Properties and Applications of Stimuli-responsive Diacetylenes

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Abstract

The topochemical reactivity of diacetylene monomers has long been established and involves the 1,4-addition polymerization reaction. This reaction is governed by well-defined parameters that allow the synthesis of diacetylene polymers. Polydiacetylenes are conjugated polymers that display unique colorimetric and fluorescent transitions when exposed to a range of stimuli, allowing them to be easily exploited in biosensors, chemosensors, and radiochromic dosimeters. In this review, we summarize recent work on polydiacetylene systems, focusing on examples involving 10,12-pentacosadiynoic acid (PCDA) that can be structured as polymerized vesicles, films, gels, and powders. Synthetic derivatives of PCDA are also reviewed, along with the effect

of incorporating guest molecules to a diacetylene system and establishing the important relationship between reversible thermochromism and noncovalent interactions.

Contents

Introduction

Diacetylenes are a well-studied class of photoactive compound, with 10,12-pentacosadiynoic acid (PCDA, Figure 1) as a common example.[1] Irradiation of PCDA with ultraviolet light, X-rays, or γ-radiation results in photopolymerization to give a polydiacetylene with an alternating ene-yne backbone.[2, 3] This monomer-to-polymer conversion is accompanied by a visible color change from colorless to blue, with additional perturbations further changing the color of the polydiacetylene from blue, to purple, to red, to yellow, and sometimes green depending on the polymer conformation and ordering, and hence extent of delocalization of the conjugated backbone.[4-6] Diacetylenes undergo topochemical photopolymerization not only as crystalline solids, but also in semi-ordered media such as liquid crystals,[7-9] thin films,[10-13] vesicles,[14-16] and gels.[17-19] The chromic properties of the resulting polydiacetylenes are typically exploited in dosimeters, biosensors, and chemosensors.[20-22]

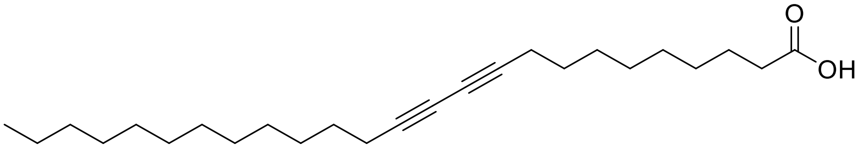
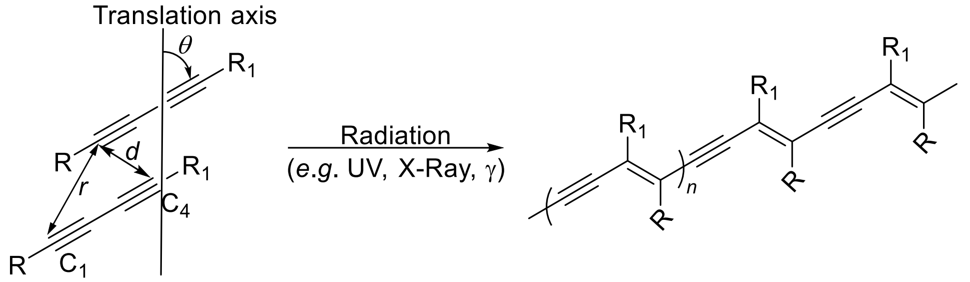


Figure 1. The structure of monomeric PCDA.

The first report of topochemical reactivity in the solid state was in 1964 by Schmidt and coworkers who investigated the [2+2] cycloaddition of *trans*-cinnamic acid polymorphs.[23-26] From extensive crystallographic and photochemical studies, Schmidt formulated the topochemical postulate which states that the carbon-carbon double bonds must be separated by a maximum distance of 4.2 Å for polymerization to be successful.[27] Five years after the postulate was described for alkene systems, Wegner reported the first example of diacetylene polymerization in the solid state,[28, 29] with Enkelmann proposing strict criteria for diacetylene reactivity in 1984 (Scheme 1).[30] Enkelmann's conditions suggest that adjacent diacetylene monomers react at a distance less than or equal to the van der Waals contact distance (d) of 3.8 Å, with a translational period repeat spacing (r) of 4.9 Å or less, along with the monomers at an orientation angle (θ) to the crystal axis at 45°.[30] These parameters for diacetylene polymerization aid in understanding the importance of molecular organization in the topochemical reaction.[31, 32] There are two possible mechanisms responsible for the topochemical polymerization of a diacetylene, known as the 'turnstile' and 'swinging gate' mechanisms, outlined in Figure 2. In the turnstile mechanism, when the monomers are exposed to radiation or heat, they pivot approximately 1 Å around the centroid of the diacetylene at 30° to bring carbon atoms C1 and C4’ together to create a new bond.[33] This mechanism is most favored for disubstituted diacetylenes,[33-36] while the swinging gate mechanism is typical for terminal diacetylenes.[37] In the swinging gate mechanism, the monomers pivot at C4’ (with the R-group remaining stationary) allowing the C1 to move approximately 3 Å to join the rest of the polymer.[33, 34]



Scheme 1. Parameters required for the topochemical polymerization of diacetylene monomers to result in a polydiacetylene. The C1-C4’ distance (*d*) of the monomers must be ≤3.8 Å, and within the translational repeat distance (*r*) of ≤4.9 Å, with a tilt angle (*θ*) of 45 °. Scheme reproduced from reference 38.

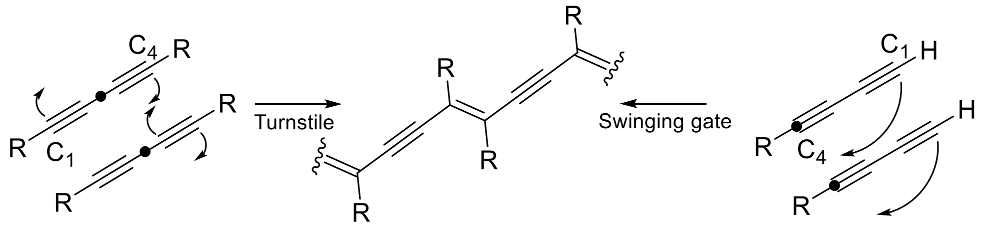


Figure 2. A simplified illustration of the two possible mechanisms of diacetylene polymerization.

Diacetylene Topochemistry

There is an abundance of diacetylene crystal structures in the literature, with some of the earlier structures arising from work by Enkelmann, that includes two bis(N-phenylcarbamate) diacetylene

(DA-*m*PhC) structures that only differ by an alkyl spacer length (*m*) of one carbon atom in DA-1PhC (Figure 3) and four carbon atoms in DA-4PhC.[39] Both structures photopolymerize, as the inter-alkyne distances are 3.65 and 3.53 Å,[40] respectively, and are within the topochemical postulate of 3.8 Å.[39] Monomer crystals of bis(N-phenylcarbamate) with a five (DA-5PhC) and six (DA-6PhC) alkyl spacer groups have also been structurally characterized, with inter-alkyne distances of 5.20 Å and 3.57 Å, respectively.[40] The large carbon-carbon distance of DA-5PhC is out of the range for topochemical reactivity, and as a result, the compound does not polymerize.[40] The topochemical parameters of DA-5PhC indicate that alkyl spacer length has an impact on how the diacetylenes react in the solid state. It has been reported that the physical properties of similar compounds can be dictated by whether there is an odd or an even number of methylene spacer groups in the spacer.[40, 41] The angle between the diacetylene and stacking axis in DA-5PhC is also vastly different from the topochemical criteria for diacetylene reactivity, at an angle of 69.3°.[40]

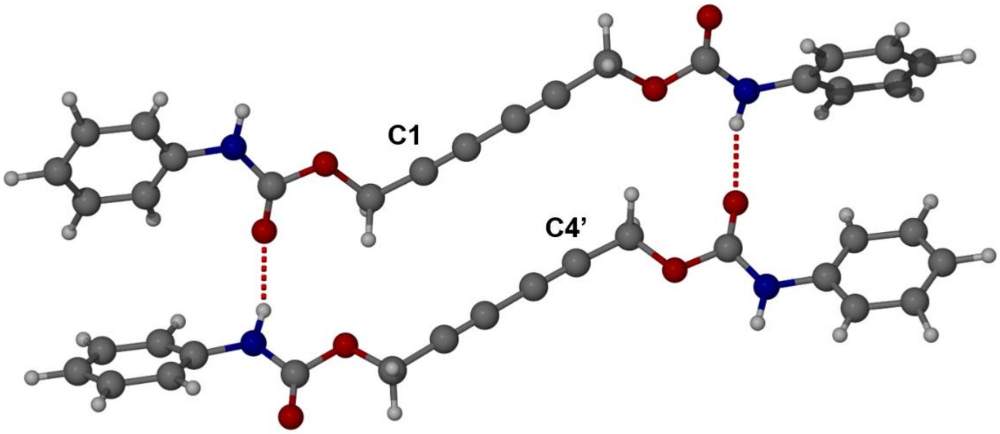


Figure 3. The X-ray structure of DA-1PhC.[40]

A different diacetylene crystal structure 4-(hexadeca-1,3-diyn-1-yl)benzoic acid that has no methylene spacer between the diacetylene moiety and the benzoic acid head group, proves to be outside of Enkelmann's parameters for topochemical reactivity, however, the material still photopolymerizes (Figure 4).[42] The C1-C4' contact distance on adjacent diacetylene moieties is reported to be 4.41 Å,[42] although a C2-C3' contact distance of 4.03 Å was identified. These observations show that exceptions to the postulate are possible.[30, 42, 43] Polydiacetylene crystal structures have also been reported in the literature, including a polymer structure of poly(1,2-bis(phenylaminomethyl)-but-1-em-3-ynyl) (Figure 5), with complete monomer-to-polymer conversion obtained by thermal annealing at temperatures below the monomer melting point (no monomer crystal structure is available).[44]

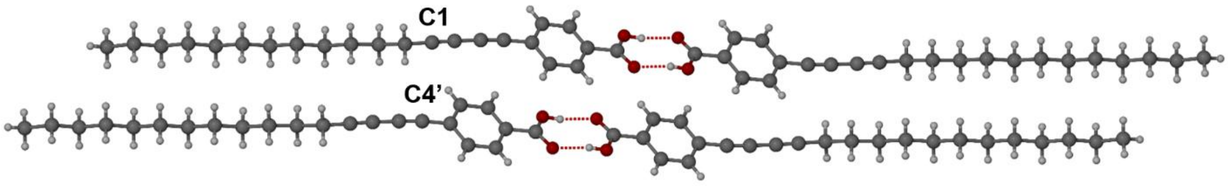


Figure 4. The X-ray structure of 4-(hexadeca-1,3-diyn-1-yl)benzoic acid with adjacent reactive groups outside of the range for topochemical reactivity, though still photopolymerizes in response to radiation.[42]

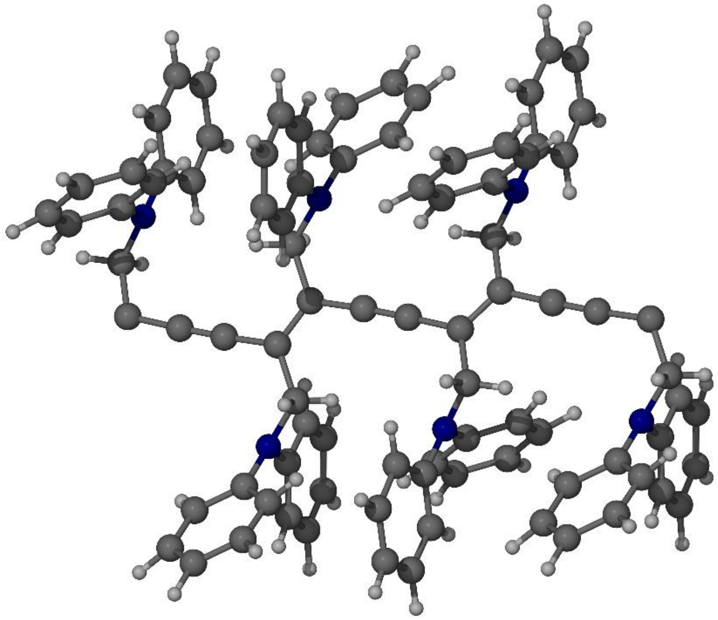


Figure 5. The structure of the polydiacetylene poly(1,2-bis(phenylaminomethyl)-but-1-en-3-ynyl).[44]

Diacetylene Cocrystals and Salts

In terms of diacetylene cocrystals, acetylene gas itself has been cocrystallized with a wide range of small molecule coformers by condensing acetylene into quartz capillaries that already contain the coformer.[45] Diacetylenes have also been cocrystallized in more complex systems. For instance, a host-guest cocrystal approach has been used to design a hydrogen bonded network of a ureylene dicarboxylic acid host with 1,6-bis(4-pyridylcarboxylato)hexa-2,4-diyne guests (Figure 6).[46] The host molecules are able to control the intermolecular spacing of the substituted diacetylene guest through the utilization of the pyridine-carboxylic acid OH···N and amino-carboxylic acid NH···O hydrogen bond synthons.[47] In this cocrystal system, the carbon-carbon triple bonds of the diacetylenes are separated by a distance of 3.94 Å with an orientation angle of 56.3 °, which is outside the values for topochemical polymerization, however, the translational period repeat spacing is within the polymerization range, at 4.71 Å.[46] Though this system is not topochemically reactive, the host molecule can be fine-tuned to design a system that allows the diacetylenes to be within the distance for reactivity. Another host-guest cocrystal system involves a 1,5-bis(4'-pyridyl)ureylene host with a deca-4,6-diyne-1,10-dicarboxylic acid guest in a hydrogen-bonded network (Figure 7).[46] In this system, adjacent diacetylenes stack with a reactive inter-alkyne distance of 4.06 Å and an orientation angle relative to the translation axis of 61.0°. These values are outside of the range for polymerization, though the translation repeat distance is within the criteria at 4.63 Å. Even though polymerization does not occur, a host-guest strategy for cocrystallization is a creative way to control and manipulate the reactivity of a diacetylene systems.[46, 48]

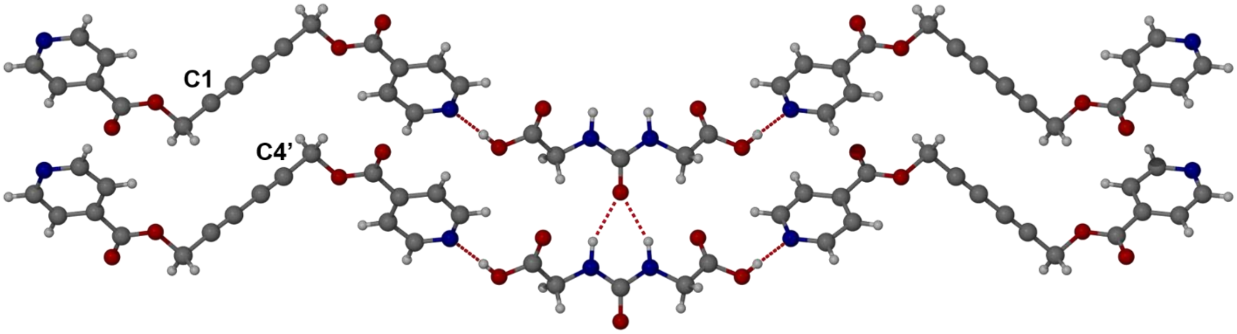


Figure 6. The X-ray structure of a ureylene dicarboxylic acid molecule interacting with 1,6-bis(4-pyridylcarboxylato)hexa-2,4-diyne by OH···N hydrogen bonds, with intermolecular NH···O hydrogen bonds forming urea tapes from the ureylene dicarboxylic acid portion of the cocrystal.[46]

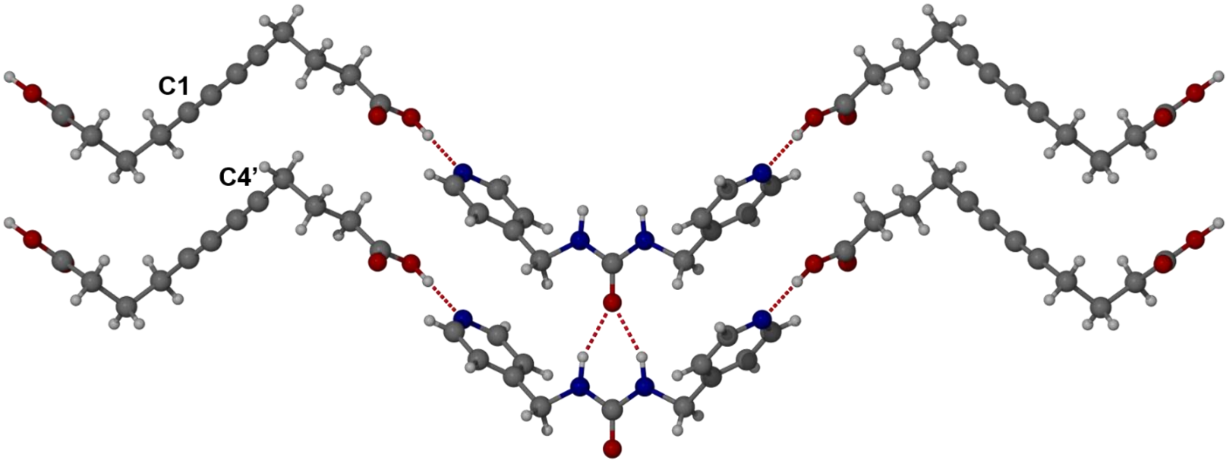


Figure 7. The X-ray structure of 1,5-bis(4'-pyridyl)ureylene and deca-4,6-diyne-1,10-dicarboxylic acid, joined by OH···N hydrogen bonds, with intermolecular NH···O hydrogen bonds forming urea tapes between 1,5-bis(4'-pyridyl)ureylene molecules.[46]

Other examples of diacetylenes cocrystallized in a host-guest matrix involve the ability of N,N'-bis(pyridine-4-ylmethyl)oxalamide to control the reactivity of the terminal diacetylene penta-2,4-

diynyl 3,5-dihydroxybenzoate (Figure 8A).[37] The resulting structure is a triple helix of alternating diacetylene and oxalamide molecules, with the diacetylene motif in the center of the helix.[37] The acetylenic C1-C4’ intermolecular distance is 3.64 Å and conforms to the topochemical postulate for reactivity.[37] As a result, after heating at 150 °C for 24 hours the diacetylene cocrystal polymerizes to give a cocrystal polydiacetylene structure, with the translational repeat distance shortening from 5.09 Å to 4.93 Å in the polymer (Figure 8B).[37]

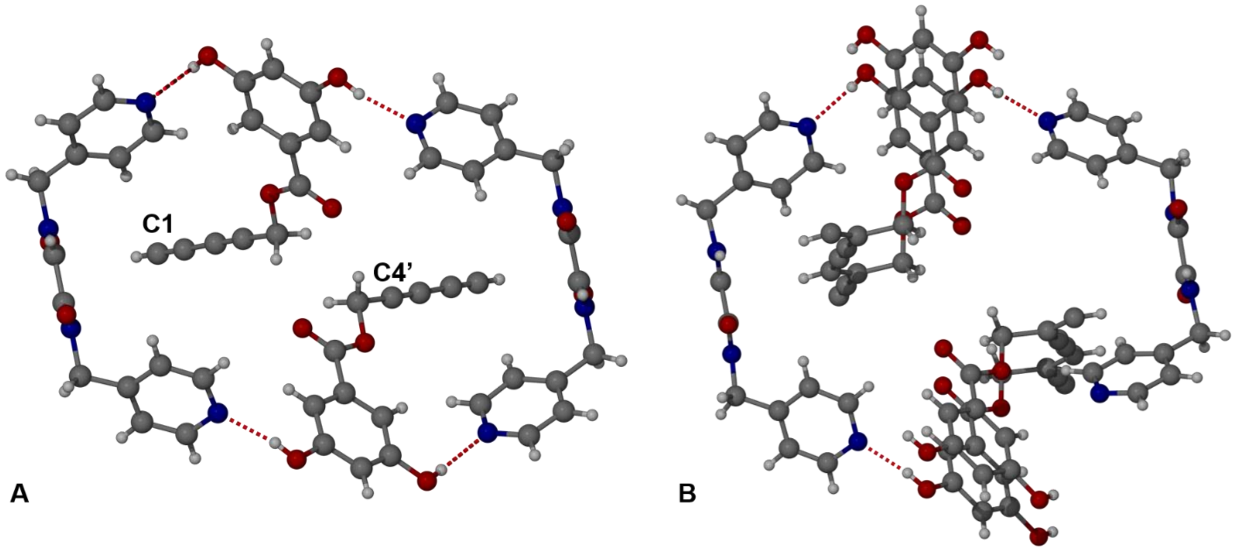


Figure 8. A) The X-ray structure of the terminal diacetylene penta-2,4-diynyl 3,5-dihydroxybenzoate cocrystallized with an oxalamide host, N,N’-bis(pyridine-4-ylmethyl)oxalamide. B) The polymerized cocrystal of penta-2,4-diynyl 3,5-dihydroxybenzoate and N,N’-bis(pyridine-4-ylmethyl)oxalamide, showing the ene-yne bonds of adjacent reactive groups.[37]

In addition to host-guest systems, bispyridyl diacetylenes have been cocrystallized with oxalamide derivatives with different length spacer chains. Eight such cocrystal structures were reported in a single publication by Curtis and coworkers.[49] The two bispyridyl diacetylenes are 1,4-bis(3-pyridyl)buta-1,3-diyne[50] and 1,4-bis(4-pyridyl)buta-1,3-diyne[51] and before cocrystallization, their closest C1-C4’ intermolecular distances are 4.48 Å and 4.52 Å, which are outside the ranges for topochemical reactivity.[49] When the diacetylene hosts are combined with varying oxalamide guests such as N,N'-oxalyldiglycine, oxalamide-N,N'-bis(3-propionic acid), oxalamide-N,N'-bis(5-pentanoic acid), and oxalamide-N,N'-bis(6-hexanoic acid), only the cocrystal of 1,4-bis(4-pyridyl)buta-1,3-diyne and N,N'-oxalyldiglycine is able to polymerize (Figure 9).[49] In this instance, the inter-alkyne distance is 3.62 Å, with a repeat distance of 4.93 Å and an orientation angle of 47.7°.[49] No other combination of the bispyridyl diacetylene and oxalamide cocrystal underwent polymerization.[49]

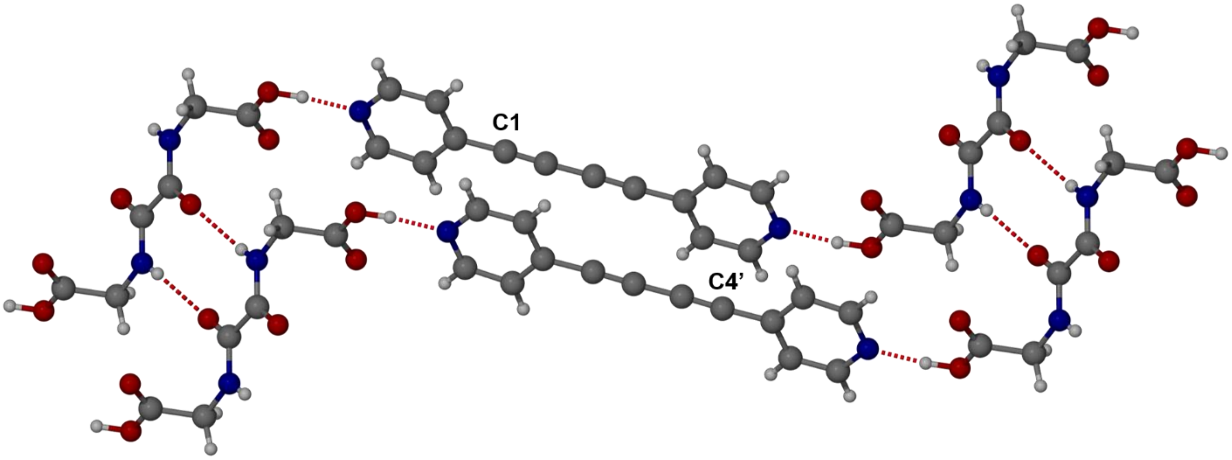


Figure 9. The X-ray crystal structure of 1,4-bis(4-pyridyl)buta-1,3-diyne and N,N'-oxalyldiglycine.[49]

Additional cocrystal systems involve the use of light-stable host molecules and light-sensitive guest molecules that crystallize as two different isomers that dimerize upon UV irradiation. An example is the cocrystallization of 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol and bis(isoquinolin-3(2H)-one, which crystallizes in a monoclinic *C*2/*c* polymorph **1** (Figure 10A) and in an orthorhombic *Pbcn* polymorph **2** (Figure 10B).[52] Though the diacetylene hosts in the cocrystals are separated by too great a distance to polymerize, the isoquinolone guest is able to dimerize upon exposure to radiation, as the carbon double bonds are separated by 3.71 Å (Schmitt's postulate suggests <4.2 Å).[29, 52] Polymorph **1** yields two identical isoquinolone isomers, while polymorph **2** also yields the same isomer as polymorph **1**, and an additional isomer, which is related by an inversion center (Scheme 2).[52]

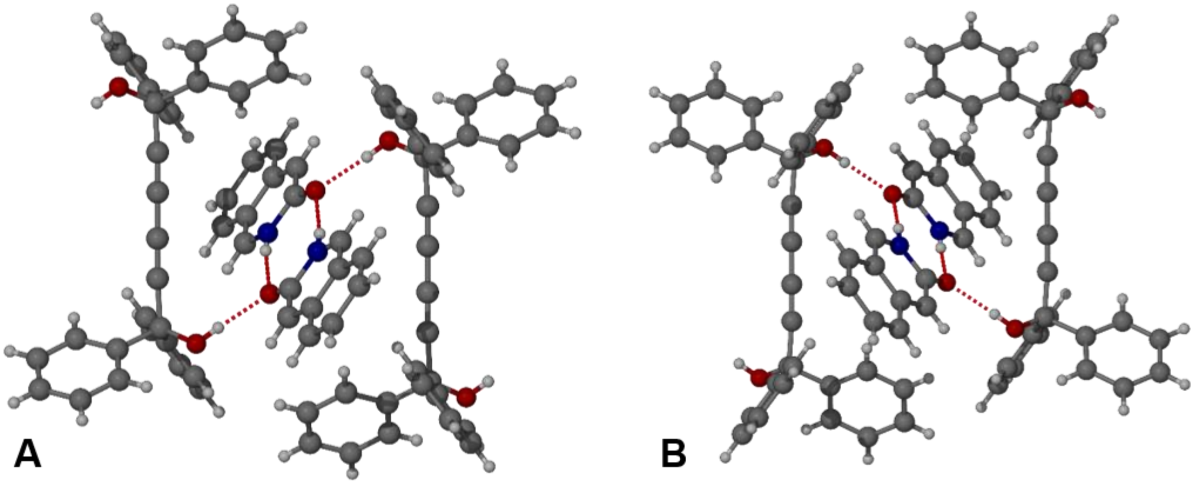
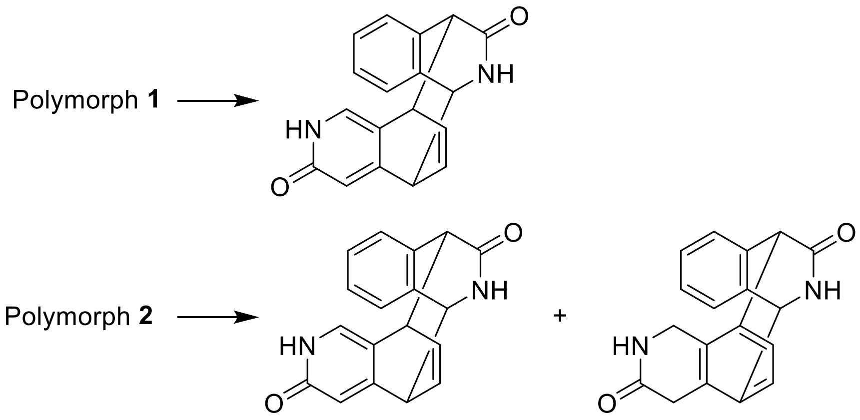


Figure 10. The X-ray structures of A) polymorph **1** B) polymorph **2** of 1,1,6,6-tetraphenyl-2,4-hexadiyne-1,6-diol and bis(isoquinolin-3(2H)-one.[52]



Scheme 2. The dimerized bis(isoquinolin-3(2H)-one isomers formed after irradiation of polymorph **1** and polymorph **2**.[52]

The importance of topochemistry has been shown by Goroff and coworkers through 1,4-di-iodobuta-1,3-diyne cocrystals with bis(3-pyridylmethyl)oxalamide (Figure 11).[53] A hydrogen bond network is formed between neighboring oxalamide molecules, consisting of O···NH hydrogen bonds, along with N···I halogen bonds between the pyridyl nitrogen of the oxalamide, and the iodine atom of the diiodoalkyne at a distance of 2.83 Å. Both hydrogen bonds and halogen bonds contribute to the control of the alignment of the diacetylene moiety. However, the intramolecular C1-C4' distance is greater than the desired value, at 3.90 Å, along with a greater value for the repeat distance of the diacetylene units, at 5.11 Å, and a tilt axis of 51 °. All of these values contribute to the fact that the diacetylene monomer units do not topochemically react when exposed to radiation.[53] A para derivative of bipyridyl oxalamide was also synthesized, bis(4-pyridylmethyl)oxalamide, and cocrystallized with diiodobutadiyne, though still, the parameters for topochemical polymerization remain outside of the necessary range.[53]

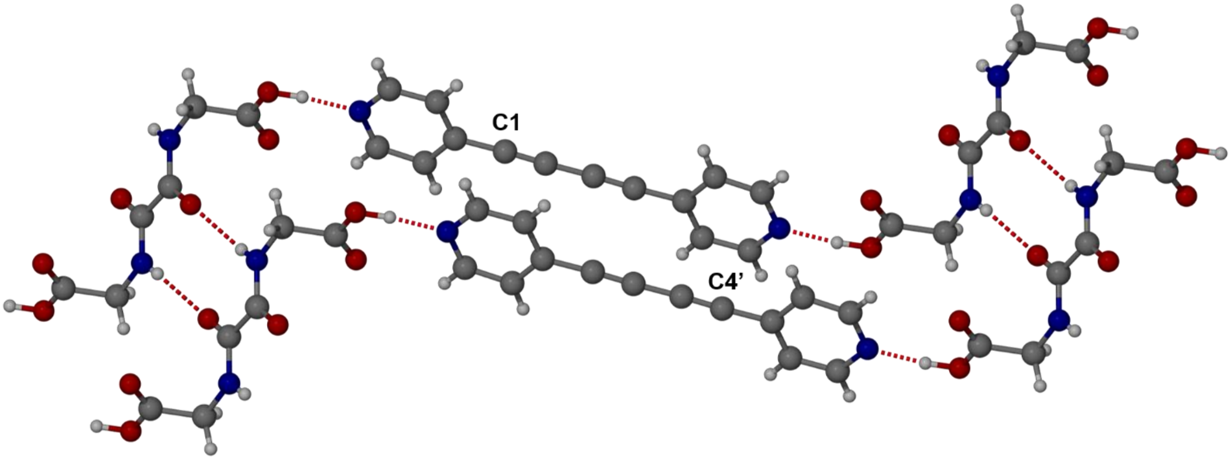


Figure 11. The halogen-bonded cocrystal of 1,4-di-iodobuta-1,3-diyne and bis(3-pyridylmethyl)oxalamide.[53]

Other diiodobutadiyne cocrystals involve N,N'-bis(4-cyano)oxalamides with different length spacer groups in a further attempt to customize the topochemical reactivity. For example, N,N'-

bis(4-cyanopropyl)oxalamide and 1,4-di-iodobuta-1,3-diyne forms a cocrystal that becomes dark and decomposes at room temperature without any evidence of polymerization (Figure 12).[54] However, bis(4-cyanobutyl)oxalamide does polymerize,[55] even though the C1-C4' distance is slightly greater than the distances suggested by the topochemical postulate, at 3.88 Å (Figure 13).[54] In the monomeric cocrystal structure, the iodine atoms of 1,4-di-iodobuta-1,3-diyne are either halogen bonded to nitrile nitrogen atoms or oxygen atoms belonging to the oxalamide group.[54] Hydrogen bonds also form between molecules of bis(4-cyanobutyl)oxalamide, via the NH···O supramolecular synthon.[54] Cocrystals of bis(4-cyanopentyl)oxalamide and 1,4-di-iodobuta-1,3-diyne also polymerize, though the X-ray coordinates could not be determined for both the monomeric and polymeric structures.[54] In conclusion, the effect of different length alkyl spacer groups can drastically change the topochemical parameters for diacetylene cocrystal polymerization. In this instance, the main difference between the cocrystals that do and do not polymerize are the number of hydrogen bonding interactions, which contribute to the control of the diacetylene units.

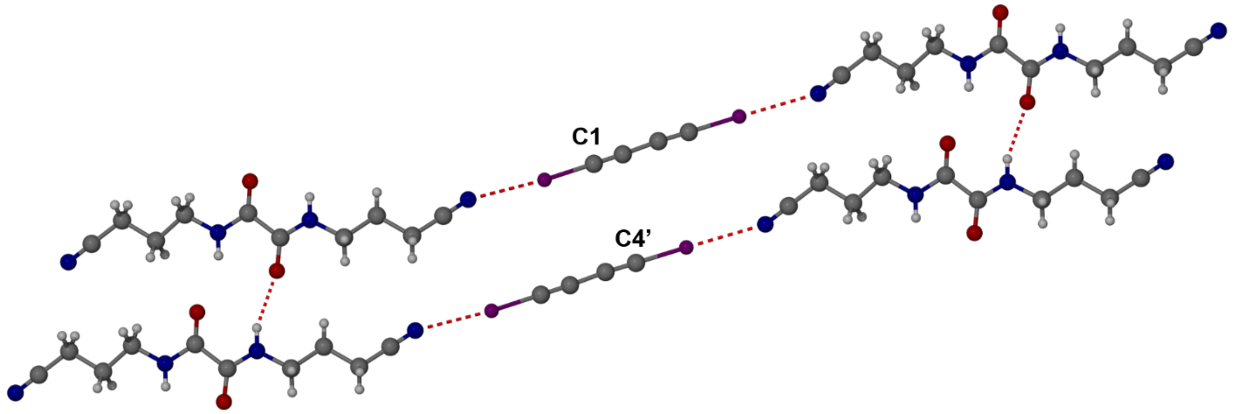


Figure 12. The X-ray structure of N,N'-bis(4-cyanopropyl)oxalamide and 1,4-di-iodobuta-1,3-diyne which does not undergo topochemical polymerization.[54]

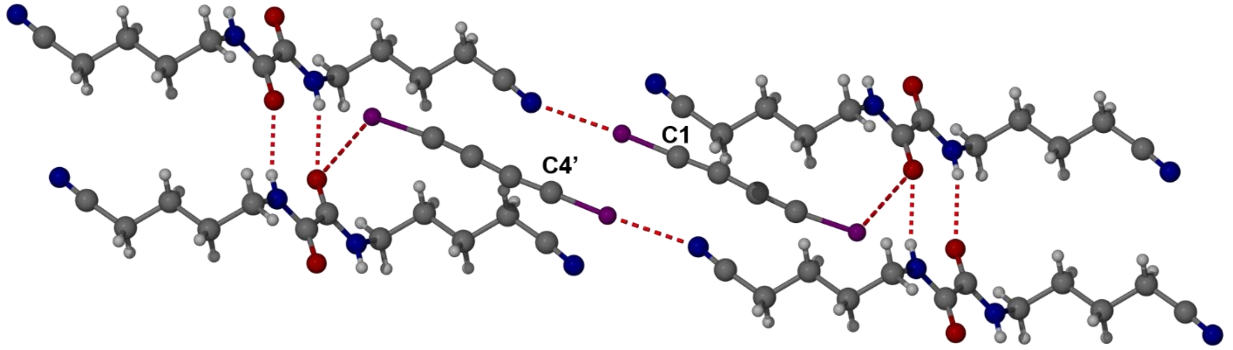


Figure 13. The X-ray structure of N,N’-bis(4-cyanobutyl)oxalamide and 1,4-di-iodobuta-1,3-diyne, which is able to topochemically polymerize.[54]

Diacetylene salts, typically as ammonium salts, have been reported. For example, 1-naphthylmethylammonium octa-2,4-diynoate contains a network of NH···O hydrogen bonds (Figure 14).[56] However this salt does not meet the criteria for topochemical polymerization as the closest inter-alkyne distance is 4.97 Å, the translational distance is 7.72 Å and the tilt angle is only 31°.[56] However, a derivative of this material, 1-naphthylmethylammonium nona-2,4-diynoate, readily undergoes polymerization in the solid-state in response to UV and γ-radiation.[56] The topochemical parameters for this salt are ideal for polymerization as the inter-dialkyne distance is 3.66 Å, the translational distance is 4.88 Å, and the tilt angle is 47°.[56]

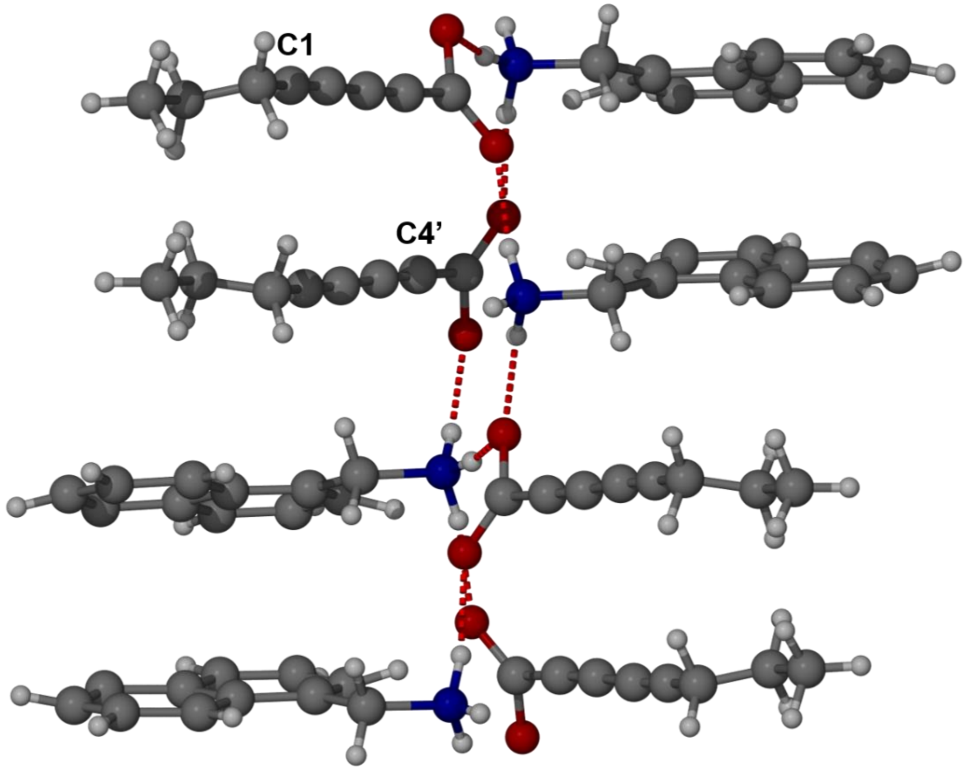


Figure 14. The X-ray structure of 1-naphthylmethylammonium octa-2,4-diynoate.[56]

The solid-state polymerization of 4,4'-butadiynedibenzylammonium disorbate has also been described.[57] [58] However, the diacetylene portion of the salt does not polymerize, rather it is the diene moieties that are separated by 5.33 Å, with a monomer repeat distance of 4.88 Å and a tilt angle of 60 ° that react. These parameters are within the diene reactivity criteria (Figure 15).[57, 59] The X-ray structure of the 4,4'-butadiynedibenzylammonium disorbate polymer shows polymerization of the diene units as expected, with a shortened repeat distance when compared to the monomer, at a distance of 4.82 Å (Figure 16).[57]

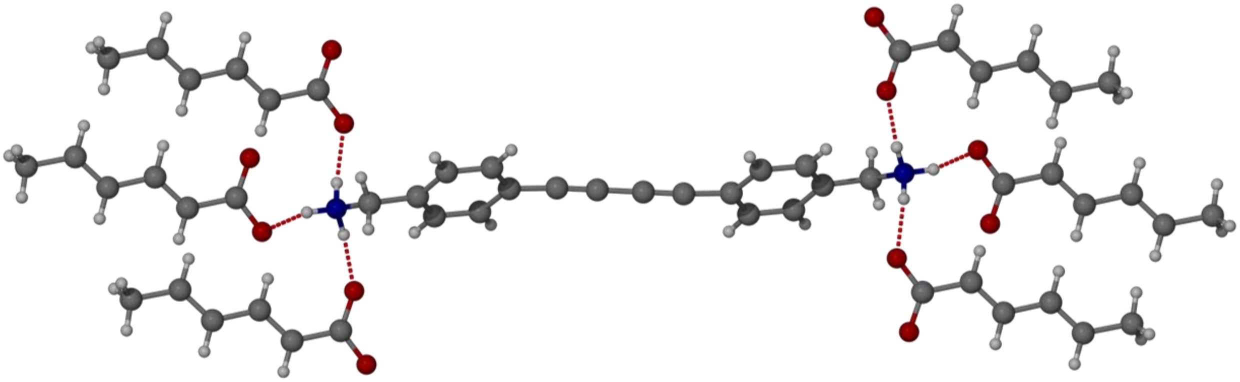


Figure 15. The X-ray structure of 4,4'-butadiynedibenzylammonium disorbate.[57]

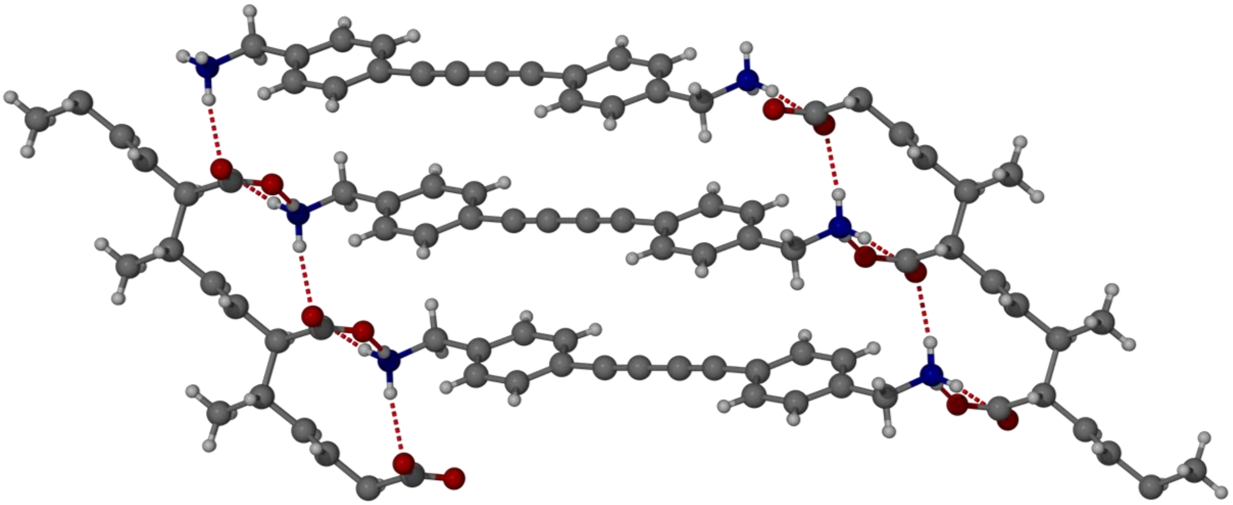


Figure 16. The X-ray structure of poly(4,4'-butadiynedibenzylammonium disorbate).[57]

PCDA Salts and Cocrystals

As PCDA is one of the most commercially used diacetylenes, the X-ray structure of PCDA has only recently been reported,[60] likely due to its known photosensitivity to ionizing radiation. The structure of PCDA centrosymmetric with a head-to-head bilayer arrangement with the alkyl chains adopting an *anti*-conformation (Figure 17).[60] As expected, all three of the topochemical criteria are met, with C1-C4’ distance and translational repeat distance of 3.712(1) Å and 4.574(1) Å, respectively. The tilt angle of the PCDA monomers relative to the translational axis is also within the desired value at 44.7°.[60]

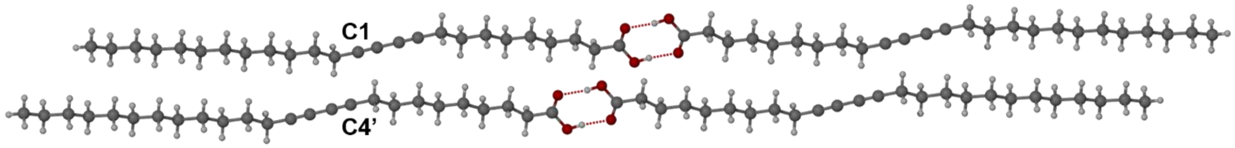


Figure 17. The X-ray structure of photosensitive monomeric PCDA.[60]

The crystal engineering of solid state structures can play a large role in diacetylene reactivity.[61] Salt formation and cocrystallization of pharmaceutical drugs can significantly change their properties,[62] this concept can also be applied to how diacetylenes respond to external stimuli. For instance, salts of PCDA with short-chain amines such as diethylamine and *n*-butylamine, along with a bifunctional linker, 4,4'-bipiperidine, have been studied.[60] The X-ray structure of PCDA-diethylamine reveals a salt cocrystal with an additional neutral molecule of PCDA (Figure 18) and has a C1-C4' inter-alkyne distance of 3.78 Å, a translational repeat distance of 4.64 Å, and a tilt angle of 41.9 ° – all values which are within the postulate for reactivity.[60] Additionally, the structure of PCDA-butylamine shows a simple 1:1 stoichiometry (Figure 19) with a C1-C4' distance of 3.78 Å, a translational repeat distance of 4.59 Å and a tilt angle of 43.7 °, which are all values within the optimum range for reactivity.[60] The 2:1 X-ray structure of PCDA-bipiperidine (Figure 20) has desirable values for the C1-C4' distance (3.76 Å) and the tilt angle (24.1 °) that are within the postulate, however, the translational repeat distance is too large for any photoreactivity to occur at a distance of 5.58 Å.[60] The photoreactivity of PCDA and its powdered salts in response to UV irradiation (254 nm) can be observed in Figure 21. The striking visual differences between the powdered salts further reinforces the importance of the topochemical postulate as a prediction tool for the reactivity of diacetylenes.

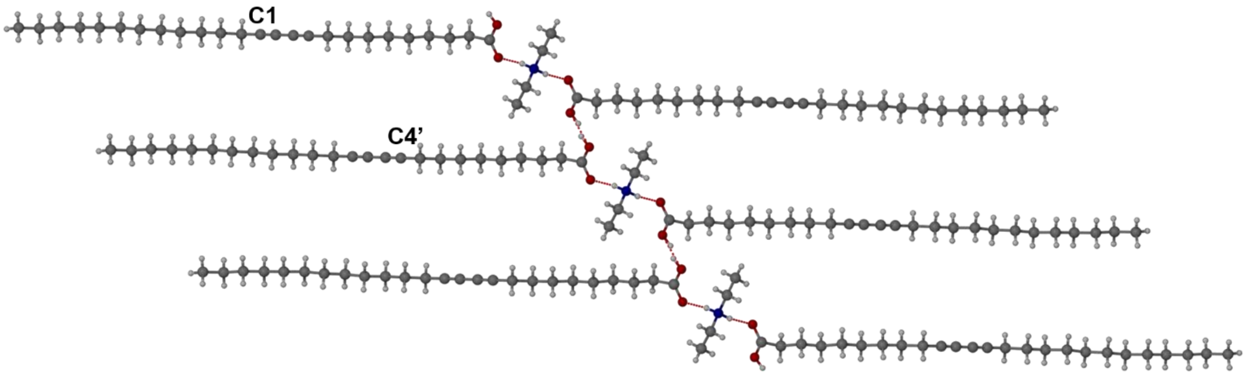


Figure 18. The X-ray structure of a PCDA with a diethylammonium cation and a neutral molecule of PCDA.[60]

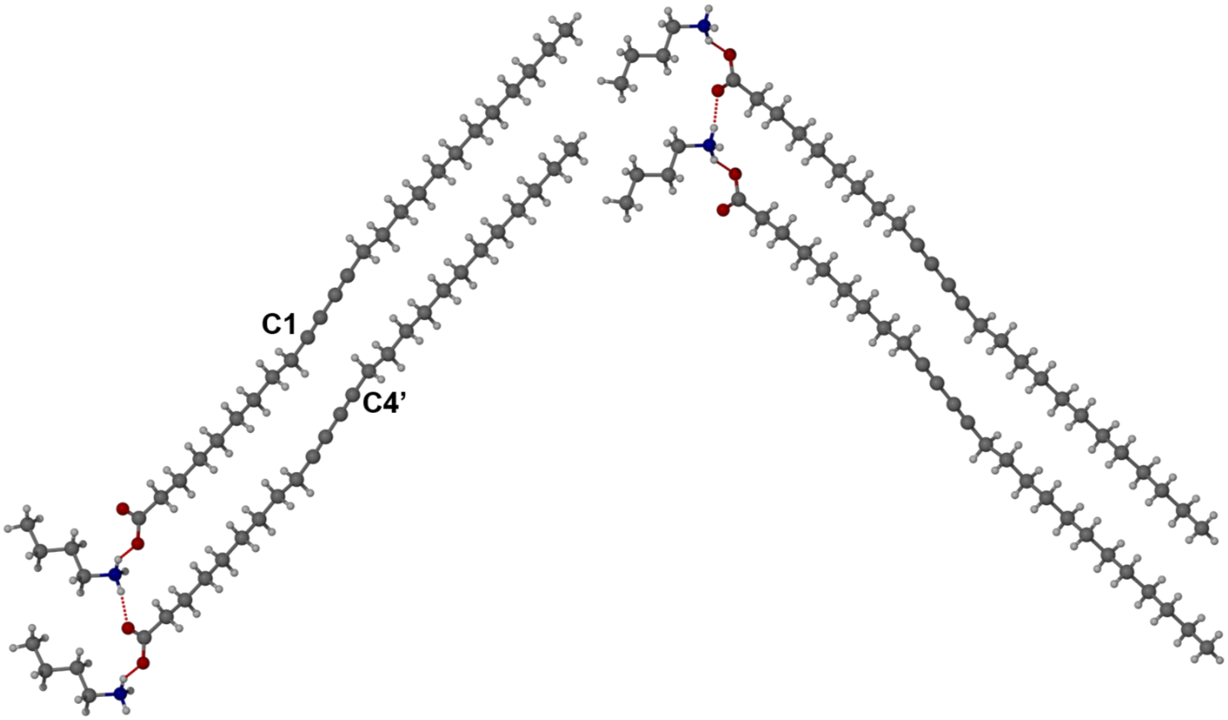


Figure 19. The X-ray structure of a 1:1 PCDA and a butylammonium cation.[60]

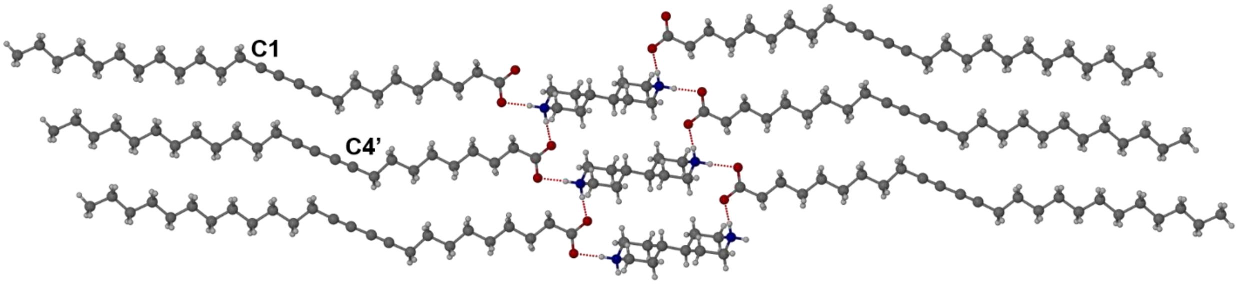


Figure 20. The X-ray structure of a PCDA with a bipiperidinium cation in a 2:1 stoichiometry, respectively.[60]

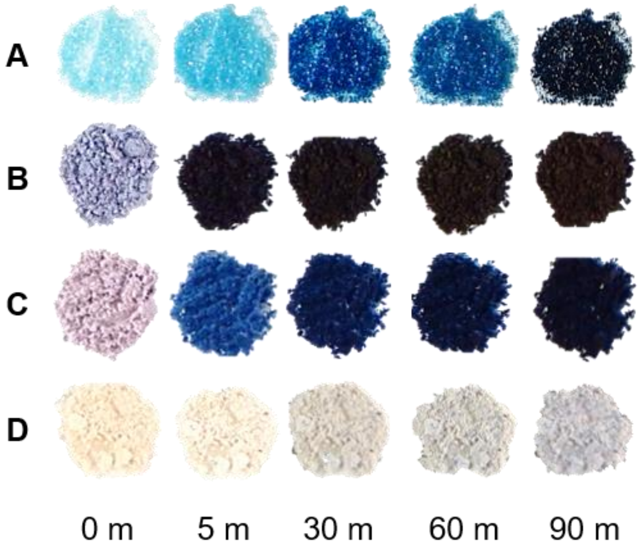


Figure 21. The UV irradiation (254 nm) studies for different durations of A) PCDA, B) PCDA-diethylamine 2:1 salt cocrystal, C) PCDA-butylamine 1:1 salt cocrystal show the darkening of each powder sample with irradiation time, whereas D) the 2:1 salt cocrystal PCDA-bipiperidine only changes slightly due to residual PCDA in the sample. Figure adapted with permission from reference 60.

Metal salts of PCDA are also important in dosimetry, with the lithium salt of PCDA (Li-PCDA) used as the photosensitive component in GAFchromic EBT films. Recently, two solid forms of Li-

PCDA have been discovered – a monohydrate and an anhydrous form.[38] The anhydrous form displays an enhanced photoresponse when compared to the monohydrate, however, the anhydrous form is more difficult to process and so the radiochromic films are based on the monohydrate form of Li-PCDA.[38] Heating the films to 100 °C for one hour can convert the monohydrated form to the anhydrous form.[38] Though no X-ray structures of either Li-PCDA form were obtained, characterization suggests the water molecule is coordinated to the lithium ion in the monohydrate, and both forms have a chelating bridging bidentate coordination mode of the carboxylate ligands.[38] Additionally, the two forms must adhere to the postulate due to their obvious photoreactivity. Another alkali metal salt of PCDA, Na-PCDA, was synthesized by mechanical grinding to give an ionic cocrystal with a formula of $Na^+PCDA^-\cdot 3PCDA$. The PCDA and $PCDA^-$ ligands display monodentate and bridging bidentate coordination to the sodium ion, in contrast to the coordination sphere of the Li-PCDA forms.[38] However, Na-PCDA is photostable in contrast to its lithium analogues as the topochemical parameters do not adhere to the postulate (C1-C4' distance = 4.25 Å, tilt angle = 33.0 °, translational repeat distance = 4.05 Å (Figure 22).[38]

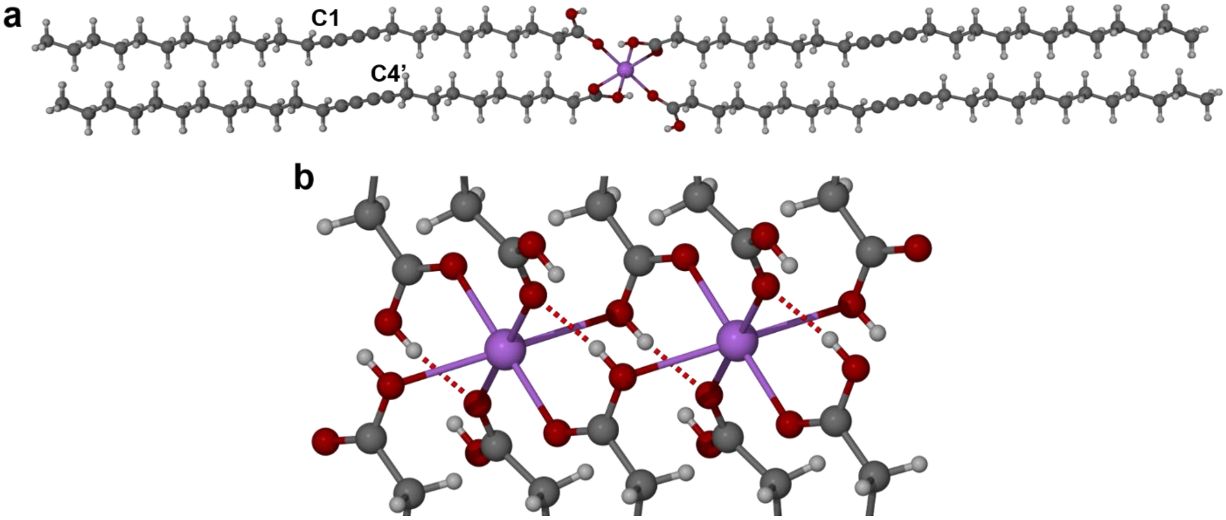


Figure 22. a) The X-ray structure of Na-PCDA. b) An enlarged section of Na-PCDA head groups to show the hydrogen bonds between PCDA acid ligands and the salt ligands (with a disordered proton). Figure adapted from reference 38.

Known PCDA cocrystals include coformers such as 4,4'-azopyridine (Figure 23), 4,4'-bipyridyl, and *trans*-1,2-bis(4-pyridyl)ethylene (Figure 24) have been cocrystallized with PCDA in a 1:2 stoichiometry, respectively.[60] In each case, all three cocrystals have two out of the three ideal parameters for the 1,4-addition polymerization of PCDA. However, as the desired translational repeat distance value is not met for each cocrystal, they are not photoresponsive.[60]

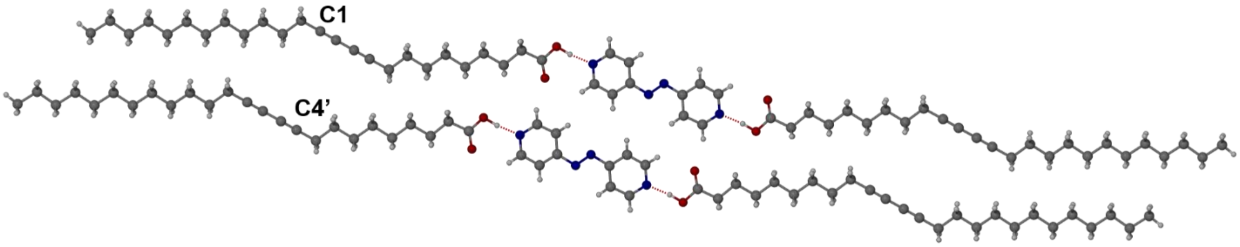


Figure 23. The X-ray structure of PCDA cocrystallized with 4,4'-azopyridine, with the diacetylene portion of the cocrystal adopting an *anti*-conformation, analogous to PCDA itself.[60]

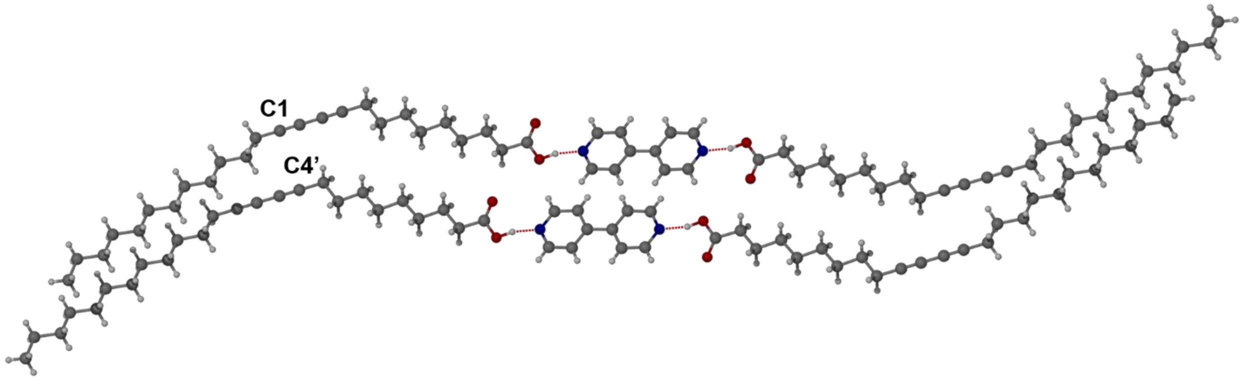


Figure 24. The X-ray structure of PCDA cocrystallized with 4,4'-bipyridyl, which is isostructural to PCDA and *trans*-1,2-bis(4-pyridyl)ethylene. The diacetylene substituents of the cocrystal adopt a *syn*-conformation compared to PCDA-azopyridine and PCDA itself.[60]

Another PCDA cocrystal system involves the successful cocrystallization with melamine (MA).[63] The cocrystals were synthesized in a two-step process involving the co-assembly of PCDA and MA in water by a non-covalently connected micelle method (NCCM), and the annealing of the co-assembly at the melting point of PCDA (approx. 65 °C) for 6 hours but lower than the melting point of the cocrystals (87 °C) (Figure 25).[63] The hydrogen bond in the cocrystal is between the carboxylic acid OH group of PCDA and an amine nitrogen atom of MA, alongsidearomatic stacking that is present between neighboring layers of MA.[63] The presence of numerous noncovalent interactions within the polymerized cocrystal stabilize it and allow for the reversible thermochromism that is displayed when heated from 25 – 90 °C.[63]

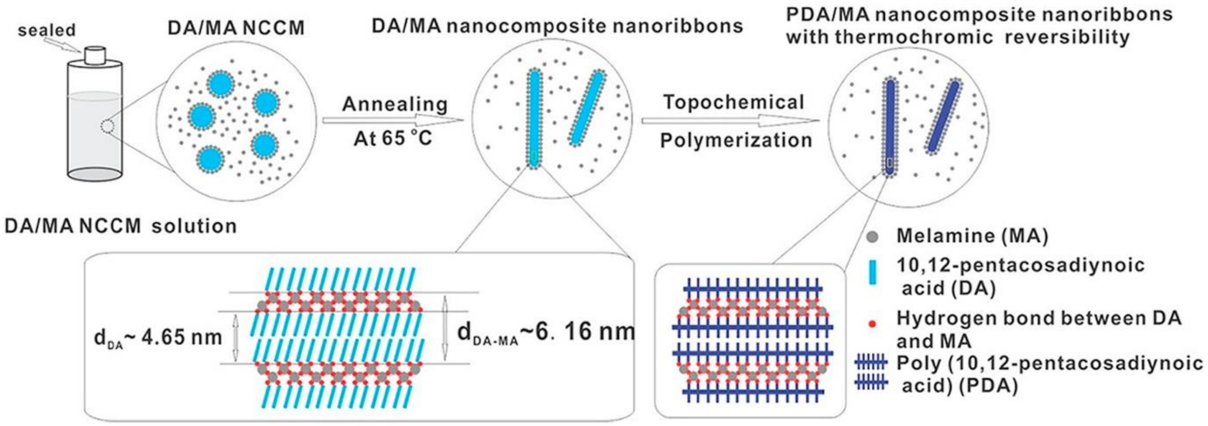


Figure 25. The preparation process for PCDA-MA cocrystals. Reproduced with permission from reference 63.

Optical and Electronic Properties of Polydiacetylenes

The monomer-to-polymer transition of diacetylenes is accompanied by a color change from colorless to blue, due to the formation of a conjugated ene-yne chromophore. The blue color arises from π-π* transitions in the ordered, conjugated chain with the efficiency of the reorganization controlling the degree of polymerization of the diacetylene monomers.[64] The color of the photoproduct can be further influenced by factors such as extended heating, pH change, mechanical stress, ligand-receptor interactions, and treatment with organic solvents. Additional stimuli upon the polydiacetylene applies strain within the structure, causing it to distort and give a blue (absorption maxima ~640 nm) to red (absorption maxima ~500 nm) chromic shift, which correspond to different chain conformations and ordering.[65] The different chain conformations are caused by segmental rearrangement within the polydiacetylene assembly to alleviate strain through rotations around the C-C bonds.[66] These C-C rotations break the planarity of the backbone, which disrupt the delocalization of the π electrons of the conjugated chain, and therefore, reduces the π orbital overlap so that the HOMO-LUMO energy gap is widened to allow the polydiacetylene to absorb light at a higher energy.[67-70] Calculations suggest that a rotation of only 5 degrees is required to change the π orbital overlap and shift the color of the polydiacetylene from blue to red, which correlates to a planar structure adopting a non-planar conformation with rotated and/or distorted side chains.[71-74] Figure 26 shows the chromic properties of the blue-to-red chromic shift in response to a difference in the conjugation of the polydiacetylene chain.[65]

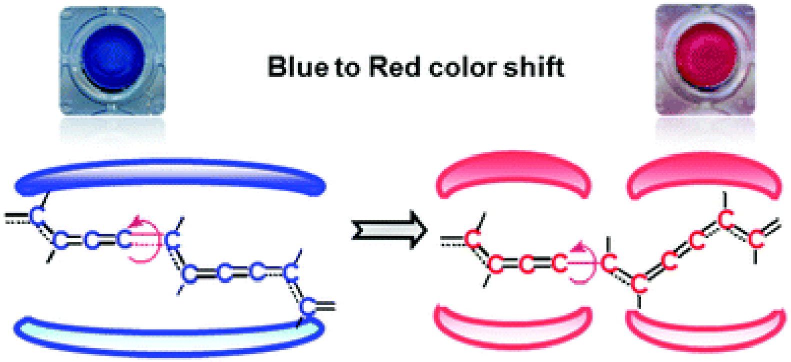


Figure 26. The chromic properties of polydiacetylenes caused by the rotations around the C-C bonds. Reproduced from reference 65.

Understanding the mechanism of the chromic changes of polydiacetylenes is imperative to control polydiacetylene-based colorimetric sensors. The control and interfacial properties of the order-disorder transition of PCDA vesicles when irradiated has been explored, through the adsorption behavior of probe material ((4-(4-diethylaminostyry)-1-methylpyridinium iodide) on the vesicle surface.[75] Surface-specific second harmonic generation and zeta potential measurements show that the order-disorder transition largely involves the gradual distortion of the carboxyl terminated chains driven by backbone perturbation (Figure 27).[75] Additionally, as UV irradiation time increases, the adsorption and chain-chain interactions between the probe molecule and the surface of the vesicles become weaker, resulting in a decrease in adsorption density of the probe molecules as UV irradiation increases.[75] This result suggests that as the duration of UV irradiation increases, structural changes occur that reduce conjugation and the planarity of the polydiacetylene through distorted side chains.

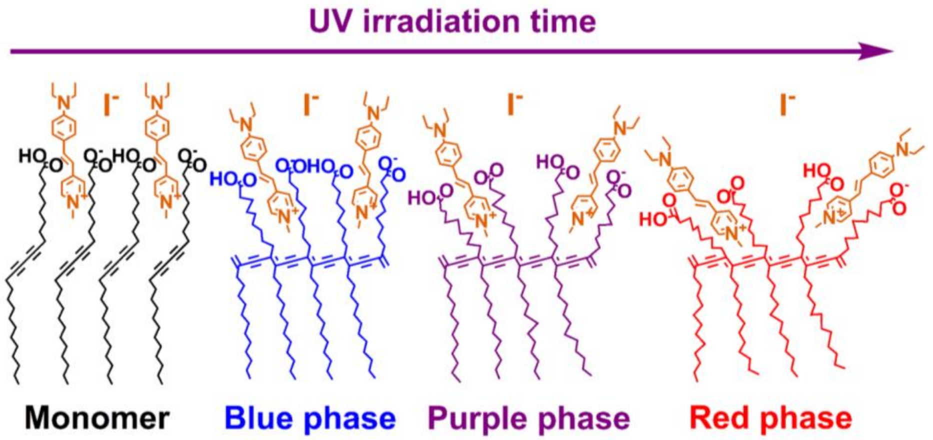


Figure 27. A model illustrating the movement of the carboxyl terminated chains from monomer to polymer forms, in the presence of probe materials on the PCDA vesicle surface. Figure reproduced with permission from reference 75.

The Effect of Extended Heating on PCDA Polymer Properties

Since the first report of the color-changing properties of polydiacetylenes in response to heat in 1976,[76] thermochromism has become an important property for many functional materials, with thermochromic liquid crystals and leuco dyes as some of the more popular examples.[77, 78] Thermochromism in diacetylenes, especially PCDA, has been extensively studied and potential sensing applications include electrothermochromic displays,[79] counterfeiting detection,[80] printable[81] and microfluidic[82] thermal sensors, and smart textiles.[83] PCDA itself exhibits irreversible thermochromism, though if monomeric or polymeric PCDA is modified in any way, this can dramatically influence the color exhibited and the reversibility of its color changes. Vesicles containing only polymeric PCDA were heated to above 55 °C, an absorption band at approx. 540 nm (red) grows while the band at approx. 620 nm (blue) simultaneously decreases.[84] When the PCDA vesicles were heated to around 65 °C, only the red species is observed (Figure 28).[84, 85] The thermochromic transition temperatures of polymeric PCDA are very close to the melting temperature of monomeric PCDA, which is also around 65 °C.[84]

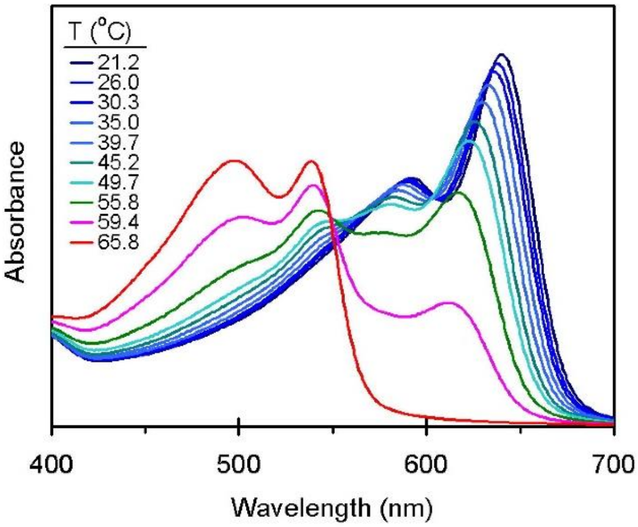


Figure 28. The UV-Vis absorbance spectra of PCDA heated from 21.2 – 65.8 °C. Figure reproduced with permission from reference 84.

An example of the thermochromic properties of PCDA changing when in a modified environment is illustrated in a study involving the nanocomposites of PCDA intercalated with low molecular weight (10,000 g/mol) polyvinylpyrrolidone (PVP).[86] This nanocomposite system provides a reversible blue-to-purple color change up to temperatures of 90 °C, with the color transition occurring at around 85 °C.[86] The PCDA color transition temperature is high compared to polydiacetylenes with shorter alkyl chains to PCDA, which illustrates greater interactions within the PCDA nanocomposite system.[84, 86, 87] Similar results were found in films of PCDA and PVP that were heated to temperatures of 30, 50, 65 and 85 °C.[88] Differential scanning calorimetry (DSC) thermograms of the heated films suggest that the films do not display reversible thermochromism as PCDA is unable to reach its melting point (~ 65 °C) and diffuse into the surrounding PVP chains. However, the film heated to 65 °C has a high melting point of 75 °C and exhibits reversible thermochromism due to the intercalation of PCDA and PVP by hydrogen bonding in a "bricks and mortar" fashion (Figure 29). Surprisingly, the film heated to 85 °C melts at only 47 °C which suggests poor crystalline packing and an insight into its lack of its photoreactivity, as the 85 °C heated film was unresponsive to 254 nm of UV exposure, unlike the other films which polymerized without resistance.[88]

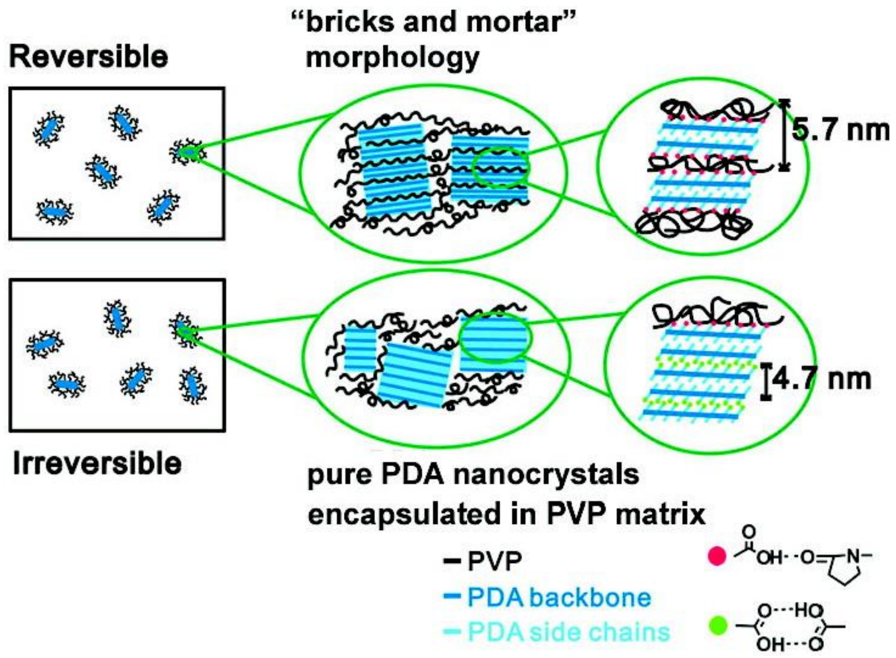


Figure 29. An illustration of the "bricks and mortar" analogy to explain the differences between reversible and irreversible thermochromism shown by films of PCDA and PVP. Polydiacetylene is abbreviated to 'PDA'. Reprinted with permission from reference 88.

Changes in the environment of PCDA also alters its thermochromic behavior. The color-change properties of films consisting of layers of PCDA monomer crystals intercalated with metals ions, in response to heating and cooling studies has been explored.[89] When the films were heated to 60

°C, thermal motion of the alkyl portion of PCDA is observed, regardless of the type of guest used.[89] However, when further heat (150 °C and 200 °C) is applied to the PCDA films containing divalent nickel and zinc respectively, a range of colors are observed, from an irreversible blue-to-yellow thermochromism with films of PCDA-Ni^{2+} (Figure 30c), and a reversible blue-to-purple-to-red thermochromism exhibited by PCDA-Zn^{2+} (Figure 30d).[89]

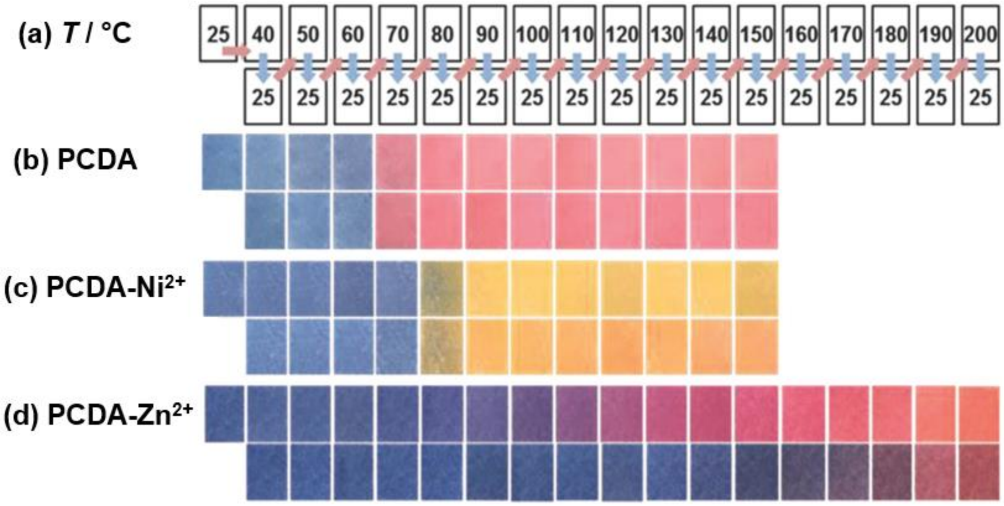


Figure 30. The temperature control (a) of the temperature-induced color changes of films containing PCDA (a color transition temperature (T_{trs}) of 65.4 °C) (b) and PCDA-Ni^{2+} from 25 °C – 150 °C (T_{trs} 77.9°C) (c), and PCDA-Zn^{2+} from 25 °C – 200 °C (T_{trs} 113.7 °C) (d). Figure adapted with permission from reference 89.

In situ X-ray diffraction (XRD) measurements were undertaken to assess the differences in crystallinity of the metal ion films before and after heat treatment. The XRD patterns of PCDA-Ni^{2+} changed considerably when heated above 100 °C and the original pattern could not be obtained on cooling, suggesting a strong link between visual irreversible thermochromism and the internal structure of the film.[89] In contrast, PCDA-Zn^{2+} visually exhibits reversible thermochromism, and the *in situ* XRD pattern displays no differences before and after heating, suggesting that the internal structure has not become strained to a high degree and subsequently allows for the electronic properties of the polydiacetylene backbone to be regained.[89] In summary, the XRD experiments reveal that the PCDA films with intercalated metal ions within the layers change in three stages. Firstly, in both PCDA-Ni^{2+} and PCDA-Zn^{2+}, there is evidence of the thermal motion of the alkyl chains when the films are heated to 60 °C. Secondly only the PCDA-Zn^{2+} film displays torsion of the polydiacetylene backbone to show a color change above 100 °C. Finally both PCDA-Ni^{2+} and PCDA-Zn^{2+} films become deformed with conformational changes, resulting in a lower crystallinity when heated to above 140 °C.[89] The differences in the behavior of the two films can be attributed to the different metal ions present between the organic layers changing the behavior of PCDA through the rigidity of the ions in the layered structure.[89] Additional work on PCDA films involves the effect of PCDA derivatives on their thermochromic properties.[67] By incorporating aromatic head groups to PCDA such as the 3-aminobenzoic acid derivative (PCDA-mBzA) and 6-amino-2-naphthoic acid compound (PCDA-NPA), the polydiacetylenes exhibit reversible thermochromism rather than the typical observed irreversible process.[67] The increasing size of the PCDA derivatives also affects how the monomers pack in the solid state, and as a result, their color and the response time of the film to heat.[67] The morphology of the polydiacetylenes also changes with the different head groups. When PCDA is structured as a vesicle, it obtains a spherical morphology, while PCDA-mBzA exhibits large rod-like shape assemblies (suggesting high molecular order), in contrast to PCDA-NPA which exists in large irregularly shaped particles.[67] These findings suggest that an increase in the head group size changes the packing parameter of the surfactant molecules, which dictates the morphology of polydiacetylene assemblies.[67, 90] The addition of aromatic groups to PCDA enhances the inter- and intramolecular interactions between polymerized layers to allow reversible thermochromism up to temperatures of 220 °C for PCDA-mBzA and 180 °C for PCDA-NPA, with polydiacetylene films ranging in color from blue, to purple, to red, until the films become yellow and exhibit irreversible thermochromism at higher temperatures (230 °C for PCDA-mBzA and 190 °C for PCDA-NPA).[67] It was also found that dried films containing the different polydiacetylenes gave an enhanced colorimetric response compared to the same polydiacetylenes suspended in aqueous solution.[67]

The Importance of Hydrogen Bonds in Reversible Thermochromism

The process of reversible thermochromism is largely dependent on non-covalent interactions, such as hydrogen bonding, van der Waals forces, and π-π stacking.[42, 91-94] However, hydrogen bond interactions are the strongest and most important type of non-covalent interaction for thermochromic reversibility, as they allow the material to exhibit reversible thermochromism in a wider temperature range.[95-97] Monomeric PCDA displays irreversible thermochromism at temperatures above 65 °C due to the increased thermal motion and consequent weakening of the hydrogen bond as temperature increases. Modification of the PCDA carboxylic acid head group can result in reversibility as a result of enhanced hydrogen bonding interactions by incorporating amine groups or changing the position of the carboxylic acid group on an aromatic ring to allow for intermolecular hydrogen bonding.[42, 67, 94, 98] A study involving vesicles containing polymeric PCDA derivatives prove that hydrogen bonding is important for thermochromic reversibility and exhibits blue-red and red-blue color transitions.[98] The PCDA derivative that exhibited the strongest reversibility to 100 °C heat for three minutes in this study was a diacetylene with a terminal 3-aminobenzoic acid (mBzA) group. The link between hydrogen bonding and reversible thermochromism exists due to strong head group interactions reducing the strain on the conjugated backbone when exposed to heat, which ultimately prevents the permanent distortion of the chain when the polydiacetylene is cooled.[99] Figure 31 illustrates the *π-π* stacking and carboxylic acid and amide hydrogen bonding in PCDA-mBzA that allow the polydiacetylene to adopt its original blue coloration before heat treatment.[95] Although PCDA-mBzA shows thermochromic reversibility when compared to PCDA, the mBzA derivative of another diacetylene, 10,12-tricosadiynoic acid (TCDA) displayed enhanced reversibility when compared to PCDA-mBzA.[95]

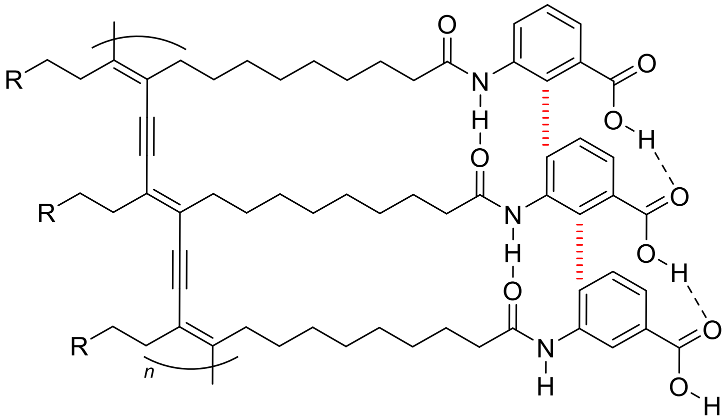


Figure 31. The intermolecular forces of PCDA-mBzA. Black dashed lines indicate hydrogen bonding, while red hashed lines indicate π-π stacking. R = $C_{12}H_{26}$.

Another study focusing on the thermochromic reversibility of PCDA-mBzA also investigated the importance of hydrogen bonds in the PCDA-mBzA films upon heating by the adsorption and desorption of cadmium(II) ions.[100] The adsorption of Cd^{2+} onto the film surface breaks the outer carboxylic O-H···O hydrogen bonds while keeping the amide N-H···O hydrogen bonds intact.[100] The removal of the carboxylic hydrogen bonds is due to the formation of a carboxylate salt of PCDA-mBzA which results in the film displaying irreversible thermochromism.[100] The desorption of Cd^{2+} allows the PCDA-mBzA film to partially regain its thermochromic reversibility through the recovery of the carboxyl hydrogen bonds, which is displayed by a visible blue-to-red transition upon heating and a red-to-blue transition on cooling.[100] Therefore, the use of metal ions in polydiacetylene films is a useful way to adjust the thermochromic properties for the required application.

A well-known class of molecules known for their hydrogen bond forming capabilities are ureas, and when incorporated into a PCDA analogue, 10,12-docosadiynoic acid (DCDA) are able to provide excellent reversible thermochromic properties up to temperatures of 200 °C when appended with hydrophilic polyethyleneglycidyl moieties (Figure 32).[81] The reason for the impressive thermoreversibility is due to the bisurea tape formation that forms hydrogen-bonded networks throughout the polydiacetylene.[81] The substituted DCDA monomer can be transferred to paper substrates as ink and will photopolymerize from clear to blue when irradiated. Moreover the system exhibits a range of colors from blue, purple, red and yellow upon heating to different temperatures.[81] A system with PCDA and a combined acetylurea group displays thermochromic reversibility up to temperatures of 150 °C.[101] The melting temperature of the polydiacetylene plays a large role in the thermochromic reversibility. In reversible thermochromic systems, if the sample is heated to greater than its melting temperature, then it is likely that the transition from reversible to irreversible thermochromism will occur.[101, 102]

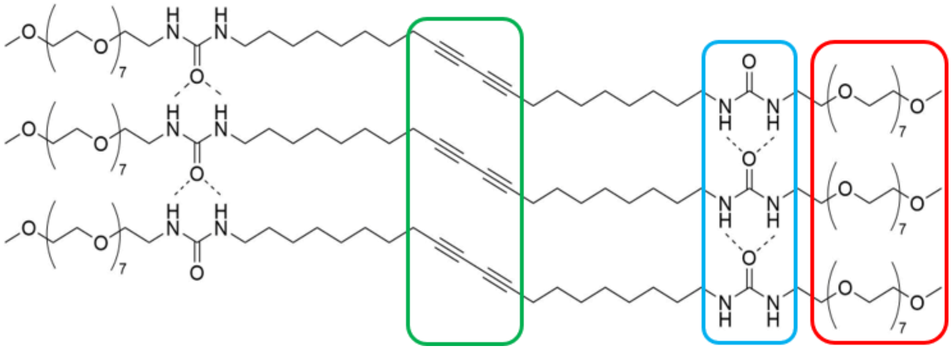


Figure 32. The hydrogen bonded networks of a DCDA urea PEG derivative. The green box shows the region responsible for polymerization, while the urea tapes in the blue box enhances self-assembly, and the region in the red box increases the water compatibility of the molecule.

Thermochromism has also been observed in conductive fibers comprised of aligned carbon nanotubes dip-coated with a PCDA derivative and an attached alternating glycine-alanine peptide segment with a terminal tyrosine group (GAGAGAGY; Figure 33).[103] However, unlike most thermochromic studies with PCDA, the apparent thermochromism was not observed by direct heat, but through the application of electrical current to the fibres.[103] Milliseconds after the application of the electric current, a blue-to-red color change was observed and then a red-to-purple transition. The response time of the fiber is correlated with the applied current.[103] Upon cooling for only 20 seconds, the fibers returned to their original blue color, and even after 1000 cycles of current, scanning electron microscopy revealed that the fibers remained unchanged.[103] The impressive reversible thermochromism of the fibers are due to the multiple hydrogen bonds that are able to form from the peptide portion of the polydiacetylene between adjacent molecules.[103]

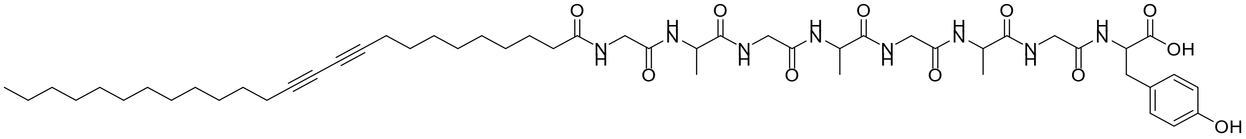


Figure 33. The molecular structure of monomeric PCDA modified with a peptide sequence.

Thermochromism has also been recognized in cyclic dipeptides (CDP) containing a PCDA derivative in which the PCDA is covalently bonded to (3*S*)-3-(hydroxymethyl)-piperazine-2 5-dione *via* an ester linkage.[104] The CDPs have a *cis*-amide functionality consisting of two hydrogen bonding acceptors and donors which allows for strong intermolecular bonding with adjacent CDPs.[104] Additionally, the chiral center of the head group allows helical packing to self-assemble into bilayers which transform into either single-wall or multiwall structures (Figure 34).[104] These hydrogen-bonded supramolecular assemblies exhibit blue-to-red reversible thermochromism even after ten consecutive heat cycles from 25 – 90 °C, thereby adding to the list of thermally responsive functional materials that contain PCDA.[104]

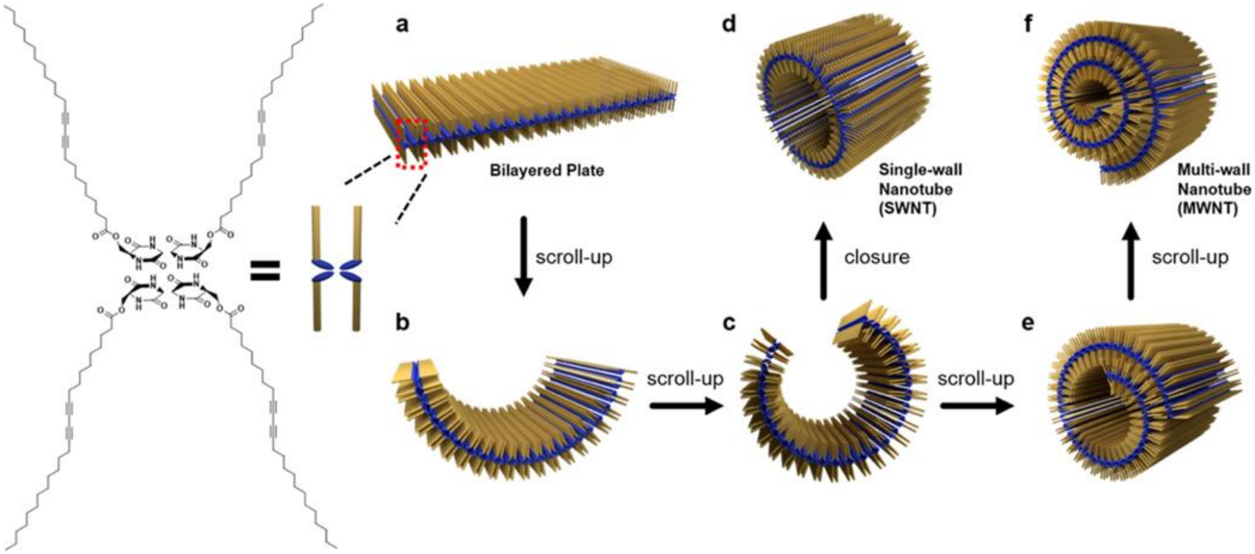


Figure 34. The self-assembly of CDP-PCDA nanotubes into bilayers leading to tubular structures of either single wall structures or multi-wall nanotubes. Reprinted with permission from 104.

The Effect of pH on PCDA Polymer Properties

The stability of PCDA films in response to pH changes can be modified, depending on the temperature at which the film was polymerized. Research into multi-layered Langmuir-Schaefer films of polymerized PCDA have been prepared at the air/water interface by irradiation with 254 nm UV radiation at 25 °C and 50 °C.[105] The polymerized films were treated with different pH levels ranging from pH 2-11, to investigate the chromic stability (blue-to-red transition) of the films in response to a change in pH.[105] The results show that the PCDA films polymerized at 50 °C display considerable chromatic stability against pH changes, when compared to the 25 °C film equivalent, which was shown to be more sensitive to external stimuli due to its shorter intermolecular packing distance.[105] In contrast to polymerized PCDA films, polymerized PCDA vesicles also change color with increasing pH.[105] At pH 4 – 8.8, the carboxylic acid protons of

PCDA are deprotonated, which causes the breakage of the hydrogen bonds at the vesicle surface and allows a partial rearrangement of the polydiacetylene segments.[105] This partial rearrangement is accompanied by growth in the absorbance spectra at 650 nm to observe a blue color.[105] At pH 8.9-10, the absorption spectra display a sharp increase at 500 nm, to exhibit a blue to red color transition. The red phase is due to a segmental rearrangement in the entire polymerized PCDA vesicles, opposed to only partial rearrangement at pH 4-8.8.[84] Additional work on the effect of pH on PCDA vesicles involves synthesizing PCDA with a 1,4-bis(octyloxy)-2,3-diaminobenzene headgroup.[15] When the vesicle was irradiated, the color changed from blue to red, and exhibited an irreversible red-yellow transition when exposed to a pH of 1. No colorimetric change occurred when the PCDA derivative was further exposed to a pH range of 2-13.[15]

An interesting application of the colorimetric response of PCDA to pH changes is the detection of *Escherichia coli* bacteria through electrospun fibers containing polymerized PCDA and a supporting polymer, either poly(ethylene oxide) (PEO) or polyurethane (PU).[106, 107] PCDA and polymer fiber composites that are blue in color were immersed in *E. coli* culture and instantly changed from blue to red, indicating that the proteins secreted by the bacteria initiated the color change.[108] There is also a positive correlation between a clearer color change of the fibers and the increasing pH and concentration of bacteria, due to the concentration of the hydroxide ion at pH 11-13, which disrupts the hydrogen bonding of the polydiacetylene head groups. This colorimetric sensing system has the capabilities to be applied to medical textiles such as wound dressings and bandages to detect the presence of *E. coli*.[106] Also, a polydiacetylene-pH sensing system has been developed for the detection of the virulence-factor enzyme urease.[109] Ureolytic activity is catalyzed by urease and is used in the diagnosis of a *Helicobacter sp.* infection,[110] and so a pH-sensitive colorimetric system has been designed for urease sensing, through the use of polymeric PCDA vesicles in different solutions.[109] As the pH increased, the PCDA vesicles gradually changed from blue, to purple, to red, with each color indicating a specific pH value (blue = pH < 7, purple = pH of 7.5-8, red = pH of > 8.5). The color transitions corresponding to the level of deprotonation of the polydiacetylene vesicles in basic solutions, which is also enhanced formation of ammonia in the urease-catalyzed hydrolysis of urea, which increases the pH of the system.[109] The concentration of alkali ions can also be determined by polymerized PCDA when it is combined with nanoporous rice husk silica to form a pH indicator with a sensitivity that can detect alkali ions at concentrations less than 122 μM, and is able to distinguish pH ranges from pH 9.9 to pH 11.4.[111] When this nanocomposite material is coated onto paper for mobile purposes, it forms the basis of a convenient colorimetric detector that changes color in the presence of OH^- ions from blue-to-red (Figure 35).[111] The paper detector is quick and simple to use, making the pH sensor useful for a primary water testing kit for relevant applications, with future work on amending the paper detectors so they are capable of detecting specific heavy metals.[111]

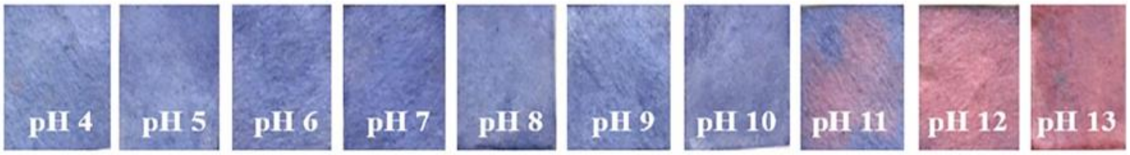


Figure 35. The color change of the paper pH-sensor as the alkali concentration increases. Figure reproduced with permission from reference 111.

The Effect of Organic Solvents on PCDA Polymer Properties

Many different approaches have been used to demonstrate that PCDA is capable of recognizing various organic solvents, with some systems able to specifically identify individual solvents.[112, 113] Solvatochromic materials have been developed that are able to distinguish between different organic solvents, mainly through the use of polymer films.[114, 115] Sensors have been designed to consist of hydrogen-bonded alternating layers of polystyrene, a mixture of poly(4-vinylpyridine) and PCDA which are transparent until exposed to UV radiation, and subsequently become blue.[115] Upon the addition of tetrahydrofuran, dichloromethane, chloroform, ethyl acetate, or toluene, the film elicits a blue-to-red transition along with the generation of fluorescence, while acetone, ethanol, isopropanol, and hexane have no effect on the PCDA/copolymer film.[115] These results suggest that the solvents have a weak affinity for the polystyrene layer of the film which results in the inability to penetrate the PCDA layer and therefore, the failure to interact and change color or generate fluorescence (Figure 36).[115] The ability of the PCDA/copolymer films to change color to specific solvents makes for a simple but effective solvatochromic and fluorescence sensor.

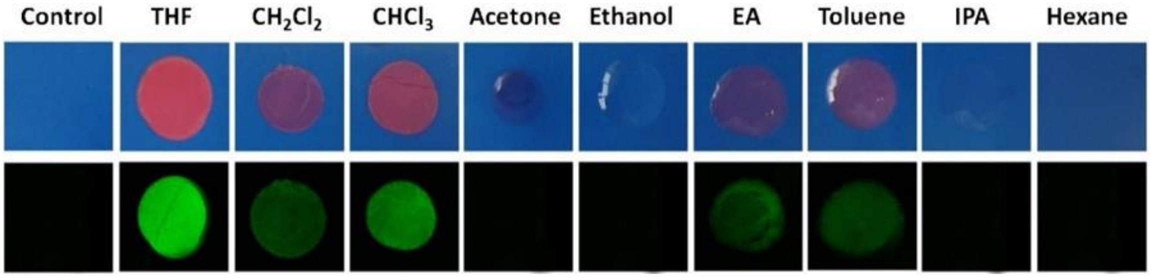


Figure 36. Images of different solvents on the PCDA/copolymer films (top) and their fluorescent microscopy images (bottom), reproduced with permission from reference 115.

Interaction of linear alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol) with polymerized PCDA vesicles shows a typical blue-to-red color transition after exposure, though the longer the alkyl length of the alcohol, the greater the colorimetric response.[116] This is due to the swelling of the alcohols into the inner layers of the vesicles which weakens the hydrogen bond interactions and results in the rearrangement of the PCDA side chains and conjugated backbone to absorb different wavelengths of light.[116] The polarity of the alcohol also plays an important part in the penetration ability to the inner layers of the polydiacetylene vesicles, as a less polar alcohol promotes the penetration into the hydrophobic layer of the vesicle, thus, induces a color transition easier than solvents of higher polarity.[116] The degree of penetration of the solvent is also influenced by the position of the –OH group within the alcohol molecule; a higher concentration of 2-propanol is required to induce a color transition, compared to 1-propanol, and branched alcohols result in a steric effect that hinders the penetration of the polydiacetylene vesicle.[116] However, when PCDA is modified with an ethylenediamine head group, the polydiacetylene is able to distinguish between 1-propanol and 2-propanol, or 1-propanol and ethanol, which provides an important structure-specific insight into the chemical sensing properties of polydiacetylene-based materials.[116] The presence of ethanol to PCDA vesicles results in swelling and increases in size with increasing ethanol concentrations.[117] The swelling of the vesicle results in the hydrogen bonds between the PCDA head groups breaking and weakens the dispersion interactions between the polydiacetylene side chains.[84] Low concentrations of ethanol do not result in a typical blue-to-red color change, however, when the ethanol concentration is 60 % v/v or above, the color transition occurs. This result suggests that a high degree of ethanol penetration is required to overcome the interactions of the PCDA head groups and side chains to yield segmental rearrangement of the chains.[84] A similar result was also found with acetone.[118]

An investigation of the behavior of polymerized PCDA and PCDA derivatives in vesicles in water *vs*. heavy water produces interesting results.[119] PCDA derivatives include 2-(2-aminoethoxyl)ethanol (HEEPCDA) and *p*-phenylenediamine (APPCDA) which are attached to the carboxylic acid group of PCDA (Figure 37).[119] For PCDA, there is no difference to the thermochromic properties in D_2O or H_2O as the color of the vesicles remain red and does not revert to the initial blue coloration on cooling, opposed to HEEPCDA that shows reversible thermochromism with D_2O but not in H_2O in the temperature range of 25 - 70 °C.[119] The preference of HEEPCDA for D_2O in the color reversibility may be due to stronger hydrogen bond interactions present with D_2O than in H_2O.[119] For the case of vesicles of APPCDA, the vesicles are thermochromically reversible in H_2O but not in D_2O from 25 - 90 °C, which is the opposite behavior to that observed for HEEPCDA. For APPCDA, the greater number of non-covalent interactions contributes to the reversibility of APPCDA to heating and cooling cycles.[119] Therefore, it is important what solvent is used in PCDA systems as a small change in the molecular composition of solvent can have vast changes in the observed chromic properties of the system.

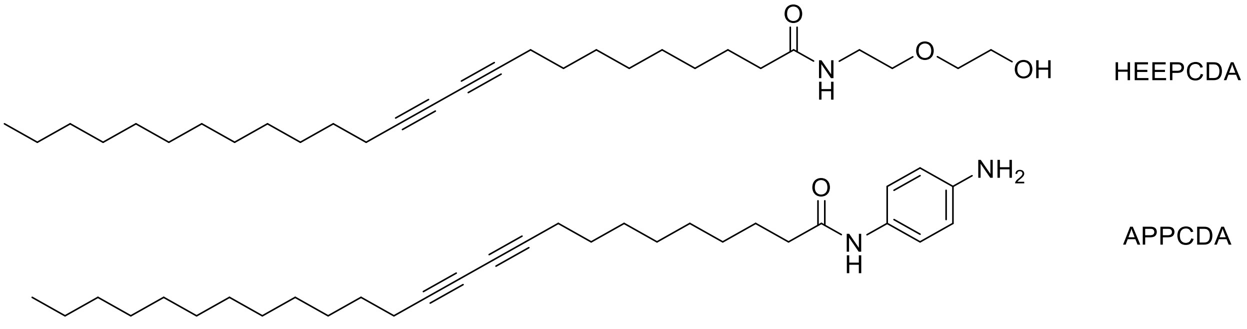
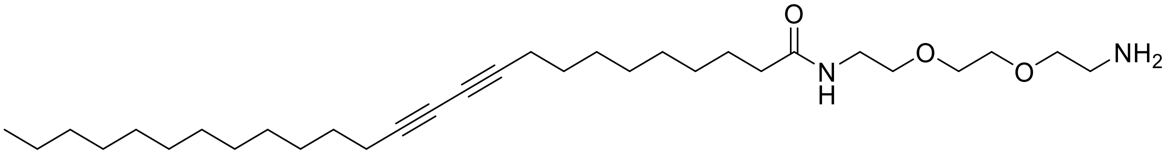


Figure 37. Structures of PCDA derivatives, HEEPCDA and APPCDA.

The Effect of Metal Ions on PCDA Polymer Properties

Materials containing PCDA and PCDA derivatives have been successful at the detection of different metal ions including alkali metals (lithium,[120] sodium,[121, 122] and caesium[123, 124]), transition metals (chromium(III),[125] manganese(II),[126] nickel(II),[127] copper(II),[127] zinc(II),[127-136] silver(I),[126, 137] cadmium(II),[100, 126, 138] iridium(III),[139] gold(III),[140] mercury(II),[125, 126, 141]) and post-transition metals and metalloids (aluminum(III),[125] arsenic(III),[125, 141] tin(IV),[125] and lead(II)[125, 137, 142-144]), and the lanthanide element terbium(III).[145, 146] Many PCDA systems incorporating metal ions exhibit reversible thermochromism due to the enhanced electrostatic interactions between the cations and the carboxylate head group of PCDA, allowing the structural recovery of the conjugated backbone after the heat stimulus is removed.[129] Nanocomposites comprising of the intercalation of zinc oxide nanoparticles into PCDA assemblies have been studied by powder X-ray diffraction to investigate the effect of metal ions on the interlamellar *d*-spacing of PCDA.[129] The interlamellar *d*-spacing of polymerized PCDA itself in the blue phase is 4.50 nm compared to 4.45 nm in the red phase (achieved by annealing the nanocomposites to 200 °C), however, when ZnO is incorporated into the PCDA assemblies, the blue phase *d*-spacing increases to 5.22 nm and the red phase of the nanocomposite has an interlamellar *d*-spacing of 5.54 nm.[129] Therefore suggesting that when the PCDA-ZnO nanocomposites are heated, the PCDA polymer side chains rearrange to incorporate the strain on the system.[129] Additional work on PCDA-Zn(II) nanocomposites includes the behavior of monocarboxylic polydiacetylenes with different alkyl chain lengths, with the polydiacetylenes nanocomposites combined with zinc(II) ions and zinc oxide.[130, 147, 148] Shortening the length of the alkyl chain and the alkyl segment between the reactive alkyne moiety and the carboxyl head group in these nanocomposites drastically changes and their color transition properties when heated, even though all polydiacetylene nanocomposites in this study exhibit reversible thermochromism.[130] When only the terminal alkyl chain is shortened by two methylene units, the color-transition temperature of blue-to-purple is reduced by approximately 20 °C due to the weakening of dispersion interactions in the polydiacetylene nanocomposite layers.[84, 130] However, when the alkyl segment adjacent to the carboxyl head group is reduced, the color-changing temperature trend is unpredictable in the Zn(II)/ZnO nanocomposites.[130]

Iridium complexes situated on the surface of PCDA vesicles are able to provide long fluorescence lifetime properties and when combined with a polydiacetylene, can also exhibit responsive blue-red properties.[139] Polymerized PCDA itself is fluorescent, though only in the red form, while the blue polymer form is non-emissive.[140, 149] The PCDA vesicles modulate the emission properties of the iridium complex through the blue-to-red color transition, which enhances the fluorescence lifetime of the polydiacetylene system and allows a simpler way to spectrally differentiate the blue and red phases of the PCDA vesicles.[139] The fluorescence properties of PCDA can also be changed by heat. A structurally modified polymerized PCDA derivative, PCDA-EDEA that was blue in coloration and was placed in a microfluidic temperature sensor and was heated until the polydiacetylene became red and emitted fluorescence (Figure 38).[82] It was observed that the fluorescence of the red phase became more intense with increasing temperature (40-60 °C) until the polydiacetylene is exposed to excessive heat (70-78 °C), where the fluorescence is then quenched and cannot be reversed.[82, 85] The sensing properties of PCDA vesicles have also been explored with the lanthanides, specifically though the use of PCDA-functionalized thiacalix[4]arene vesicles.[150] Calixarenes are three-dimensional host molecules that can be easily modified to act as supramolecular receptors for molecular recognition and sensing applications. In this case, the calixarene-PCDA vesicles display a colorimetric response to metal ions in the lanthanide series of elements (with a 10 mol % content of calixarene), with an enhanced blue-to-red color change influenced by lanthanum(III) ions in particular. The transition is not observed when the two components are individually exposed to lanthanide ions.[150] The structure of the functional thiacalix[4]arene-PCDA vesicles are shown in Figure 39, with the PCDA-**1** combination displaying an increased colorimetric response to lanthanum(III) when compared to PCDA-**2**.[150] The color transition of the vesicles when in contact with lanthanide ions is due to the distortion of the calixarene cavity which ultimately disturbs the polydiacetylene backbone, alongside metal-induced aggregation and sedimentation of the vesicles.[150] An additional lanthanide ion that has been used in combination with PCDA is terbium(III) with bilayers of PCDA intercalated with terbium(III) ions positioned at the carboxyl head group of PCDA.[146] The nanosheets of PCDA-Tb(III) exhibited reversible thermochromism and reversible fluorescence up to temperatures of 90 °C.[146]



PCDA-EDEA

Figure 38. Structure of the PCDA diacetylene derivative, PCDA-EDEA.

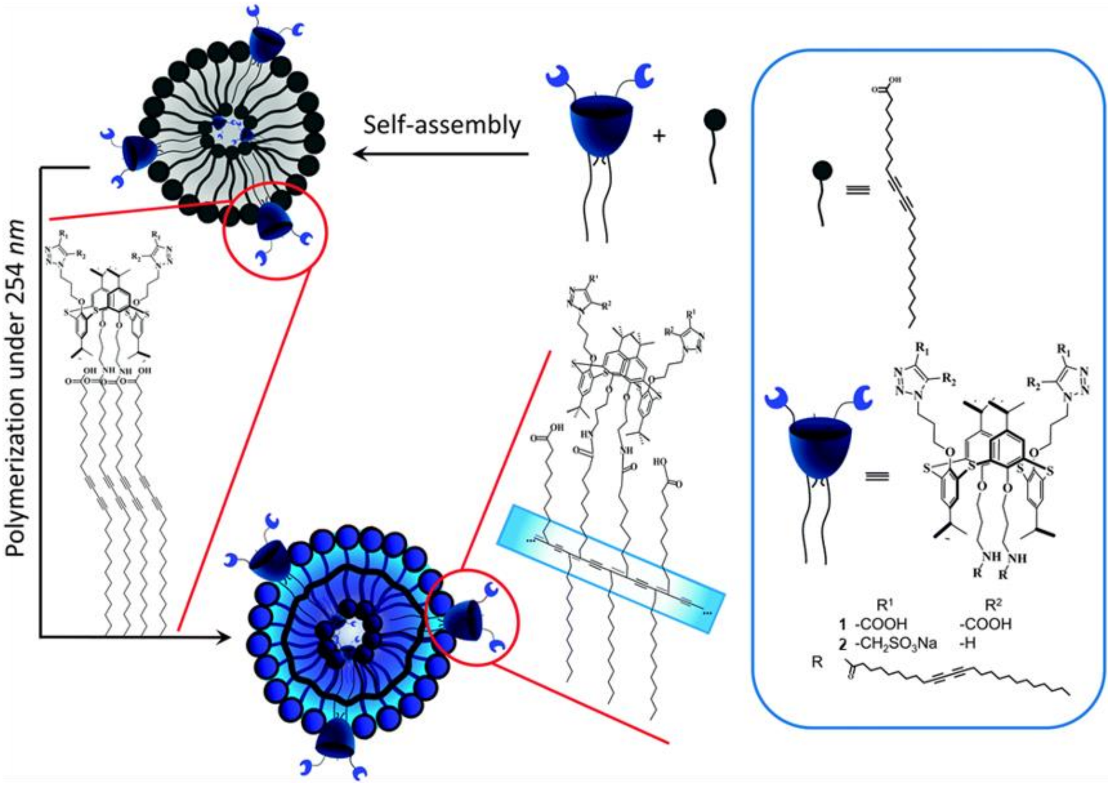


Figure 39. A schematic representation of functional thiacalix[4]arene-PCDA vesicles. Reproduced with permission from reference 150.

The Effect of Mechanical Stress on PCDA Polymer Properties

The first observation of mechanochromism in PCDA films at the nanometer scale was reported by Carpick and coworkers by atomic force microscopy (AFM) and near-field scanning optical microscopy (NSOM) accompanied by interfacial force microscopy.[151] It was observed that structural changes in PCDA films result in a blue-red color change of the PCDA polymers caused by the shear forces between the cantilever/scanning tip of the AFM and NSOM experiments.[151] The blue-to-red transition will only occur if the AFM scan direction is perpendicular to the backbone direction, as the color will not change if the film is scanned in a direction parallel to the polydiacetylene backbone.[152] The chromic transition exists even without the excitation laser present and without any heating of the contact zone.[151] It was found that the strongly anisotropic red polymer propagates along the backbone direction of the polydiacetylene by the red domains nucleating at film defects.[151] Once the red phase is established, additional tip-induced mechanochromism does not affect the red phase of polymerized PCDA.[151]

Films of PCDA and perfluorotetradecanoic acid (PF) in a 1:2 ratio respectively, were characterized by dual atomic force and fluorescence microscopy (AFM-FM) and were irradiated by lasers with wavelengths of 532 nm and 254 nm.[10] Upon irradiation, all the PCDA was polymerized, with around 80 % of the polymer existing in the red phase (which is fluorescent), with the remaining ~20 % in the blue polymer phase.[10] The presence of PCDA polymer can also be determined by AFM height differences when compared to the underlying bare glass substrate the polymer is placed on, with a height difference of approximately 5 nm.[153] The addition of PF to PCDA films compresses the films to give a 1 $Å^2$ reduction in film area, as PF induces mechanical stress which results in the formation of the irreversible red polymer phase of PCDA upon irradiation.[154] Figure 40A and Figure 40B show AFM images of a polymerized PCDA derivative at the blue-to-red interface adjacent to a silicon dioxide defect in the film, with the heights of the blue and red phases to the substrate are approximately 22 and 9 Å, respectively.[152] Figure 40C shows a schematic representation of the two colored polydiacetylene forms, with the planar "blue" form to the right of the image, becoming twisted and distorting the conjugation of the backbone, to result in the "red" form.[152]

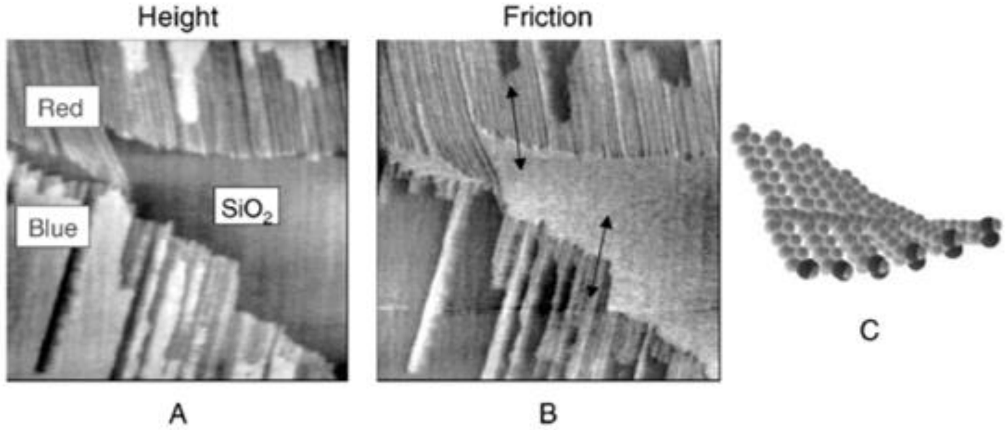


Figure 40. The AFM images of a region of polymerized N-(-2-ethanol)-10,12-pentacosadinamide film that was transformed under shear forces on a silicon dioxide substrate, with the fast scan direction along the x-axis. A) The blue phase = brightest, red phase = darkest. B) The blue phase = darkest, red phase = brightest, with the arrows indicating the backbone direction. C) A schematic of the blue-to-red transition of the polymer. Figure reproduced with permission from reference 152.

Conductive carbon nanotubes (CNT) coated in polymerized PCDA readily exhibit a blue-to-red color change when exposed to an electric current. Unlike other PCDA systems, the PCDA-CNT composites are reversible with the color change retained when exposed to current cycles lower than 30 mA, with the CNTs reversing to the original blue state after only 2 seconds from the removal of the current.[155] The color transition is reversible at 30 mA as the polydiacetylene backbone only temporarily deforms through the polarization of the carbonyl group in the PCDA side chains, which decreases the conjugation of the backbone while the CNTs are exposed to the applied current.[155, 156] At higher current values, it is expected that the polydiacetylene will permanently deform, resulting in irreversible chromism of the PCDA-CNTs.[155] It was discovered that when the PCDA-CNTs are exposed to mechanical stress, the color of the CNTs is dependent on the applied tensile stress to the CNT. A CNT fiber was exposed to a tensile strain of 0.55 GPa and remained blue, while at tensile stress values below 0.48 GPa, the PCDA-CNT fibers immediately became red in color.[155] However, if the applied tensile stress reached the range of 0.48-0.51 GPa and the mechanical stress was removed, the color transition reversed from red-to-blue.[155] Electrochromic and mechanochromic PCDA-CNTs make for impressive functional materials with sensing properties that can be applied to many fields.

Powders of polymerized PCDA intercalated with guest organic amines reveal a mechano-responsive color change that is clearly visible to the naked eye, with the responsiveness of the powders tuned by the type of alkyl amine or diamine used (with varying alkyl lengths from 4 – 16 carbon atoms long).[157] Powder XRD of the composites revealed that PCDA was no longer dimerized by O-H···O hydrogen bonds at the carbonyl head groups, and instead exist as ammonium salts.[157] The responsivity of the PCDA-powders to heat and mechanical stress were similar, as both stimuli resulted in an irreversible blue-to-red color change, however, the color change after rubbing the powder was found to be caused by shear stress, rather than by the frictional heat caused by rubbing.[157] As the effects of mechanical stress and heating were similar on the powders, the effect of rubbing the powders must have the same internal mechanism of accumulated torsion on the polydiacetylene backbone, which dictates the observed colorimetric changes. These stimuli-responsive powders have the potential to be applied to a variety of sensing and diagnostic materials.[157]

Applications of PCDA

Dosimetry Technology

Dosimeters are typically two-dimensional films that work on the premise that when irradiated, the color of the film changes from clear to blue, with the intensity of blue color proportional to the amount of irradiation the film has received. This correlates with the degree of polymerization of the diacetylenes present in the film. One of the most commonly used diacetylene based radiochromic sensors for therapeutic purposes are Gafchromic films, which contain a lithium salt of PCDA.[120] The most used radiochromic film, Gafchromic EBT®, comprises of an active layer which is surrounded by a polyester cover (Figure 41) and is intended for recording radiation doses between 1 cGy and 40 Gy (with 1 cGy equivalent to 1 rad).[158] Alternative models of Gafchromic films are able to detect different dosage ranges than the EBT model due to changes in their chemical composition and thicknesses of the active layer in the films, with the different models detecting doses from 0.2 cGy – 1000 Gy.[159] Previous discontinued radiochromic films models such as MD-55 contained PCDA as the diacetylene in the active layer, however, the MD-55 film was only useful at doses greater than 5 Gy.[160, 161] Additionally, PCDA has also been incorporated into films using polyvinyl alcohol (PVA)[20] and polyvinyl butyral (PVB)[162] as the polymer layer, compared to polyester in the Gafchromic films. The PCDA-PVA film exhibits a color change from clear to dark blue at a dose range of 100 Gy – 6000 Gy,[20] while the PVB film displays a dose range of 5 – 4000 Gy, though the range is dependent on the PCDA content within the films.[162] An important application of radiochromic films is their use on blood bags to indicate if the blood has been irradiated with gamma radiation before the blood is transferred between patients.[163] Once the film has been irradiated, the film will change color from transparent red with the word "NOT" across the film, to opaque, which makes it clear to the handler which blood is safe to use (Figure 42).[164] This irradiation process prevents the spread of transfusion-associated graft-versus-host disease which is rare but can be fatal if an immunocompromised patient is exposed to the disease.[163] An alternative to 2D radiochromic films is the utilization of 3D PCDA gel dosimeters which display a linear irradiation response in the dose range of 2 – 100 Gy.[165] The gel dosimeters are prepared through the dispersion of self-assembled nanovesicles of PCDA into a gel matrix, Figure 43. When compared to existing 3D dosimeters,[166, 167] the PCDA gel system provides excellent tissue equivalence, has high spatial resolution and dose accuracy, and does not exhibit any dose rate, energy, or temperature dependent effects.[165]

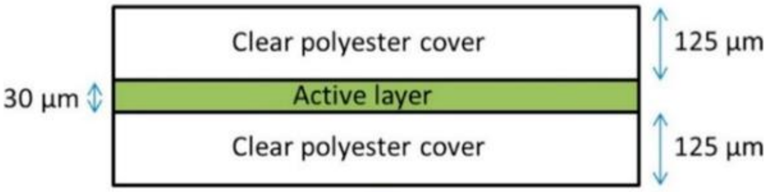


Figure 41. The composition of Gafchromic EBT3 film, reproduced with permission from reference 158.

Figure 42. Radiochromic film labels used for irradiation detection on blood bags. Figure reproduced from reference 164.

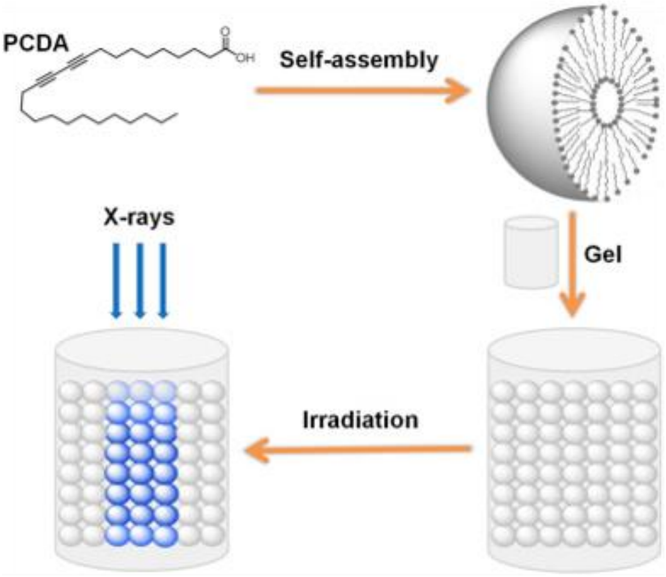


Figure 43. The preparation and application of PCDA vesicles to create a gel dosimeter. Reproduced with permission from reference 165.

PCDA Biosensors

Polydiacetylenes have the potential to produce a colorimetric response to a wide range of biomolecules such as proteins/enzymes,[109, 168-171] viruses,[172-174] bacteria,[106, 175-177] sugars,[178-180] and active ingredients.[181] A recent review on polydiacetylene-based sensors categorizes the sensor application by the type of chromism that is used *e.g.* thermochromism, solvatochromism, or electrochromism.[182] Polydiacetylene biosensors have a real-world application within the field of food safety, with PCDA vesicles able to detect the presence of *Salmonella* bacteria,[183] along with the detection of eight commonly used sanitizers and surfactants used in the food industry.[184] Recent work on treating bacterial infections includes the detection of pore-forming toxins by PCDA.[175] A polymerized PCDA nanoparticle-functionalized microgel has been designed to manage topical bacterial infections, with the specific nanoparticle morphology prepared by a 3D bioprinting process.[175] The 3D nanoparticle gel diffuses and neutralizes the pore-forming toxins released from bacteria and has shown in mouse models that the microgel promotes tissue recovery after bacterial infection, and, therefore, has the potential to be developed into a larger-scale treatment in the future.[175] PCDA has also been extensively studied for its chromic properties when combined with biomolecules, for example, nucleic acids have been detected by modifying the head group of PCDA with an antibiotic, neomycin, which inhibits bacterial protein synthesis through binding to the 30S subunit of the bacterial ribosome.[185-187] Therefore, the neomycin head group of PCDA will act as a binding site for RNA resulting in a conformational change of the polymerized PCDA-neomycin complex and hence a blue-to-purple colorimetric change.[181] The detection of the veterinary fluoroquinolone antibiotic, enrofloxacin, has also been achieved through the synthesis of a nanoblend consisting of polymerized PCDA, triblock copolymer (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)), and sodium dodecyl sulfate (SDS).[188] The detection of enrofloxacin residues are important for human health, especially in terms of food safety and antimicrobial resistance. The colorimetric response of enrofloxacin to the nanoblend depends on the SDS concentration suggesting that the surfactant is as important as PCDA in the detection of enrofloxacin residues.[188] Alongside antibiotics, PCDA has also been used in enzyme-free systems to amplify the presence of miRNA in human serum at ultralow concentrations, as miRNA expression is dysregulated in human cancer and therefore, is able to serve as a potential biomarker for cancer diagnosis.[189, 190] The presence of DNA has also been detected through the utilization of a *p*-*tert*-butyl thaicalix[4]arene with PCDA moieties on either side of the macrocyclic cavity.[191] When the PCDA residues are polymerized by UV exposure and the calixarene is in contact with calf thymus DNA, the macrocycle intercalates to form a lipoplex and displays a typical blue-to-red color change from concentrations as low as 20 μmol L^{-1}.[191] Polymerized PCDA has been incorporated into a microtube waveguide system whereby single-stranded miRNA is attracted to the surface of the PCDA microtube which facilitates an amplification reaction within the surface of the PCDA microtube, ultimately able to distinguish between cancer patients and healthy humans.[189] The detection of specific proteins is also possible when combining enzymes such as glutathione *S*-transferase,[168] phospholipase D,[21] and alkaline phosphatase[192] to PCDA head groups which elicits a colorimetric response. Interestingly, polymerized PCDA vesicles have also been combined with phospholipids (1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC), 1,2-dimyristoyl-*sn*-glycero-3-phospho-(1′-*rac*-glycerol) (DMPG), and stearamide) to tune the surface potentials of vesicles designed for gene therapy (Figure 44A).[169] When model gene vectors Lipofectamine 2000, Entranster TM-H4000, and polyethylenimine are added to the phospholipid/polydiacetylene vesicles, a color change is observed in less than five minutes from blue-to-red (Figure 44B).[169] From the UV-Vis data, the affinity constant was calculated to determine the sensitivity of each type of phospholipid/polydiacetylene vesicle combination used and revealed that the vesicles consisting of DMPC/PDA show the highest sensitivity towards gene vectors.[169] This polydiacetylene biosensing system demonstrates a rapid visualization technique of gene vectors that has the potential for screening of carrier molecules for drug delivery.[169]

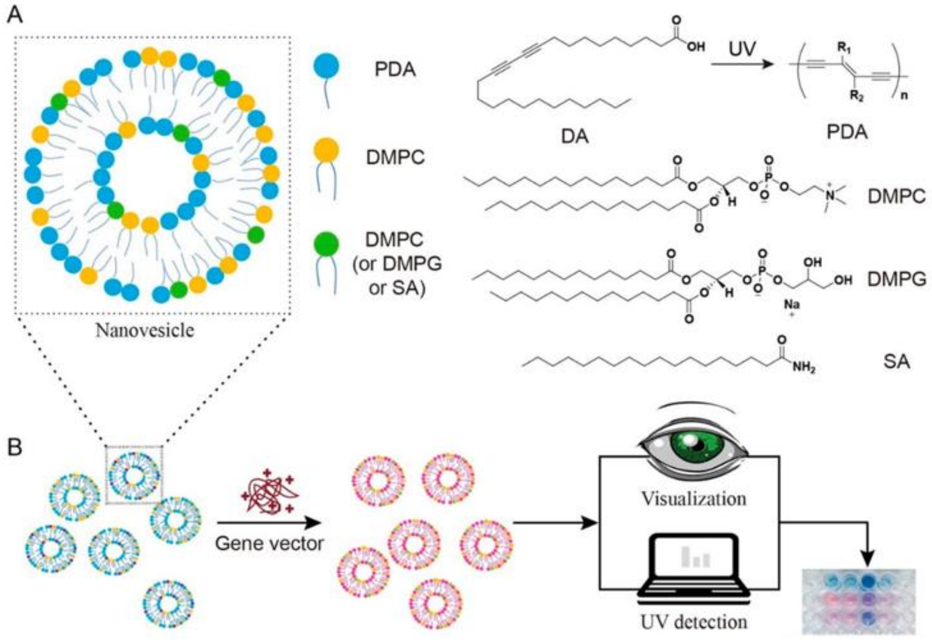


Figure 44. A) An illustration of the incorporation of different phospholipids into the polydiacetylene (PDA) nanovesicles. B) The rapid color change of the phospholipid/polydiacetylene vesicles when in contact with gene vectors and the quantification of the color change by UV-Vis analysis. Reprinted with permission from reference 169.

Research has been conducted for the colorimetric detection of the influenza A virus (pH1N1), through the modification of PCDA materials.[170] For instance, a recent study involves designing paper chips that contains a polymerized PCDA-imide derivative that detects the pH1N1 influenza strain with high sensitivity by an obvious blue-to-red color change, ultimately for quick and easy point-of-care testing of the influenza A virus.[172] The PCDA derivative was then mixed with PCDA and 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and a polyvinylidene difluoride (PVDC) membrane, with PCDA secured to the PVDC membrane through UV irradiation for one minute.[172] A colorimetric change occurs on the chip due to the binding events of the pH1N1 virus by the interaction of the influenza A virus nucleoprotein and nucleoprotein antibodies on the surface of the chip, and to intensify the color change, the chip can be incubated or physically touched to enhance the thermochromic properties of the polydiacetylene system.[172] Though the sensitivities of the polydiacetylene-paper chip are too low for clinical applications, a smartphone application has been designed to visually detect a high concentration of viruses based on the colorimetric response of the paper chip results.[172]

PCDA Chemosensors

The detection of specific chemicals that pose a risk to human health and environmental welfare is of high importance, and multiple polydiacetylene systems have been developed to combat the issues. A World Health Organization 1990 review of the impact of pesticides on human health, estimated that over 3 million cases of severe acute poisoning were due to pesticides, and of these around 220,000 were the cause of death, indicating the need for an practical pesticide detection system.[193] A recent study uses a commonly used organophosphate insecticide, malathion, that is able to be detected by PCDA with pralidoxime (PAM) functionalized terminal group, enabling PCDA to bind to organophosphates and which would inhibit the pesticides' mechanism of action through the binding of acetylcholinesterases present in the synaptic cleft.[194] When polymerized PCDA/PAM binds to malathion, a blue-to-purple-to-red color change is observed within seconds of binding and can be observed by the naked eye and quantified by electronic absorption studies.[194] Polymerized PCDA also has the capability to detect the presence of trinitrotoluene (TNT) when coupled with a TNT recognition motif comprised of a trimer peptide of tryptophan-histidine-tryptophan (Trp-His-Trp).[195] The binding of TNT to the peptide region results in a conformational change which alters the conjugated backbone of PCDA, resulting in a blue-to-red color change.[195]

Polydiacetylene-based sensors are also helpful in the food industry, with the development of low-cost films that are able to detect the early release of gases due to food spoilage and are suitable for food packaging labels.[196] The ammonia-sensitive films consist of PCDA as the sensing material, cellulose nanocrystals (CNC) as the stabilizing agent, and chitosan to provide a matrix. The components help to fabricate strong but flexible free-standing films that display a blue-to-red color change when in the presence of ammonia over a wide temperature range of -20 to 24 °C.[196]

An impressive dual-stimuli responsive dendritic diacetylene has been designed with an aromatic head group and a PCDA tail that forms a tetraphenylmethane core capable of forming pores in the tight packing structure (Figure 45).[197] Once polymerized, the tetrahedral structure (TePDA) exhibits cross-linking to give the typical ene-yne carbon backbone and displays reversible blue-red-blue thermochromism at temperatures up to 134 °C.[197] The main application of TePDA is the detection of volatile organic compounds in the vapor phase. Paper strips were coated with TePDA and exposed to the vapors of dichloromethane, tetrahydrofuran, chloroform, benzene, toluene, xylene in different concentrations (0.05 % - 1.0 %) for one hour. Chloroform provided the greatest colorimetric response with a color change from blue to light brown, while PCDA alone shows an indistinct color transition at the maximum concentration of chloroform.[197] This intrinsically porous self-assembled material has the potential to be used in multi-disciplinary fields that require a system that is sensitive to more than one stimulus at a time.

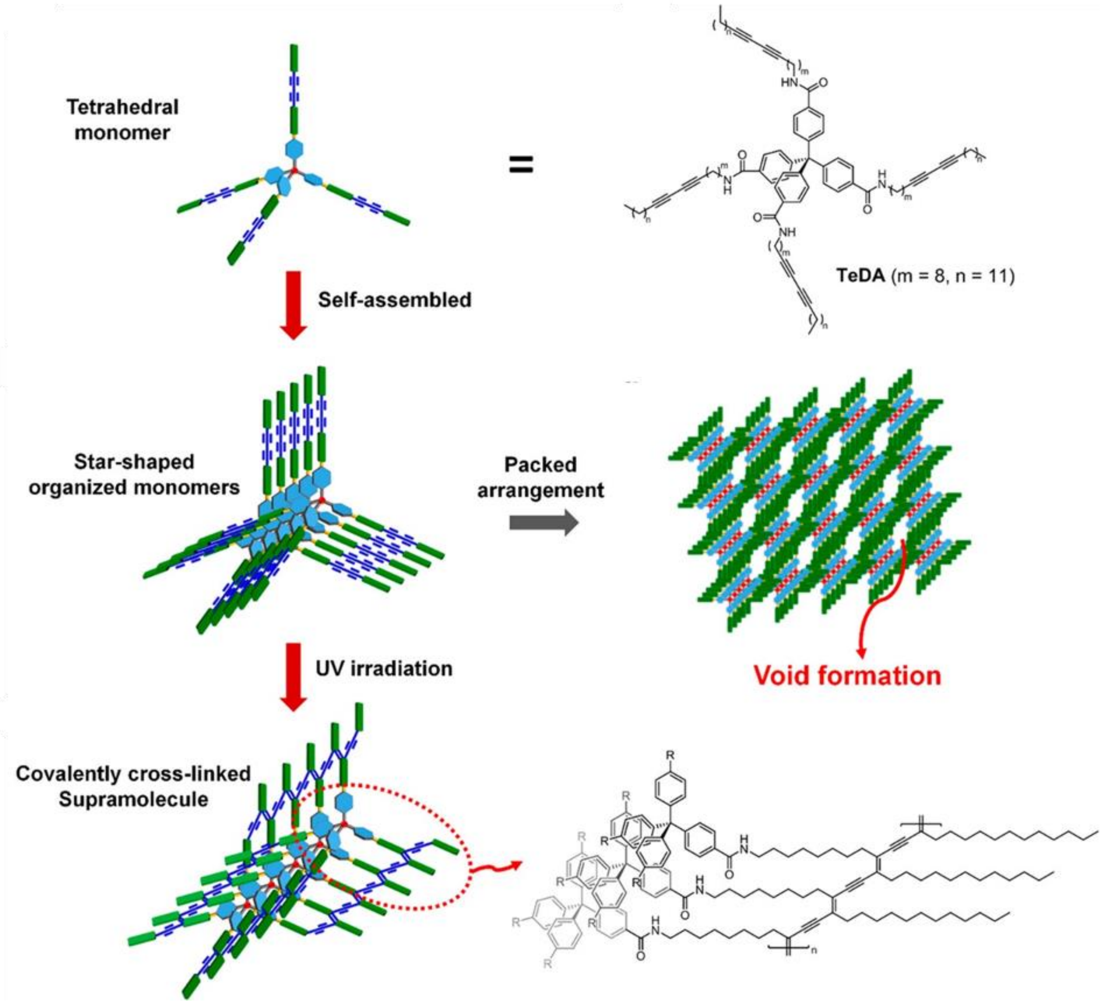


Figure 45. The formation of the self-assembled tetrahedral diacetylene in monomeric and polymeric forms. Reprinted with permission from reference 197.

The combination of PCDA and polymers have also been shown to enhance the sensing properties of the diacetylene. For instance, monomeric PCDA has been embedded in poly-ε-caprolactone polymer matrix through electrospinning and irradiated by UV exposure, which allows the polymer matrix to detect the presence of an organic solvent additives in gasoline, through a visible blue-to-red color change.[198] Another polymer matrix system involves electrodes coated with polymerized PCDA which are embedded in a porous polymer matrix containing PVP by a spin coating technique.[199] The PCDA/PVP electrode acts as a vapor-sensing system, or an "artificial nose" for detecting different organic solvents, with each vapor determining a different capacitance transformation, which is fully reversible when the vapor is no longer in contact with the electrode.[199] Figure 46 summarizes the capacitance responses of polydiacetylene/PVP thin films containing 10,12-tricosadiynoic acid (TCDA) and PCDA to different solvents, with the responses color coded to the degree of capacitance change.[199] These results illustrate the vapor selectivity for two different diacetylenes as the capacitance changes depending on the exposure of different vapors, with PCDA showing higher capacitance values in more solvents than TCDA.[199] A different study that involves electrical conductivity rather than the storage of electrical charge has focused on the effect of PCDA sulfonic acid derivatives as dopants to increase the thermal stability and maintain the electrical conductivity of polyaniline.[200] The PCDA derivatives were synthesized by derivatizing the carboxylic acid group with either a 2-aminoethanesulfonic acid group or a 4-aminobenzenesulfonic acid (pBzS) group.[200] Upon polymerization of the diacetylene dopants with polyaniline, the thermal stability was observed in the range 250-600 °C, with the sheet resistance of polymerized dopants maintained, when compared to polyaniline with dodecylbenzenesulfonic acid, which has the same functional group as PCDA-pBzS, though without the photoreactive diacetylene functionality.[200]

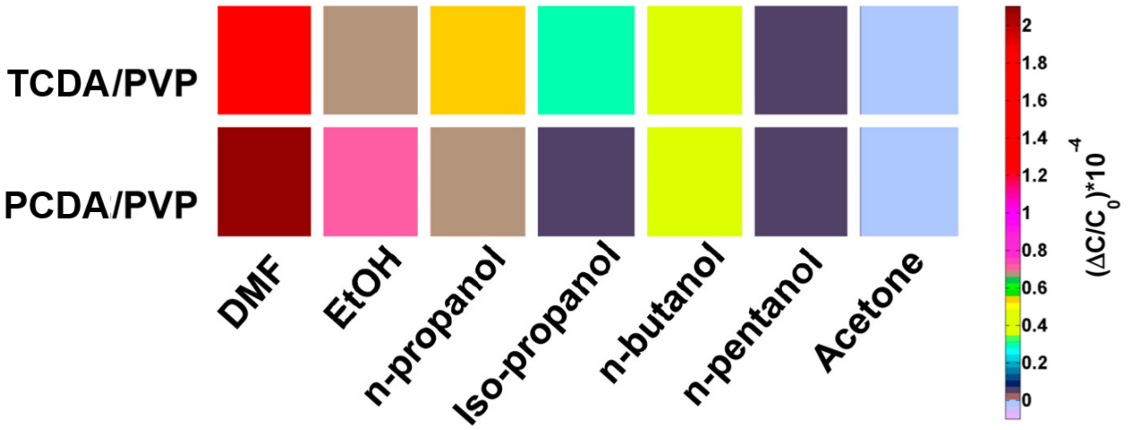


Figure 46. The capacitance responses of thin PVP composite films containing TCDA and PCDA to different gases, with the color coded to the degree of capacitance change scale on the right. Figure adapted with permission from reference 201.

Conclusions and Outlook

In this review, we have demonstrated how crystal engineering is critical in controlling the diacetylene monomer structure to allow successful polymerization. The monomeric structure can be altered to match the optimal topochemical conditions through the use of multi-component systems, such as host-guest interactions that involve cocrystallization and salt formation. Once the desired polydiacetylene is produced, the resulting polymer has a wide range of applications, especially in thermochromic sensing systems, with emphasis on non-covalent interactions (e.g. hydrogen bonding) to influence reversible thermochromism. Alongside heat, polydiacetylenes are also responsive to differences in pH, a range of solvents, metal ions, and mechanical stress, all which produce varying colorimetric responses depending on the polymer used.

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Author Contributions

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References

(1) Han, N.; Woo, H. J.; Kim, S. E.; Jung, S.; Shin, M. J.; Kim, M.; Shin, J. S., Systemized organic functional group controls in polydiacetylenes and their effects on color changes. *J. Appl. Polym. Sci.* 2017, 134, (30), 1-8.

(2) Grim, P. C. M.; De Feyter, S.; Gesquiere, A.; Vanoppen, P.; Rucker, M.; Valiyaveettil, S.; Moessner, G.; Mullen, K.; De Schryver, F. C., Submolecularly resolved polymerization of diacetylene molecules on the graphite surface observed with scanning tunneling microscopy. *Angew. Chem., Int. Ed.* 1997, 36, (23), 2601-2603.

(3) Kantha, C.; Kim, H.; Kim, Y.; Heo, J. M.; Joung, J. F.; Park, S.; Kim, J. M., Topochemical polymerization of macrocyclic diacetylene with a naphthalene moiety for a tubular-shaped polydiacetylene chromophore. *Dyes Pigm.* 2018, 154, 199-204.

(4) Kim, T.; Moon, D.; Park, J. H.; Yang, H.; Cho, S.; Park, T. H.; Ahn, D. J., Visual detection of odorant geraniol enabled by integration of a human olfactory receptor into polydiacetylene/lipid nano-assembly. *Nanoscale* 2019, 11, (16), 7582-7587.

(5) Mergu, N.; Kim, H.; Heo, G.; Son, Y. A., Development of naphthalimide-functionalized thermochromic conjugated polydiacetylenes and their reversible green-to-red chromatic transition in the solid state. *Dyes Pigm.* 2019, 164, 355-362.

(6) Barisien, T.; Fave, J. L.; Hameau, S.; Legrand, L.; Schott, M.; Malinge, J.; Clavier, G.; Audebert, P.; Allain, C., Reversible Quenching of a Chromophore Luminescence by Color Transition of a Polydiacetylene. *ACS Appl. Mater. Interfaces* 2013, 5, (21), 10836-10841.

(7) Hammond, P. T.; Rubner, M. F., Thermochromism in liquid crystalline polydiacetylenes. *Macromolecules* 1997, 30, (19), 5773-5782.

(8) Shimogaki, T.; Dei, S.; Ohta, K.; Matsumoto, A., Columnar mesophases constructed by hierarchical self-organization of rod-like diacetylene molecules. *J. Mater. Chem.* 2011, 21, (29), 10730-10737.

(9) Kim, D. Y.; Lee, S. A.; Jung, D.; Koo, J.; Kim, J. S.; Yu, Y. T.; Lee, C. R.; Jeong, K. U., Topochemical polymerization of dumbbell-shaped diacetylene monomers: relationship between chemical structure, molecular packing structure, and gelation property. *Soft Matter* 2017, 13, (34), 5759-5766.

(10) Araghi, H. Y.; Paige, M. F., Insight into diacetylene photopolymerization in Langmuir-Blodgett films using simultaneous AFM and fluorescence microscopy imaging. *Surf. Interface Anal.* 2017, 49, (11), 1108-1114.

(11) Spagnoli, S.; Briand, E.; Vickridge, I.; Fave, J. L.; Schott, M., Method for Determining the Polymer Content in,Nonsoluble Polydiacetylene Films: Application to Pentacosadiynoic Acid. *Langmuir* 2017, 33, (6), 1419-1426.

(12) Yarimaga, O.; Yoon, B.; Ham, D. Y.; Lee, J.; Hara, M.; Choi, Y. K.; Kim, J. M., Electrophoretic deposition of amphiphilic diacetylene supramolecules: polymerization, selective immobilization, pattern transfer and sensor applications. *J. Mater. Chem.* 2011, 21, (46), 18605-18612.

(13) Lee, S.; Lee, D.; Hong, C. S.; Yang, J. E.; Kang, J. S.; Sung, Y. E.; Paik, S. R., Alternative Assembly of alpha-Synuclein Leading to Protein Film Formation and Its Application for Developing Polydiacetylene-Based Sensing Materials. *Langmuir* 2019, 35, (36), 11923-11931.

(14) Kim, M.; Shin, Y. J.; Hwang, S. W.; Shin, M. J.; Shin, J. S., Chromatic detection of glucose using polymerization of diacetylene vesicle. *J. Appl. Polym. Sci.* 2018, 135, (25), 1-5.

(15) Yoo, K.; Kim, S.; Han, N.; Kim, G. E.; Shin, M. J.; Shin, J. S.; Kim, M., Stepwise blue-red-yellow color change of a polydiacetylene sensor through internal and external transitions. *Dyes Pigm.* 2018, 149, 242-245.

(16) Singh, Y.; Jayaraman, N., Visual Detection of pH and Biomolecular Interactions at Micromolar Concentrations Aided by a Trivalent Diacetylene-Based Vesicle. *Macromol. Chem. Phys.* 2017, 218, (11), 1-11.

(17) Meng, Y.; Jiang, J.; Liu, M. H., Self-assembled nanohelix from a bolaamphiphilic diacetylene via hydrogelation and selective responsiveness towards amino acids and nucleobases. *Nanoscale* 2017, 9, (21), 7199-7206.

(18) Sun, P.; Fu, Y. C.; Hu, J.; Li, L.; Wang, X.; Huang, W.; Jiang, B., Electron irradiation effects of radiochromic PCDA vesicle gel dosimeters. *Nucl. Sci. Tech.* 2015, 26, (5), 6.

(19) Fan, H. H.; Jiang, H. J.; Zhu, X. F.; Zhu, M. S.; Zhang, L.; Liu, M. H., Homo- and heterochirality regulated blue and red phase polymerization of diacetylene with enantiomeric and racemic gelators. *Eur. Polym. J.* 2019, 118, 146-152.

(20) Kozicki, M.; Sasiadek, E.; Kadlubowski, S.; Dudek, M.; Maras, P.; Nosal, A.; Gazicki-Lipman, M., Flat foils as UV and ionising radiation dosimeters. *J. Photochem. Photobiol., A* 2018, 351, 179-196.

(21) Zhang, Z. J.; Li, J.; Wang, F.; Wei, T. W.; Chen, Y. H.; Qiang, J.; Xiao, T.; Chen, X. Q., A polydiacetylenes-based sensor for the efficient detection of phospholipase D activity. *Sens. Actuators, B* 2019, 282, 636-643.

(22) Yang, J. E.; Lee, S.; Bhak, G.; Lee, M.; Jeong, D. H.; Jung, S.; Paik, S. R., Litmus-type thermochromic and solvatochromic sensors prepared with alpha-synuclein amyloid fibrils and polydiacetylene. *Sens. Actuators, B* 2016, 227, 313-319.

(23) Cohen, M. D.; Schmidt, G. M. J., 383. Topochemistry. Part I. A survey. *J. Chem. Soc.* 1964, 1996-2000.

(24) Cohen, M. D.; Schmidt, G. M. J.; Sonntag, F. I., 384. Topochemistry. Part II. The photochemistry of *trans*-cinnamic acids. *J. Chem. Soc.* 1964, 2000-2013.

(25) Schmidt, G. M. J., 385. Topochemistry. Part III. The crystal chemistry of some *trans*-cinnamic acids. *J. Chem. Soc.* 1964, 2014-2021.

(26) Bregman, J.; Schmidt, G. M. J.; Osaki, K.; Sonntag, F. I., 386. Topochemistry. Part IV. The crystal chemistry of some *cis*-cinnamic acids. *J. Chem. Soc.* 1964, 2021-2030.

(27) Hirshfeld, F. L.; Schmidt, G. M. J., Topochemical Control of Solid-State Polymerization. *J. Polym. Sci. A* 1964, 2, (5), 2181-2190.

(28) Wegner, G., Z. Topochemical reactions of monomers with conjugated triple bonds I. Polymerizations of 2,4-Hexadiynyl-1,6-diol derivatives in the crystalline state. *Z. Naturforsch., B: J. Chem. Sci.* 1969, 24, 824-832.

(29) Schmidt, G. M. J., Photodimerization in the solid state. *Pure Appl. Chem.* 1971, 27, (4), 647-678.

(30) Enkelmann, V., Structural Aspects of the Topochemical Polymerization of Diacetylenes. *Adv. Polym. Sci.* 1984, 63, 91-136.

(31) Baughman, R. H., Solid-state polymerization of diacetylenes. *J. Appl. Phys.* 1972, 43, (11), 4362-4370.

(32) Baughman, R. H.; Yee, K. C., Solid-state polymerization of linear and cyclic acetylenes. *J. Polym. Sci., Part D: Macromol. Rev.* 1978, 13, (1), 219-239.

(33) Lauher, J. W.; Fowler, F. W.; Goroff, N. S., Single-crystal-to-single-crystal topochemical polymerizations by design. *Accounts Chem. Res.* 2008, 41, (9), 1215-1229.

(34) Li, Z.; Fowler, F. W.; Lauher, J. W., Weak Interactions Dominating the Supramolecular Self-Assembly in a Salt: A Designed Single-Crystal-to-Single-Crystal Topochemical Polymerization of a Terminal Aryldiacetylene. *J. Am. Chem. Soc.* 2009, 131, (2), 634-643.

(35) Day, D.; Lando, J. B., Morphology of Crystalline Diacetylene Monolayers Polymerized at the Gas-Water Interface. *Macromolecules* 1980, 13, (6), 1478-1483.

(36) Nakanishi, H.; Matsuda, H.; Kato, M.; Theocharis, C. R.; Jones, W., Single-crystal study of the solid-state polymerisation of butadiynylenebis-(*m*-acetamidobenzene). *J. Chem. Soc., Perkin Trans. 2* 1986, (12), 1965-1967.

(37) Ouyang, X.; Fowler, F. W.; Lauher, J. W., Single-crystal-to-single-crystal topochemical polymerizations of a terminal diacetylene: two remarkable transformations give the same conjugated polymer. *J. Am. Chem. Soc.* 2003, 125, (41), 12400-1.

(38) Hall, A. V.; Musa, O. M.; Hood, D. K.; Apperley, D. C.; Yufit, D. S.; Steed, J. W., Alkali Metal Salts of 10,12-Pentacosadiynoic Acid and Their Dosimetry Applications. *Cryst. Growth Des.* 2021, 21, (4), 2416-2422.

(39) Enkelmann, V., Crystal Structure of 2 Diacetylene Monomers. *J. Chem. Res., Synop.* 1981, (11), 344-345.

(40) Tachibana, H.; Kumai, R.; Hosaka, N.; Tokura, Y., Crystal structures, polymerization, and thermochromic phase changes in urethane-substituted diacetylenes crystals with varying alkyl chain lengths. *Chem. Mater.* 2001, 13, (1), 155-158.

(41) Smith, A. E., The Crystal Structure of the Normal Paraffin Hydrocarbons. *J. Chem. Phys.* 1953, 21, (12), 2229-2231.

(42) Tanioku, C.; Matsukawa, K.; Matsumoto, A., Thermochromism and Structural Change in Polydiacetylenes Including Carboxy and 4-Carboxyphenyl Groups as the Intermolecular Hydrogen Bond Linkages in the Side Chain. *ACS Appl. Mater. Interfaces* 2013, 5, (3), 940-948.

(43) Kaupp, G., Solid-state molecular syntheses: complete reactions without auxiliaries based on the new solid-state mechanism. *CrystEngComm* 2003, 5, (23), 117-133.

(44) Enkelmann, V.; Schleier, G., Poly[1,2-bis(diphenylaminomethyl)-1-buten-3-ynylene]. *Acta Crystallogr., Sect. B: Struct. Sci.* 1980, 36, 1954-1956.

(45) Kirchner, M. T.; Blaser, D.; Boese, R., Co-crystals with Acetylene: Small Is not Simple! *Chem.-Eur. J.* 2010, 16, (7), 2131-2146.

(46) Kane, J. J.; Liao, R. F.; Lauher, J. W.; Fowler, F. W., Preparation of Layered Diacetylenes as a Demonstration of Strategies for Supramolecular Synthesis. *J. Am. Chem. Soc.* 1995, 117, (48), 12003-12004.

(47) Desiraju, G. R., Supramolecular Synthons in Crystal Engineering—A New Organic Synthesis. *Angew. Chem., Int. Ed. Engl.* 1995, 34, (21), 2311-2327.

(48) Fowler, F. W.; Lauher, J. W., A rational design of molecular materials. *J. Phys. Org. Chem.* 2000, 13, (12), 850-857.

(49) Curtis, S. M.; Le, N.; Fowler, F. W.; Lauher, J. W., A rational approach to the preparation of polydipyridyldiacetylenes: An exercise in crystal design. *Cryst. Growth Des.* 2005, 5, (6), 2313-2321.

(50) Rodriguez, J. G.; MartinVillamil, R.; Cano, F. H.; Fonseca, I., Synthesis of 1,4-di(n-pyridyl)buta-1,3-diyne and formation of charge-transfer complexes. X-Ray structure of 1,4-di(3-pyridyl)buta-1,3-diyne. *J. Chem. Soc., Perkin Trans. 1* 1997, (5), 709-714.

(51) Allan, J. R.; Barrow, M. J.; Beaumont, P. C.; Macindoe, L. A.; Milburn, G. H. W.; Werninck, A. R., The crystal structure of 1,4-bis-(4-pyridyl)butadiyne and a study of its complexes with cobalt(II), nickel(II) and copper(II). *Inorg. Chim. Acta* 1988, 148, (1), 85-90.

(52) Cao, D. K.; Sreevidya, T. V.; Botoshansky, M.; Golden, G.; Benedict, J. B.; Kaftory, M., Formation of different photodimers of isoquinolinone by irradiation of solid molecular compounds. *CrystEngComm* 2011, 13, (9), 3181-3188.

(53) Goroff, N. S.; Curtis, S. M.; Webb, J. A.; Fowler, F. W.; Lauher, J. W., Designed cocrystals based on the pyridine-iodoalkyne halogen bond. *Org. Lett.* 2005, 7, (10), 1891-1893.

(54) Luo, L.; Wilhelm, C.; Sun, A. W.; Grey, C. P.; Lauher, J. W.; Goroff, N. S., Poly(diiododiacetylene): Preparation, isolation, and full characterization of a very simple poly(diacetylene). *J. Am. Chem. Soc.* 2008, 130, (24), 7702-7709.

(55) Sun, A. W.; Lauher, J. W.; Goroff, N. S., Preparation of poly(diiododiacetylene), an ordered conjugated polymer of carbon and iodine. *Science* 2006, 312, (5776), 1030-1034.

(56) Matsumoto, A.; Kunisue, T.; Tanaka, A.; Tohnai, N.; Sada, K.; Miyata, M., Solid-state photopolymerization of diacetylene-containing carboxylates with naphthylmethylammonium as the countercation in a two-dimensional array. *Chem. Lett.* 2004, 33, (2), 96-97.

(57) Odani, T.; Okada, S.; Kabuto, C.; Kimura, T.; Matsuda, H.; Matsumoto, A.; Nakanishi, H., Single-crystal-to-single-crystal polymerization of 4,4 '-butadiynedibenzylammonium disorbate. *Chem. Lett.* 2004, 33, (10), 1312-1313.

(58) Odani, T.; Okada, S.; Kabuto, C.; Kimura, T.; Shimada, S.; Matsuda, H.; Oikawa, H.; Matsumoto, A.; Nakanishi, H., Solid-State Reactions of Crystals Containing Two Kinds of Polymerizable Moieties of Diene and Diyne. *Cryst. Growth Des.* 2009, 9, (8), 3481-3487.

(59) Matsumoto, A.; Sada, K.; Tashiro, K.; Miyata, M.; Tsubouchi, T.; Tanaka, T.; Odani, T.; Nagahama, S.; Inoue, K.; Saragai, S.; Nakamoto, S., Reaction principles and crystal structure

design for the topochemical polymerization of 1,3-dienes. *Angew. Chem., Int. Ed.* 2002, 41, (14), 2502-2505.

(60) Hall, A. V.; Yufit, D. S.; Apperley, D. C.; Senak, L.; Musa, O. M.; Hood, D. K.; Steed, J. W., The crystal engineering of radiation-sensitive diacetylene cocrystals and salts. *Chem. Sci.* 2020, 11, (30), 8025-8035.

(61) Biradha, K.; Santra, R., Crystal engineering of topochemical solid state reactions. *Chem. Soc. Rev.* 2013, 42, (3), 950-967.

(62) Steed, J. W., 21st century developments in the understanding and control of molecular solids. *Chem. Commun.* 2018, 54, (94), 13175-13182.

(63) Guo, J.; Fu, K. Y.; Zhang, Z. B.; Yang, L. Y.; Huang, Y. C.; Huang, C. I.; Zhu, L.; Chen, D. Y., Reversible thermochromism via hydrogen-bonded cocrystals of polydiacetylene and melamine. *Polymer* 2016, 105, 440-448.

(64) Mueller, A.; O'Brien, D. F., Supramolecular materials via polymerization of mesophases of hydrated amphiphiles. *Chem. Rev.* 2002, 102, (3), 727-757.

(65) Jelinek, R.; Ritenberg, M., Polydiacetylenes - recent molecular advances and applications. *RSC Adv.* 2013, 3, (44), 21192-21201.

(66) Carpick, R. W.; Sasaki, D. Y.; Marcus, M. S.; Eriksson, M. A.; Burns, A. R., Polydiacetylene films: a review of recent investigations into chromogenic transitions and nanomechanical properties. *J. Phys.: Condens. Matter* 2004, 16, (23), 679-697.

(67) Khanantong, C.; Charoenthai, N.; Kielar, F.; Traiphol, N.; Traiphol, R., Influences of bulky aromatic head group on morphology, structure and color-transition behaviors of polydiacetylene assemblies upon exposure to thermal and chemical stimuli. *Colloids Surf., A* 2019, 561, 226-235.

(68) Pang, J.; Yang, L.; McCaughey, B. F.; Peng, H.; Ashbaugh, H. S.; Brinker, C. J.; Lu, Y., Thermochromatism and structural evolution of metastable polydiacetylenic crystals. *J. Phys. Chem. B* 2006, 110, (14), 7221-5.

(69) Khanantong, C.; Charoenthai, N.; Wacharasindhu, S.; Sukwattanasinitt, M.; Traiphol, N.; Traiphol, R., Influences of solvent media on chain organization and thermochromic behaviors of polydiacetylene assemblies prepared from monomer with symmetric alkyl tails. *J. Ind. Eng. Chem.* 2018, 58, 258-265.

(70) Schaefer, J. J.; Fox, C. B.; Harris, J. M., Confocal Raman microscopy for monitoring the membrane polymerization and thermochromism of individual, optically trapped diacetylenic phospholipid vesicles. *J. Raman Spectrosc.* 2012, 43, (3), 351-359.

(71) Scoville, S. P.; Shirley, W. M., Investigations of Chromatic Transformations of Polydiacetylene with Aromatic Compounds. *J. Appl. Polym. Sci.* 2011, 120, (5), 2809-2820.

(72) Eckhardt, H.; Boudreaux, D. S.; Chance, R. R., Effects of substituent-induced strain on the electronic structure of polydiacetylenes. *J. Chem. Phys.* 1986, 85, (7), 4116-4119.

(73) Schott, M., The colors of polydiacetylenes: a commentary. *J. Phys. Chem. B* 2006, 110, (32), 15864-15868.

(74) Lifshitz, Y.; Golan, Y.; Konovalov, O.; Berman, A., Structural Transitions in Polydiacetylene Langmuir Films. *Langmuir* 2009, 25, (8), 4469-4477.

(75) Chen, S. L.; Zhu, X. F.; Yang, F. Y.; Pan, X. C.; Gan, W.; Yuan, Q. H., Order-Disorder Transition of Carboxyl Terminated Chains in Polydiacetylenes Vesicles Probed by Second Harmonic Generation and Two-Photon Fluorescence. *Chin. J. Chem. Phys.* 2018, 31, (3), 269-276.

(76) Exarhos, G. J.; Risen, W. M.; Baughman, R. H., Resonance Raman study of the thermochromic phase transition of a polydiacetylene. *J. Am. Chem. Soc.* 1976, 98, (2), 481-487.

(77) Smith, C. R.; Sabatino, D. R.; Praisner, T. J., Temperature sensing with thermochromic liquid crystals. *Exp. Fluids* 2001, 30, (2), 190-201.

(78) Basnec, K.; Perse, L. S.; Sumiga, B.; Huskic, M.; Meden, A.; Hladnik, A.; Boh Podgornik, B.; Gunde, M. K., Relation between colour- and phase changes of a leuco dye-based thermochromic composite. *Sci. Rep.* 2018, 8, 1-10.

(79) Shin, H.; Yoon, B.; Park, I. S.; Kim, J. M., An electrothermochromic paper display based on colorimetrically reversible polydiacetylenes. *Nanotechnology* 2014, 25, (9), 1-8.

(80) Yoon, B.; Lee, J.; Park, I. S.; Jeon, S.; Kim, J. M., Recent functional material based approaches to prevent and detect counterfeiting. *J. Mater. Chem. C* 2013, 1, (13), 2388-2403.

(81) Yoon, B.; Shin, H.; Kang, E. M.; Cho, D. W.; Shin, K.; Chung, H.; Lee, C. W.; Kim, J. M., Inkjet-Compatible Single-Component Polydiacetylene Precursors for Thermochromic Paper Sensors. *ACS Appl. Mater. Interfaces* 2013, 5, (11), 4527-4535.

(82) Ryu, S.; Yoo, I.; Song, S.; Yoon, B.; Kim, J. M., A Thermoresponsive Fluorogenic Conjugated Polymer for a Temperature Sensor in Microfluidic Devices. *J. Am. Chem. Soc.* 2009, 131, (11), 3800-3801.

(83) Hansen, R. V.; Zhong, L.; Khor, K. A.; Zheng, L. X.; Yang, J. L., Tuneable electrochromism in weavable carbon nanotube/polydiacetylene yarns. *Carbon* 2016, 106, 110-117.

(84) Charoenthai, N.; Pattanatornchai, T.; Wacharasindhu, S.; Sukwattanasinitt, M.; Traiphol, R., Roles of head group architecture and side chain length on colorimetric response of polydiacetylene vesicles to temperature, ethanol and pH. *J. Colloid Interf. Sci.* 2011, 360, (2), 565-573.

(85) Joung, J. F.; Baek, J.; Kim, Y.; Lee, S.; Kim, M. H.; Yoon, J.; Park, S., Electronic relaxation dynamics of PCDA-PDA studied by transient absorption spectroscopy. *Phys. Chem. Chem. Phys.* 2016, 18, (33), 23096-104.

(86) Kamphan, A.; Khanantong, C.; Traiphol, N.; Traiphol, R., Structural-thermochromic relationship of polydiacetylene (PDA)/polyvinylpyrrolidone (PVP) nanocomposites: Effects of PDA side chain length and PVP molecular weight. *J. Ind. Eng. Chem.* 2017, 46, 130-138.

(87) Kamphan, A.; Traiphol, N.; Traiphol, R., Versatile route to prepare reversible thermochromic polydiacetylene nanocomposite using low molecular weight poly(vinylpyrrolidone). *Colloids Surf., A* 2016, 497, 370-377.

(88) Gu, Y.; Cao, W. Q.; Zhu, L.; Chen, D. Y.; Jiang, M., Polymer mortar assisted self-assembly of nanocrystalline polydiacetylene bricks showing reversible thermochromism. *Macromolecules* 2008, 41, (7), 2299-2303.

(89) Takeuchi, M.; Gnanasekaran, K.; Friedrich, H.; Imai, H.; Sommerdijk, N.; Oaki, Y., Tunable Stimuli-Responsive Color-Change Properties of Layered Organic Composites. *Adv. Funct. Mater.* 2018, 28, (45), 11.

(90) Nagarajan, R., Molecular packing parameter and surfactant self-assembly: The neglected role of the surfactant tail. *Langmuir* 2002, 18, (1), 31-38.

(91) Huo, J. P.; Hu, Z. D.; He, G. Z.; Hong, X. X.; Yang, Z. H.; Luo, S. H.; Ye, X. F.; Li, Y. L.; Zhang, Y. B.; Zhang, M.; Chen, H.; Fan, T.; Zhang, Y. Y.; Xiong, B. Y.; Wang, Z. Y.; Zhu, Z. B.; Chen, D. C., High temperature thermochromic polydiacetylenes: Design and colorimetric properties. *Appl. Surf. Sci.* 2017, 423, 951-956.

(92) Zhang, L.; Yuan, Y. Z.; Tian, X. H.; Sun, J. Y., A thermally reversible supramolecular system based on biphenyl polydiacetylene. *Chin. Chem. Lett.* 2015, 26, (9), 1133-1136.

(93) Niu, R.; Meng, X. L.; Yang, D. D.; Chang, Y.; Zha, F., Preparation of Reversible Thermochromism Supramolecules of 4-Aminophenol-Modified Polydiacetylene. *Arabian J. Sci. Eng.* 2015, 40, (10), 2867-2872.

(94) Wacharasindhu, S.; Montha, S.; Boonyiseng, J.; Potisatityuenyong, A.; Phollookin, C.; Tumcharern, G.; Sukwattanasinitt, M., Tuning of Thermochromic Properties of Polydiacetylene toward Universal Temperature Sensing Materials through Amido Hydrogen Bonding. *Macromolecules* 2010, 43, (2), 716-724.

(95) Park, S. H.; Roh, J.; Ahn, D. J., Optimal Photoluminescence Achieved by Control of Photopolymerization for Diacetylene Derivatives That Induce Reversible, Partially Reversible, and Irreversible Responses. *Macromol. Res.* 2017, 25, (9), 960-962.

(96) Bloor, D., Dissolution and thermochromism of polydiacetylenes with chiral pendent groups. *Chem. Phys. Lett.* 1998, 295, (1-2), 63-69.

(97) Bloor, D., Dissolution and spectroscopic properties of the polydiacetylene poly(10,12-docosadiyne-1,12-diol-bisethylurethane). *Macromol. Chem. Phys.* 2001, 202, (8), 1410-1423.

(98) Kim, J. M.; Lee, J. S.; Choi, H.; Sohn, D.; Ahn, D. J., Rational design and in-situ FTIR analyses of colorimetrically reversibe polydiacetylene supramolecules. *Macromolecules* 2005, 38, (22), 9366-9376.

(99) Ahn, D. J.; Lee, S.; Kim, J. M., Rational Design of Conjugated Polymer Supramolecules with Tunable Colorimetric Responses. *Adv. Funct. Mater.* 2009, 19, (10), 1483-1496.

(100)Lee, G. S.; Kim, T. Y.; Ahn, D. J., Modulation of chromatic reversibility of polydiacetylene Langmuir Schafer (LS) films by cadmium ion Ad/desorption. *J. Ind. Eng. Chem.* 2018, 67, 312-315.

(101)Mapazi, O.; Matabola, P. K.; Moutloali, R. M.; Ngila, C. J., A urea-modified polydiacetylene-based high temperature reversible thermochromic sensor: Characterisation and evaluation of properties as a function of temperature. *Sens. Actuators, B* 2017, 252, 671-679.

(102)Yu, X. W.; Luo, Y. H.; Wu, W. X.; Yan, Q.; Zou, G.; Zhang, Q. J., Synthesis and reversible thermochromism of azobenzene-containing polydiacetylenes. *Eur. Polym. J.* 2008, 44, (9), 3015-3021.

(103)Lu, X.; Zhang, Z. D.; Sun, X. M.; Chen, P. N.; Zhang, J.; Guo, H.; Shao, Z. Z.; Peng, H. S., Flexible and stretchable chromatic fibers with high sensing reversibility. *Chem. Sci.* 2016, 7, (8), 5113-5117.

(104)Seo, M. J.; Song, J.; Kantha, C.; Khazi, M. I.; Kundapur, U.; Heo, J. M.; Kim, J. M., Reversibly Thermochromic Cyclic Dipeptide Nanotubes. *Langmuir* 2018, 34, (28), 8365-8373.

(105)Lee, G. S.; Hyun, S. J.; Ahn, D. J., Temperature-Dependent Phase Behavior of Langmuir Films of 10,12-Pentacosadiynoic Acid at the Air/Water Interface and Its Effects on Chromatic Stability of the Polymerized Langmuir-Schaefer Films. *Macromol. Res.* 2018, 26, (6), 566-570.

(106)Yapor, J. P.; Alharby, A.; Gentry-Weeks, C.; Reynolds, M. M.; Alam, A.; Li, Y. V., Polydiacetylene Nanofiber Composites as a Colorimetric Sensor Responding To Escherichia coli and pH. *ACS Omega* 2017, 2, (10), 7334-7342.

(107)Hassan, F.; Gentry-Weeks, C.; Reynolds, M.; Li, Y. V., Study on microstructure and mechanical properties of polydiacetylene composite biosensors. *J. Appl. Polym. Sci.* 2019, 136, (34), 1-14.

(108)Silbert, L.; Ben Shlush, I.; Israel, E.; Porgador, A.; Kolusheva, S.; Jelinek, R., Rapid chromatic detection of bacteria by use of a new biomimetic polymer sensor. *Appl. Environ. Microbiol.* 2006, 72, (11), 7339-7344.

(109)Jannah, F.; Kim, J. M., pH-sensitive colorimetric polydiacetylene vesicles for urease sensing. *Dyes Pigm.* 2019, 169, 15-21.

(110)Celli, J. P.; Turner, B. S.; Afdhal, N. H.; Keates, S.; Ghiran, I.; Kelly, C. P.; Ewoldt, R. H.; McKinley, G. H.; So, P.; Erramilli, S.; Bansil, R., Helicobacter pylori moves through mucus by reducing mucin viscoelasticity. *Proc. Natl. Acad. Sci. U. S. A.* 2009, 106, (34), 14321-14326.

(111)Song, S.; Cho, H. B.; Lee, H. W.; Kim, H. T., Onsite paper-type colorimetric detector with enhanced sensitivity for alkali ion via polydiacetylene-nanoporous rice husk silica composites. *Mater. Sci. Eng., C* 2019, 99, 900-904.

(112)Park, D. H.; Kim, B.; Kim, J. M., A Tetrahydrofuran-selective Optical Solvent Sensor Based on Solvatochromic Polydiacetylene. *Bull. Korean Chem. Soc.* 2016, 37, (6), 793-794.

(113)Wang, X. N.; Sun, X. L.; Hu, P. A.; Zhang, J.; Wang, L. F.; Feng, W.; Lei, S. B.; Yang, B.; Cao, W. W., Colorimetric Sensor Based on Self-Assembled Polydiacetylene/Graphene-Stacked Composite Film for Vapor-Phase Volatile Organic Compounds. *Adv. Funct. Mater.* 2013, 23, (48), 6044-6050.

(114)Lee, J.; Chang, H. T.; An, H.; Ahn, S.; Shim, J.; Kim, J. M., A protective layer approach to solvatochromic sensors. *Nat. Commun.* 2013, 4, 1-9.

(115)Guo, L. M.; Wang, Y., Retarded evaporation-induced synthesis of lamellar block copolymer supramolecules for solvatochromic sensing. *Sens. Actuators, B* 2018, 277, 172-178.

(116)Pattanatornchai, T.; Charoenthai, N.; Wacharasindhu, S.; Sukwattanasinitt, M.; Traiphol, R., Control over the color transition behavior of polydiacetylene vesicles using different alcohols. *J. Colloid Interface Sci.* 2013, 391, 45-53.

(117)Shin, M. J.; Shin, J. S., Effect of ethanol on the color transition of the polydiacetylene vesicle of 10,12-pentacosadiynoic acid for butylamine detection. *J. Appl. Polym. Sci.* 2019, 136, (26), 1-7.

(118)Kassis, R.; Bassil, M.; Al Choueiry, A., Evaluating the effect of the surface morphology on the colorimetric sensitivity of poly-vinyl-pyrrolidone polydiacetylene composites. *Mater. Res. Express* 2019, 6, (1), 1-7.

(119)Shin, M. J.; Kim, J. D., Reversible Chromatic Response of Polydiacetylene Derivative Vesicles in D2O Solvent. *Langmuir* 2016, 32, (3), 882-888.

(120)Balakrishnan, S.; Lee, S.; Kim, J. M., Thermochromic reversibility of conjugated polymers derived from a diacetylenic lipid containing lithium salt. *J. Mater. Chem.* 2010, 20, (12), 2302-2304.

(121)Pang, J. B.; Yang, L.; McCaughey, B. F.; Peng, H. S.; Ashbaugh, H. S.; Brinker, C. J.; Lu, Y. F., Thermochromatism and structural evolution of metastable polydiacetylenic crystals. *J. Phys. Chem. B* 2006, 110, (14), 7221-7225.

(122)Yu, L.; Hsu, S. L., A Spectroscopic Analysis of the Role of Side Chains in Controlling Thermochromic Transitions in Polydiacetylenes. *Macromolecules* 2012, 45, (1), 420-429.

(123)Gwon, Y. J.; Kim, C.; Lee, T. S., Chromatic detection of Cs ions using polydiacetylene-based vesicles containing crown-ether-like ethylene glycol units. *Sens. Actuator, B* 2019, 281, 343-349.

(124)Lee, J.; Pyo, M.; Lee, S. H.; Kim, J.; Ra, M.; Kim, W. Y.; Park, B. J.; Lee, C. W.; Kim, J. M., Hydrochromic conjugated polymers for human sweat pore mapping. *Nat. Commun.* 2014, 5.

(125)Xu, Y. Y.; Fu, S. Y.; Liu, F. Y.; Yu, H. Y.; Gao, J. G., Multi-stimuli-responsiveness of a novel polydiacetylene-based supramolecular gel. *Soft Matter* 2018, 14, (39), 8044-8050.

(126) Jose, D. A.; Konig, B., Polydiacetylene vesicles functionalized with N-heterocyclic ligands for metal cation binding. *Org. Biomol. Chem.* 2010, 8, (3), 655-662.

(127) Wu, S.; Pan, L. B.; Huang, Y. J.; Yang, N.; Zhang, Q. J., Co-assemblies of polydiacetylenes and metal ions for solvent sensing. *Soft Matter* 2018, 14, (33), 6929-6937.

(128) Seetha, S.; Saymung, R.; Traiphol, R.; Traiphol, N., Controlling self-assembling and color-transition of polydiacetylene/zinc(II) ion/zinc oxide nanocomposites by varying pH: Effects of surface charge and head group dissociation. *J. Ind. Eng. Chem.* 2019, 72, 423-431.

(129) Traiphol, N.; Chanakul, A.; Kamphan, A.; Traiphol, R., Role of Zn2+ ion on the formation of reversible thermochromic polydiacetylene/zinc oxide nanocomposites. *Thin Solid Films* 2017, 622, 122-129.

(130) Phonchai, N.; Khanantong, C.; Kielar, F.; Traiphol, R.; Traiphol, N., Low-Temperature Reversible Thermochromic Polydiacetylene/Zinc(II)/Zinc Oxide Nanocomposites for Colorimetric Sensing. *ACS Appl. Nano Mater.* 2019, 2, (7), 4489-4498.

(131) Potai, R.; Faisadcha, K.; Traiphol, R.; Traiphol, N., Controllable thermochromic and phase transition behaviors of polydiacetylene/zinc(II) ion/zinc oxide nanocomposites via photopolymerization: An insight into the molecular level. *Colloids Surf., A* 2018, 555, 27-36.

(132) Chanakul, A.; Traiphol, R.; Traiphol, N., Utilization of polydiacetylene/zinc oxide nanocomposites to detect and differentiate organic bases in various media. *J. Ind. Eng. Chem.* 2017, 45, 215-222.

(133) Chanakul, A.; Traiphol, R.; Traiphol, N., Colorimetric sensing of various organic acids by using polydiacetylene/zinc oxide nanocomposites: Effects of polydiacetylene and acid structures. *Colloids Surf., A* 2016, 489, 9-18.

(134) Okaniwa, M.; Oaki, Y.; Kaneko, S.; Ishida, K.; Maki, H.; Imai, H., Advanced Biominnetic Approach for Crystal Growth in Nonaqueous Media: Morphology and Orientation Control of Pentacosadiynoic Add and Applications. *Chem. Mat.* 2015, 27, (7), 2627-2632.

(135) Pattanatornchai, T.; Rueangsuwan, J.; Phonchai, N.; Traiphol, N.; Traiphol, R., Reversible thermochromie polydiacetylene/Zn(II) ion assemblies prepared via co-assembling in aqueous phase: The essential role of pH. *Colloids Surf., A* 2020, 594, 1-10.

(136) Phonchai, N.; Khanantong, C.; Kielar, F.; Traiphol, R.; Traiphol, N., Enhancing thermal and chemical sensitivity of polydiacetylene colorimetric sensors: The opposite effect of zinc oxide nanoparticles. *Colloids Surf., A* 2020, 589, 1-10.

(137) Guo, J.; Yang, L. Y.; Zhu, L.; Chen, D. Y., Selective detection of metal ions based on nanocrystalline ionochromic polydiacetylene. *Polymer* 2013, 54, (2), 743-749.

(138) Fujimori, A.; Ishitsuka, M.; Nakahara, H.; Ito, E.; Hara, M.; Kanai, K.; Ouchi, Y.; Seki, K., Formation of the newly greenish organized molecular film of long-chain diynoic acid derivatives by photopolymerization and its structural study using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. *J. Phys. Chem. B* 2004, 108, (35), 13153-13162.

(139) Sansee, A.; Kamphan, A.; Traiphol, R.; Kielar, F., Embedding luminescent iridium complex into polydiacetylene vesicles as a means of development of responsive luminescent system for imaging applications. *Colloids Surf., A* 2016, 497, 362-369.

(140)Tobias, A.; Rooke, W.; Hanks, T. W., Incorporation of gold nanoparticles into the bilayer of polydiacetylene unilamellar vesicles. *Colloid Polym. Sci.* 2019, 297, (1), 85-93.

(141)Motalebizadeh, A.; Bagheri, H.; Asiaei, S.; Fekrat, N.; Afkhami, A., New portable smartphone-based PDMS microfluidic kit for the simultaneous colorimetric detection of arsenic and mercury. *RSC Adv.* 2018, 8, (48), 27091-27100.

(142)Wang, D. E.; Wang, Y. L.; Tian, C.; Zhang, L. L.; Han, X.; Tu, Q.; Yuan, M. S.; Chen, S.; Wang, J. Y., Polydiacetylene liposome-encapsulated alginate hydrogel beads for Pb2+ detection with enhanced sensitivity. *J. Mater. Chem. A* 2015, 3, (43), 21690-21698.

(143)Li, Y.; Wang, L. H.; Yin, X.; Ding, B.; Sun, G.; Ke, T.; Chen, J. Y.; Yu, J. Y., Colorimetric strips for visual lead ion recognition utilizing polydiacetylene embedded nanofibers. *J. Mater. Chem. A* 2014, 2, (43), 18304-18312.

(144)Zhang, S. Y.; Shi, B. L.; Yang, G., A Selective Colorimetric Sensor for Pb2+ Detection by Using Phenylboronic Acid Functionalized Polydiacetylene Liposomes. *Macromol. Res.* 2020, 28, (1), 51-56.

(145)Wang, Q.; Wang, G.; Huang, X. Y.; Chen, D. Y., Fabrication of melamine/Tb3+-intercalated polydiacetylene nanosheets and their thermochromic reversibility. *Chin. J. Chem. Phys.* 2020, 33, (3), 357-364.

(146)Yao, Y. S.; Fu, K. Y.; Huang, X. Y.; Chen, D. Y., Polydiacetylene-Tb3+ Nanosheets of Which Both the Color and the Fluorescence Can Be Reversibly Switched between Two Colors. *Chin. J. Chem.* 2017, 35, (11), 1678-1686.

(147)Chanakul, A.; Traiphol, N.; Traiphol, R., Controlling the reversible thermochromism of polydiacetylene/zinc oxide nanocomposites by varying alkyl chain length. *J. Colloid Interface Sci.* 2013, 389, 106-114.

(148)Traiphol, N.; Rungruangviriya, N.; Potai, R.; Traiphol, R., Stable polydiacetylene/ZnO nanocomposites with two-steps reversible and irreversible thermochromism: The influence of strong surface anchoring. *J. Colloid Interface Sci.* 2011, 356, (2), 481-489.

(149)Baughman, R. H.; Chance, R. R., Comments on the optical properties of fully conjugated polymers: Analogy between polyenes and polydiacetylenes. *J. Polym. Sci., Part B: Polym. Phys.* 1976, 14, (11), 2037-2045.

(150)Burilov, V.; Valiyakhmetova, A.; Mironova, D.; Sultanova, E.; Evtugyn, V.; Osin, Y.; Katsyuba, S.; Burganov, T.; Solovieva, S.; Antipin, I., Novel amphiphilic conjugates of p-tert-butylthiacalix 4 arene with 10,12-pentacosadiynoic acid in 1,3-alternate stereoisomeric form. Synthesis and chromatic properties in the presence of metal ions. *New J. Chem.* 2018, 42, (4), 2942-2951.

(151)Carpick, R. W.; Sasaki, D. Y.; Burns, A. R., First observation of mechanochromism at the nanometer scale. *Langmuir* 2000, 16, (3), 1270-1278.

(152)Burns, A. R.; Carpick, R. W.; Sasaki, D. Y.; Shelnutt, J. A.; Haddad, R., Shear-induced mechanochromism in polydiacetylene monolayers. *Tribol. Lett.* 2001, 10, (1-2), 89-96.

(153)Araghi, H. Y.; Paige, M. F., Deposition and Photopolymerization of Phase-Separated Perfluorotetradecanoic Acid-10,12-Pentacosadiynoic Acid Langmuir-Blodgett Mono layer Films. *Langmuir* 2011, 27, (17), 10657-10665.

(154)Araghi, H. Y.; Paige, M. F., The effect of perfluorotetradecanoic acid on the structure of photopolymerized 10,12-pentacosadiynoic acid films at the air-water interface. *Can. J. Chem.-Rev. Can. Chim.* 2013, 91, (11), 1130-1138.

(155)Peng, H. S.; Sun, X. M.; Cai, F. J.; Chen, X. L.; Zhu, Y. C.; Liao, G. P.; Chen, D. Y.; Li, Q. W.; Lu, Y. F.; Zhu, Y. T.; Jia, Q. X., Electrochromatic carbon nanotube/polydiacetylene nanocomposite fibres. *Nat. Nanotechnol.* 2009, 4, (11), 738-741.

(156)Cheng, Q.; Stevens, R. C., Charge-induced chromatic transition of amino acid-derivatized polydiacetylene liposomes. *Langmuir* 1998, 14, (8), 1974-1976.

(157)Ishijima, Y.; Imai, H.; Oaki, Y., Tunable Mechano-responsive Color-Change Properties of Organic Layered Material by Intercalation. *Chem* 2017, 3, (3), 509-521.

(158)Ng, C. Y. P.; Chun, S. L.; Yu, K. N., Quality assurance of alpha-particle dosimetry using peeled-off Gafchromic EBT3 (R) film. *Radiat. Phys. Chem.* 2016, 125, 176-179.

(159)Devic, S.; Tomic, N.; Lewis, D., Reference radiochromic film dosimetry: Review of technical aspects. *Eur. J. Med. Phys.* 2016, 32, (4), 541-556.

(160)Rink, A.; Lewis, D. F.; Varma, S.; Vitkin, I. A.; Jaffray, D. A., Temperature and hydration effects on absorbance spectra and radiation sensitivity of a radiochromic medium. *J. Med. Phys.* 2008, 35, (10), 4545-55.

(161)Klassen, N. V.; van der Zwan, L.; Cygler, J., GafChromic MD-55: investigated as a precision dosimeter. *Med. Phys.* 1997, 24, (12), 1924-34.

(162)Abdel-Fattah, A. A.; Soliman, Y. S., Performance improvement of pentacosa-diynoic acid label dosimeter for radiation processing technology. *Radiat. Phys. Chem.* 2017, 141, 66-72.

(163)Moroff, G.; Luban, N. L. C., The irradiation of blood and blood components to prevent graft-versus-host disease: Technical issues and guidelines. *Transf. Med. Rev.* 1997, 11, (1), 15-26.

(164)LLP, A. RAD-SURE™ blood irradiation indicators. http://www.ashland.com/industries/medical/blood-safety/rad-sure-bood-irradiation-indicators (14/01/2018),

(165)Sun, P.; Fu, Y. C.; Hu, J.; Hao, N.; Huang, W.; Jiang, B., Development and dosimetric evaluation of radiochromic PCDA vesicle gel dosimeters. *Radiat. Meas.* 2016, 85, 116-125.

(166)Baldock, C.; De Deene, Y.; Doran, S.; Ibbott, G.; Jirasek, A.; Lepage, M.; McAuley, K. B.; Oldham, M.; Schreiner, L. J., Polymer gel dosimetry. *Phys. Med. Biol.* 2010, 55, (5), R1-R63.

(167)Nasr, A. T.; Olding, T.; Schreiner, L. J.; McAuley, K. B., Evaluation of the potential for diacetylenes as reporter molecules in 3D micelle gel dosimetry. *Phys. Med. Biol.* 2013, 58, (4), 787-805.

(168)Jung, Y. K.; Park, H. G., Colorimetric polydiacetylene (PDA) liposome-based assay for rapid and simple detection of GST-fusion protein. *Sens. Actuators, B* 2019, 278, 190-195.

(169)Wang, J. W.; Zheng, F.; Chen, H.; Ding, Y.; Xia, X. H., Rapidly Visualizing the Membrane Affinity of Gene Vectors Using Polydiacetylene-Based Allochroic Vesicles. *ACS Sens.* 2019, 4, (4), 977-983.

(170)Jeong, J. P.; Cho, E.; Yun, D.; Kim, T.; Lee, I. S.; Jung, S., Label-Free Colorimetric Detection of Influenza Antigen Based on an Antibody-Polydiacetylene Conjugate and Its Coated Polyvinylidene Difluoride Membrane. *Polymers* 2017, 9, (4), 9.

(171)Leal, M. P.; Assali, M.; Fernandez, I.; Khiar, N., Copper-Catalyzed Azide-Alkyne Cycloaddition in the Synthesis of Polydiacetylene: "Click Glycoliposome" as Biosensors for the Specific Detection of Lectins. *Chem. - Eur. J.* 2011, 17, (6), 1828-1836.

(172)Son, S. U.; Seo, S. B.; Jane, S.; Choi, J.; Lim, J. W.; Lee, D. K.; Kim, H.; Seo, S.; Kang, T.; Jung, J.; Lim, E. K., Naked-eye detection of pandemic influenza a (pH1N1) virus by polydiacetylene (PDA)-based paper sensor as a point-of-care diagnostic platform. *Sens. Actuators, B* 2019, 291, 257-265.

(173)Deng, J. L.; Sheng, Z. H.; Zhou, K.; Duan, M. X.; Yu, C. Y.; Jiang, L., Construction of Effective Receptor for Recognition of Avian Influenza H5N1 Protein HA1 by Assembly of Monohead Glycolipids on Polydiacetylene Vesicle Surface. *Bioconjugate Chem.* 2009, 20, (3), 533-537.

(174)Reichert, A.; Nagy, J. O.; Spevak, W.; Charych, D., Polydiacetylene Liposomes Functionalized with Sialic Acid Bind and Colorimetrically Detect Influenza Virus. *J. Am. Chem. Soc.* 1995, 117, (2), 829-830.

(175)Tao, J.; Xu, X.; Wang, S.; Kang, T. Y.; Guo, C. Z.; Liu, X.; Cheng, H.; Liu, Y.; Jiang, X.; Mao, J.; Gou, M. L., Polydiacetylene-Nanoparticle-Functionalized Microgels for Topical Bacterial Infection Treatment. *ACS Macro Lett.* 2019, 8, (5), 563-568.

(176)de Oliveira, T. V.; Soares, N. D. F.; de Andrade, N. J.; Silva, D. J.; Medeiros, E. A. A.; Badaro, A. T., Application of PCDA/SPH/CHO/Lysine vesicles to detect pathogenic bacteria in chicken. *Food Chem.* 2015, 172, 428-432.

(177)de Oliveira, T. V.; Soares, N. D. F.; Silva, D. J.; de Andrade, N. J.; Medeiros, E. A. A.; Badaro, A. T., Development of PDA/Phospholipids/Lysine vesicles to detect pathogenic bacteria. *Sens. Actuators, B* 2013, 188, 385-392.

(178)Kim, M.; Shin, Y. J.; Hwang, S. W.; Shin, M. J.; Shin, J. S., Chromatic detection of glucose using polymerization of diacetylene vesicle. *J. Appl. Polym. Sci.* 2018, 135, (25), 5.

(179)Wang, C.; Park, J. H.; Tan, S. W.; Cui, C. Z.; Jin, J. Y.; Ahn, D. J., The Composition-Tunable Polydiacetylenic Complex Films: Conformational Change upon Thermal Stimulation and Preferential Interaction with Specific Small Molecules. *J. Nanomater.* 2017, 1-7.

(180)Wang, D. E.; Yan, J. H.; Jiang, J. J.; Liu, X.; Tian, C.; Xu, J.; Yuan, M. S.; Han, X.; Wang, J. Y., Polydiacetylene liposomes with phenylboronic acid tags: a fluorescence turn-on sensor for sialic acid detection and cell-surface glycan imaging. *Nanoscale* 2018, 10, (9), 4570-4578.

(181)Kamphan, A.; Gong, C. J.; Maiti, K.; Sur, S.; Traiphol, R.; Arya, D. P., Utilization of chromic polydiacetylene assemblies as a platform to probe specific binding between drug and RNA. *RSC Adv.* 2017, 7, (66), 41435-41443.

(182)Qian, X. M.; Stadler, B., Recent Developments in Polydiacetylene-Based Sensors. *Chem. Mat.* 2019, 31, (4), 1196-1222.

(183)de Oliveira, T. V.; Soares, N. D. F.; Coimbra, J. S. D.; de Andrade, N. J.; Moura, L. G.; Medeiros, E. A. A.; de Medeiros, H. S., Stability and sensitivity of polydiacetylene vesicles to detect Salmonella. *Sens. Actuators, B* 2015, 221, 653-658.

(184)Zhang, Y. Y.; Northcutt, J.; Hanks, T.; Miller, I.; Pennington, B.; Jelinek, R.; Han, I.; Dawson, P., Polydiacetylene sensor interaction with food sanitizers and surfactants. *Food Chem.* 2017, 221, 515-520.

(185)Carter, A. P.; Clemons, W. M.; Brodersen, D. E.; Morgan-Warren, R. J.; Wimberly, B. T.; Ramakrishnan, V., Functional insights from the structure of the 30S ribosomal subunit and its interactions with antibiotics. *Nature* 2000, 407, (6802), 340-348.

(186)Xi, H. J.; Davis, E.; Ranjan, N.; Xue, L.; Hyde-Volpe, D.; Arya, D. P., Thermodynamics of Nucleic Acid "Shape Readout" by an Aminosugar. *Biochemistry* 2011, 50, (42), 9088-9113.

(187)Shin, M. J.; Shin, J. S., Chromatic response of cationic polydiacetylene vesicles induced by permeation of target compound. *J. Appl. Polym. Sci.* 2020, 137, 1-7.

(188)Rezende, J. D.; Pacheco, A. F. C.; Magalhaes, O. F.; Coelho, Y. L.; Vidigal, M.; da Silva, L. H. M.; Pires, A. C. D., Polydiacetylene/triblock copolymer/surfactant nanoblend: A simple and rapid method for the colorimetric screening of enrofloxacin residue. *Food Chem.* 2019, 280, 1-7.

(189)He, C. L.; Wang, M. Q.; Sun, X. B.; Zhu, Y.; Zhou, X.; Xiao, S. Y.; Zhang, Q. J.; Liu, F. N.; Yu, Y.; Liang, H. J.; Zou, G., Integrating PDA microtube waveguide system with heterogeneous CHA amplification strategy towards superior sensitive detection of miRNA. *Biosens. Bioelectron.* 2019, 129, 50-57.

(190)Peng, Y.; Croce, C. M., The role of MicroRNAs in human cancer. *Signal Transduction Targeted Ther.* 2016, 1, (15004), 1-9.

(191) Valiyakhmetova, A. M.; Sultanova, E. D.; Burilov, V. A.; Solovieva, S. E.; Antipin, I. S., New DNA-sensor based on thiacalix 4 arene-modified polydiacetylene particles. *Russ. Chem. Bull.* 2019, 68, (5), 1067-1074.

(192) Wang, D. E.; Gao, X. H.; Li, G. B.; Xue, T.; Yang, H.; Xu, H. Y., Facile colorimetric assay of alkaline phosphatase activity using polydiacetylene liposomes with calcium ions and pyrophosphate. *Sens. Actuators, B* 2019, 289, 85-92.

(193) Organization, W. H. *Public health impact of pesticides used in agriculture*; Geneva, Switzerland, 1990; p 128.

(194) Zhang, Y. F.; Bromberg, L.; Lin, Z.; Brown, P.; Van Voorhis, T.; Hatton, T. A., Polydiacetylene functionalized with charged termini for device-free colorimetric detection of malathion. *J. Colloid Interface Sci.* 2018, 528, 27-35.

(195) Jaworski, J.; Yokoyama, K.; Zueger, C.; Chung, W. J.; Lee, S. W.; Majumdar, A., Polydiacetylene Incorporated with Peptide Receptors for the Detection of Trinitrotoluene Explosives. *Langmuir* 2011, 27, (6), 3180-3187.

(196) Nguyen, L. H.; Naficy, S.; McConchie, R.; Dehghani, F.; Chandrawati, R., Polydiacetylene-based sensors to detect food spoilage at low temperatures. *J. Mater. Chem. C* 2019, 7, (7), 1919-1926.

(197) Jeong, W.; Khazi, M. I.; Lee, D. G.; Kim, J. M., Intrinsically Porous Dual-Responsive Polydiacetylenes Based on Tetrahedral Diacetylenes. *Macromolecules* 2018, 51, (24), 10312-10322.

(198)Ali, S.; Ahmed, F.; Khatri, A., Polycaprolactone-Polydiacetylene Electrospun Fibers for Colorimetric Detection of Fake Gasoline. *Mehran Univ. Res. J. Eng. Technol.* 2016, 35, (2), 287-292.

(199)Rao, V. K.; Teradal, N. L.; Jelinek, R., Polydiacetylene Capacitive Artificial Nose. *ACS Appl. Mater. Interfaces* 2019, 11, (4), 4470-4479.

(200)Choi, Y. K.; Kim, H. J.; Kim, S. R.; Cho, Y. M.; Ahn, D. J., Enhanced Thermal Stability of Polyaniline with Polymerizable Dopants. *Macromolecules* 2017, 50, (8), 3164-3170.

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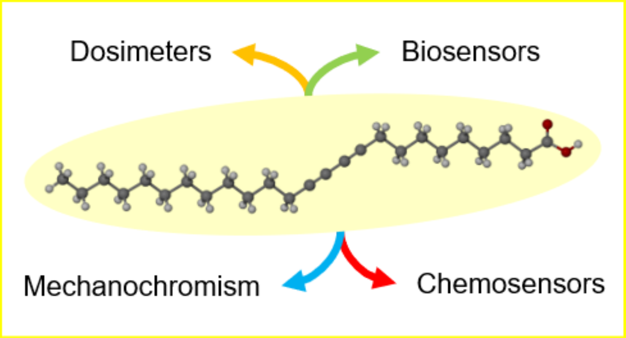
Properties and Applications of Stimuli-responsive Diacetylenes

Amy V. Hall, Osama M. Musa, and Jonathan W. Steed



Synopsis: 10,12-Pentacosadiynoic acid (PCDA) and PCDA derivatives have diverse properties with wide-ranging applications.