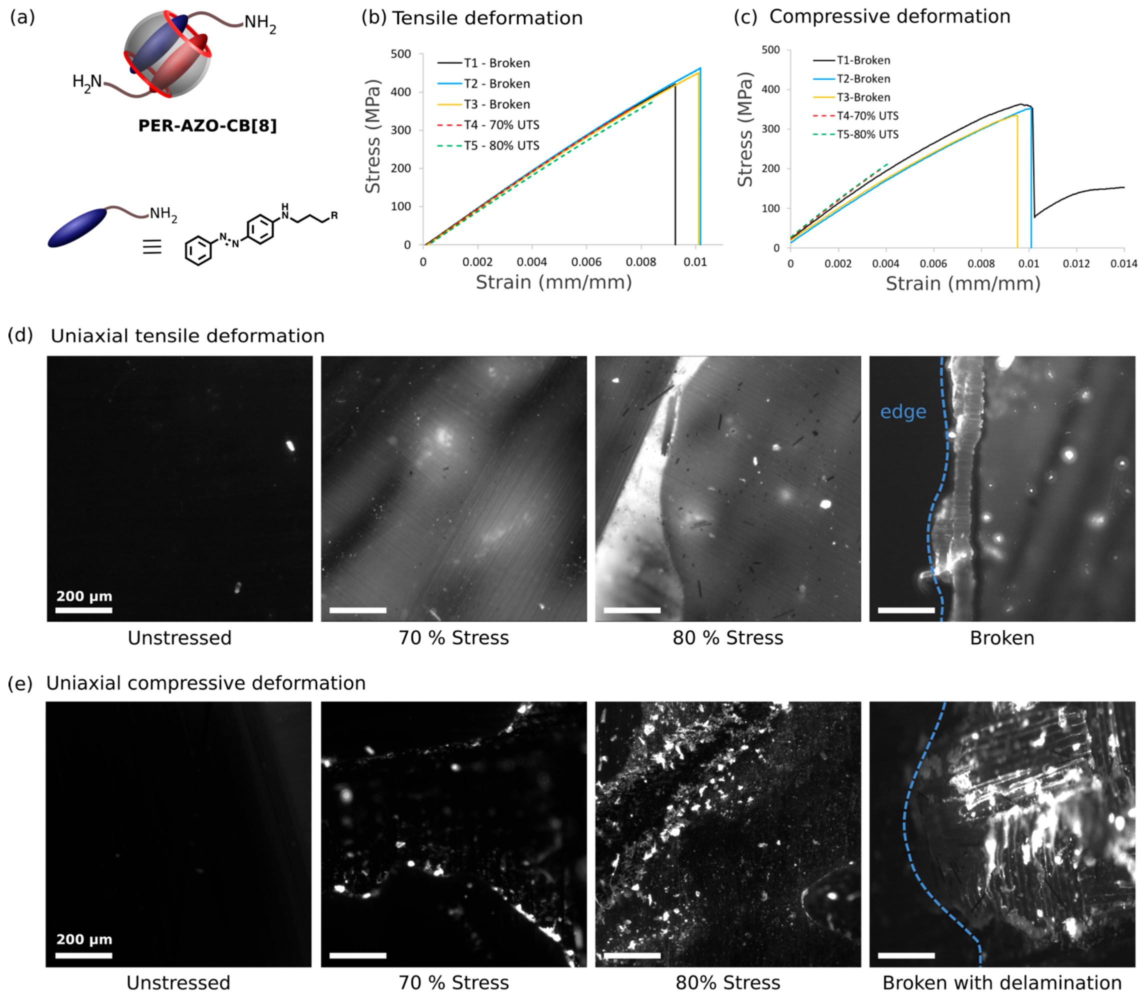


Figure 3. (a) Sketch of the employed **PER-AZO-CB**[8] reporting agent. Stress strain curves for uniaxial (b) tensile deformation and (c) compressive deformation. (d) Fluorescence microscope images (10×) under varying degrees of tensile stress represented as percent of UTS. (e) Fluorescence microscope images under increasing compressive stress represented as percent of UTS.

Upon removal of water the resulting curing agent **W152 LR** was cooled to room temperature, giving the loaded curing agent (**LCA**) containing the preformed **CB**[8] ternary complex (Scheme S3). The stability and fluorescence emission of the system in the matrix was investigated by the preparation of samples of the thermoset containing the **PER-AZO-CB**[8] ternary complex and its **PER-CB**[8] precursor in disposable polycarbonate cuvettes. The **LCA** was used in combination with the epoxy component EC 157.1 in the preparation of the thermoset using the curing procedure reported in the technical data sheet (Supporting Information). In the presence of the **AZO** quencher the emission of the **PER-CB**[8] is drastically reduced with respect to the control sample containing **PER-CB**[8] in 1:1 ratio (Figure 2b). This also confirmed the stability of the complex to curing conditions of the epoxy resin.

The same procedure was employed for the **PER-DBF-CB**[8] complex and the control complex. The formation of the heteroternary complex is necessary for the quenching of **PER** fluorescence in the matrix. The unlikely alternative of fluorescence quenching by the second guest dispersed in the matrix was ruled out by the following experiments: cured epoxy resins were prepared under standard conditions with **LCA** containing **PER** alone and **PER** plus an excess of **DBF** respectively. In both cases the fluorescence emission spectrum of **PER** remained unaltered (Figure S5).

The carbon fiber-epoxy panels were prepared via vacuum infusion of the loaded resin into carbon fiber fabric (Twill 2 × 2) The two components (**EC157** and **LCA** containing **PER-AZO-CB**[8]) were combined and the mixture was infused into the carbon fiber fabric under vacuum (Figure S6a−d). The resulting panel was then cut to obtain specimens with the direction of carbon fiber at 0°.[30] The same procedure was followed in the case of **PER-DBF-CB**[8]. Blank panels were similarly prepared using the pure hardener containing no reporting agent. Standardized specimens were then prepared from the panel.

Tensile and Compressive Testing of Self-Diagnostic Specimens. The response of the **PER-AZO-CB**[8] containing composite to stress was studied by subjecting the specimens to uniaxial deformation testing in both tensile and compression modes, in accordance with the American Society for Testing and Materials (ASTM) standards. They were subsequently examined under a fluorescence microscope to observe changes in emission. In unstressed samples, images report a random position of the sample, while in stressed samples, images report a region of maximum fluorescence. For broken samples, images were acquired in correspondence to the breaking point. Both blank and unstressed specimen showed no fluorescence under the same conditions.

The stressed specimen did not show any superficial damage compared to the pristine one. When viewed under a fluorescence microscope, a marked increase in background fluorescence was observed with a stress threshold above 70% as shown in Figure 3d. The fluorescence intensity increases with stress loading. No significant increase in fluorescence was detected below 70% (Figure S8). Upon breaking, fluorescence appears along the broken edge of the specimen (Figure 3d). The same behavior was observed under uniaxial compression testing according to the ASTM D3410 method. In this case the final breaking can also follow a delamination pathway. Again, the fluorescence appears at 70% stress, even if less strongly than in the tensile stress mode (Figure 3e).

Exchanging the quencher in the ternary complex did not alter the self-diagnostic properties of the resulting composite. The performance of the **PER-DBF-CB**[8] complex were comparable to those of the **PER-AZO-CB**[8] in terms of fluorescence intensity and stress sensitivity both in the tensile and compression modes (Figure S9). The optical resolution of strained regions was observed to be very high, with detectable fluorescent zones smaller than 20 μm. This is an important asset related to the use of turn-on fluorescence based supramolecular probes, since it combines molecular level stress response with highly sensitive fluorescence strain detection. In addition, the fluorescence of the specimens was observed to persist unaltered over the course of months.

Control Experiments. According to the proposed reporting mechanism, the cross-linking of the ternary complex within the matrix is pivotal to translate the localized strain into decomplexation-induced fluorescence. A control experiment was devised to test this tenet, using a ternary complex in which both the reactive amino groups of the **PER** fluorophore and the **DBF** quencher have been substituted by unreactive methoxy units (Figure 4a,b). The two guests were prepared adapting known literature procedures (Scheme S2). This chemically inert ternary complex was randomly dispersed within the **W152 LR** curing agent. The corresponding **LCA** underwent the same vacuum infusion protocol to fabricate specimens for mechanical testing. Very limited fluorescence appeared upon both uniaxial tensile and compression deformations compared to the corresponding cross-linked ternary complex **PER-DBF-CB**[8] (Figures 4 and S10).

Response to Fatigue Damage. In order to assess the performance of the material under conditions similar to actual use, the specimens were subjected to fatigue in addition to compressive and tensile testing. Fatigue is the weakening of a material caused by repeated application of load.[31] If the loads are above a certain threshold, microscopic cracks begin to form. The stress values that cause such damage are significantly lower than the corresponding static ultimate tensile stress limit. Tensile fatigue testing was performed on composite specimens containing the **PER-DBF-CB**[8] reporting agent, cut to the size defined in ASTM D3479 (Figure 5). The S–N (stress–number of cycles) or Wöhler diagram is a familiar way to represent the resistance of a given material to cyclic loading in addition to compressive and tensile testing. It shows graphically the material stiffness reduction with repeated application of load as the ratio of final elastic modulus/initial elastic modulus of the specimen (E_x/E_{x0}). The specimen was progressively subjected to 1000, 10 000, and 100 000 cycles under 60% UTS with a frequency of 10 Hz. The 60% UTS stress value was chosen because it is below the sensitivity threshold of the reporting agent. 1000 cycles showed no changes in fluorescence and no stiffness drop (Figure 5e). At 10 000 cycles, few fluorescence spots appeared in concomitance with an extremely limited stiffness drop (Figure 5f). After 100 000 cycles, a 40% of stiffness drop was observed and fluorescence was visible along the entire length of the specimen. Carbon fiber laminate fabrics are made of many threads woven on a warp and a weft at 0° and 90° yarn orientation.[32] The loading is usually applied in one of the two fiber directions. In our case, monotonically increased tensile load was applied along the 0-direction, resulting in multiple ply microcracks in the 90-plies (Figure 5f–h; for images of microcracks, see Figure S11). Fluorescence in the 0° orientation was observed only after significant stiffness drop (Figure 5i), as indication of extensive damage. This is particularly relevant since the presence of microscopic damage in the 0° orientation is the harbinger of catastrophic failure in a composite. The spatial resolution attainable for detecting microcracks is in the low micrometer range. This is well below the resolution achievable with highly sensitive NDT techniques such as Phased Array Ultrasonic Testing (PAUT)[33] and comparable to that obtained via incorporation of microcapsules.[10] Increasing the resolution to the nanoscale requires the application of single molecule super-resolution microscopy as shown by Wang and co-workers.[34]

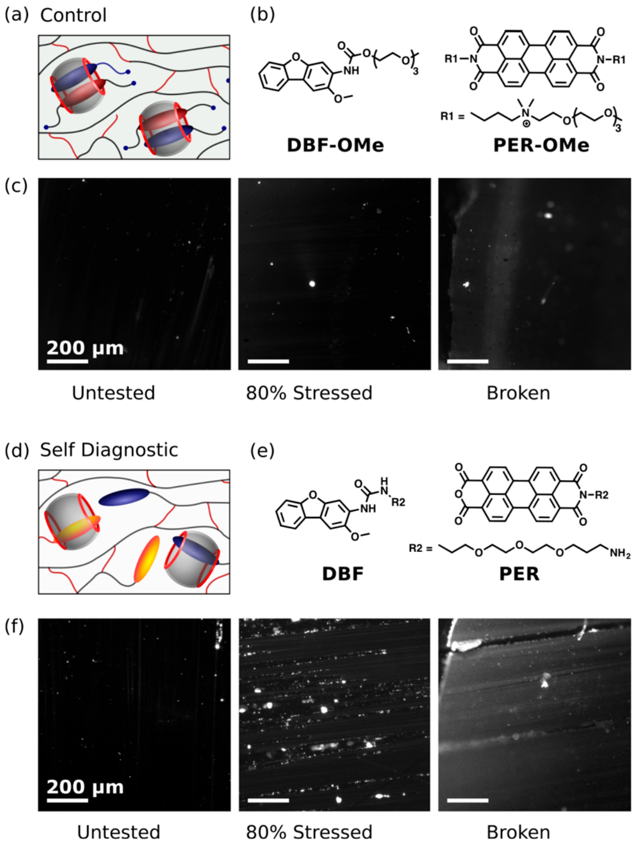
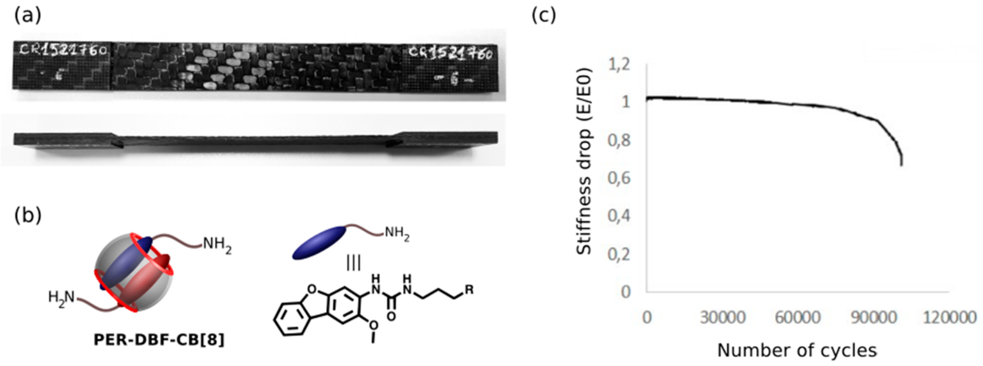


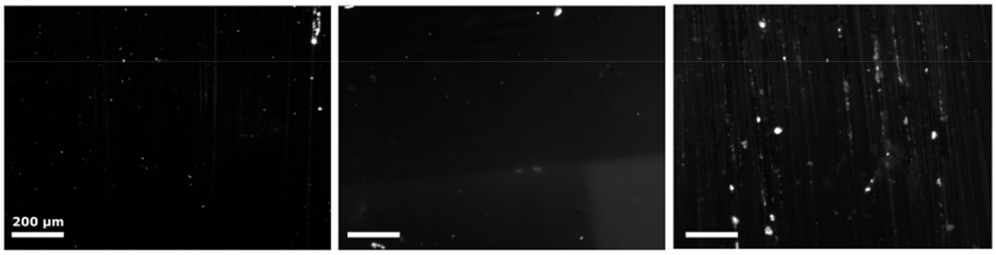
Figure 4. Illustration of the control composite and its behavior under uniaxial stress (top, a–c) compared to the self-diagnostic composite containing **PER-DBF-CB**[8] (bottom, d–f).

CONCLUSIONS

In summary, we report a novel system for early stage damage detection in a carbon fiber reinforced composite by incorporating supramolecular cross-links within the matrix facilitated by the host molecule **CB**[8]. **CB**[8] encapsulates



(d) Untested (e) 1000 cycles (f) 10,000 cycles



(g) 100,000 cycles (h) 100,000 cycles (i) 100,000 cycles

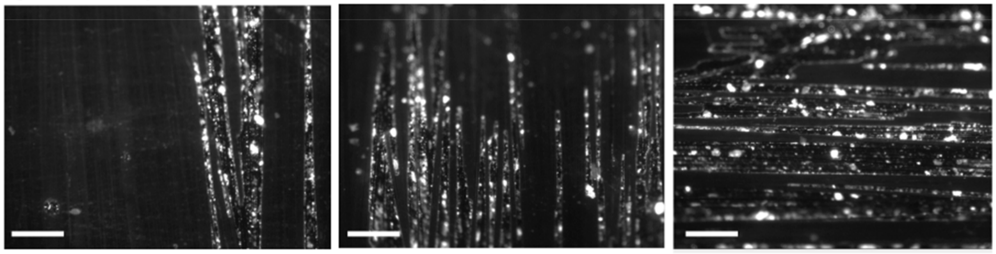


Figure 5. Fatigue testing with **PER-DBF-CB**[8] reporting agent: (a) specimen image after complete fatigue testing showing the visual integrity of the specimen; (b) structure of the **CB**[8] ternary complex used for the fatigue testing; (c) *S*−*N* diagram showing normalized stiffness drop (E_x/E_{x0}) with increasing number of cycles (see Figure S12 for all diagrams); (d−i) fluorescence microscope images (10×) under increasing cycles of stress of 60% UTS: (d) pristine specimen; (e) after 1000 cycles; (f) 90° fluorescence emission after 10 000 cycles; (g) and (h) 90° fluorescence emission after 100 000 cycles; (i) 0° fluorescence emission after 100 000 cycles.

two molecules in the matrix, a fluorophore and a quencher forming a ternary complex wherein the emission of the probe is suppressed. The epoxy matrix was used to prepare carbon fiber epoxy composite panels as per standard industrial methods, which were subjected to mechanical deformation testing. Under the application of stress, the weak supramolecular links within the matrix break apart, and the fluorescence of the probe is reinstated, assisting in the visualization of microscopic damage in the first layer of the composite material. Moreover, samples subjected to increasing stress show a commensurate increase in fluorescence intensity. Correlation of the compressive and tensile tests with emergence of fluorescence at 70% of UTS demonstrates that the proposed reporting agents are capable of detecting early damage in carbon fiber epoxy composites. In addition to tensile and compressive stress, the system shows the ability to detect fatigue damage. Compared to existing supramolecular damage reporting methodologies,[35] the proposed system is specifically tailored for structural composites.

Exploiting the dissociation of noncovalent interactions in combination with turn on fluorescence has enabled self-diagnosis in composite materials at 0.003 wt % of the reporting systems, a very low value compared to the microcapsule system for composites.[10,15] This additive-based approach allows to directly incorporate the damage-reporting probe into a commercial polymer without altering its mechanical properties (Figure S13). Overall, this approach offers an innovative, technologically viable solution to the quest of simple and effective methods of monitoring the structural integrity in composites. The proposed approach can be applied to a broad range of thermosets and related composites.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsapm.9b00694.

> Synthesis and characterization of precursors of fluorophores and quenchers. Fluorescence and ITC titrations of ternary complexes. Fluorescence microscope images, stress−strain graphs, cross section images, and mechanical properties of specimens. Technical data sheet of the used epoxy resins (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

TLC, thin layer chromatography; DMSO, dimethyl sulfoxide; DCM, dichloromethane

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