



## Research article

Acid-responsive polydiacetylene- $\text{Na}^+$  assemblies with unique red-to-blue color transitionRungarune Saymung<sup>a</sup>, Ruttayapon Potai<sup>b</sup>, Christine M. Papadakis<sup>c</sup>, Nisanart Traiphol<sup>d,e,\*</sup>, Rakchart Traiphol<sup>a,\*\*</sup><sup>a</sup> Laboratory of Advanced Polymers and Nanomaterials, School of Materials Science and Innovation, Faculty of Science, Mahidol University at Salaya, Phuttamonthon 4 Road, Salaya, Nakhon Pathom, 73170, Thailand<sup>b</sup> Division of Chemistry, Faculty of Science, Nakhon Phanom University, Nakhon Phanom, 48000, Thailand<sup>c</sup> Technical University of Munich, TUM School of Natural Sciences, Physics Department, Soft Matter Physics Group, James-Frank-Str. 1, 85748, Garching, Germany<sup>d</sup> Laboratory of Advanced Chromic Materials, Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand<sup>e</sup> Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok, 10330, Thailand

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## ABSTRACT

Polydiacetylenes (PDAs), conjugated and stimuli-responsive polymers, are of interest for colorimetric sensing technologies. Commercially available PDAs with carboxylic headgroup do not show any colorimetric response to acid. To achieve acid-responsive property, the headgroups of PDAs are often modified with some functional moieties, involving complicated synthetic processes. This contribution presents a facile approach to develop acid-responsive materials via co-assembly of PDA and excess sodium hydroxide (NaOH). After low-temperature incubation and photopolymerization, the mixtures of 10,12-tricosadiynoic acid (TCDA) and NaOH develop into red-phase poly (TCDA- $\text{Na}^+$ ) assemblies. A unique red-to-blue color transition occurs when the poly (TCDA- $\text{Na}^+$ ) assemblies are exposed to hydrogen chloride (HCl) acid both in aqueous solution and gas phase. Increasing the concentrations of NaOH and TCDA monomer during the self-assembly process affects the molecular organization and morphologies of the resultant poly (TCDA- $\text{Na}^+$ ) assemblies, which in turn govern the sensitivity to acid. The results of this study offer a simple and inexpensive method for developing acid-responsive PDAs, extending their colorimetric sensing applications.

## 1. Introduction

Polydiacetylenes (PDAs) possess alternating triple/double bonds within the backbone. The PDA side chain can be functionalized with different moieties depending on the desired properties [1–3]. PDAs are often synthesized from well-organized diacetylene (DA) monomers via topotactic 1,4-addition photopolymerization [4–6]. This process usually yields a metastable blue phase of PDA. External stimuli induce segmental rearrangement of PDAs, which consequently cause color transition [1–3,7]. These color-responsive

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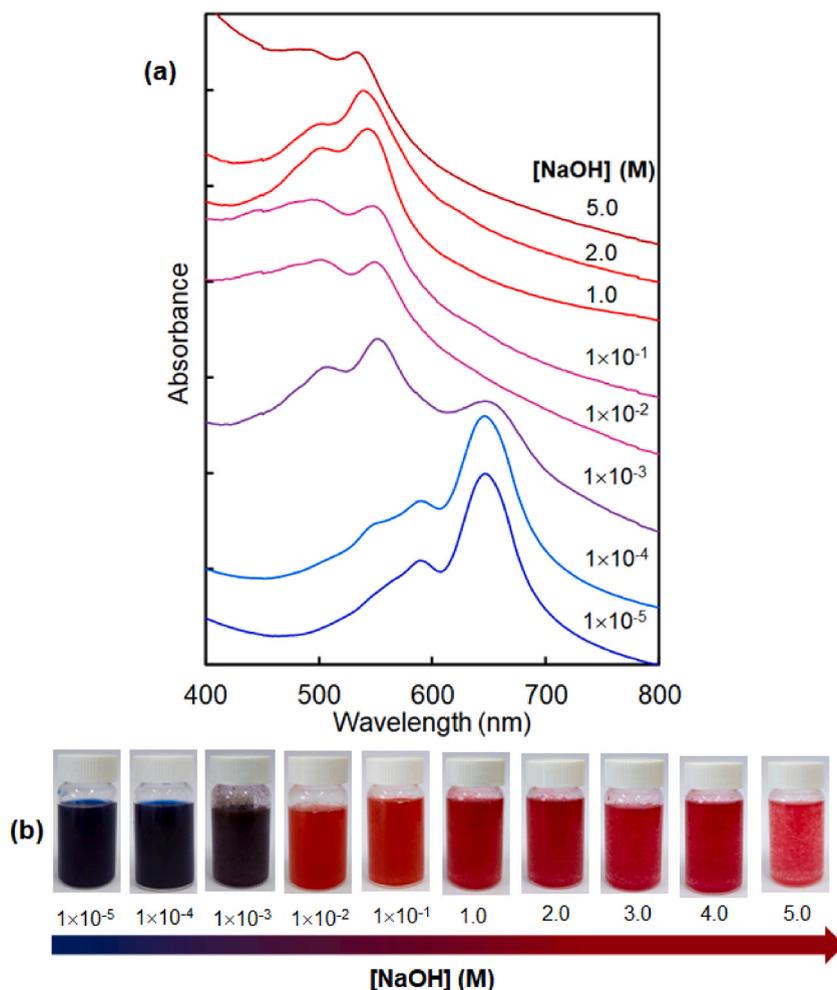
E-mail addresses: [nisanart.t@chula.ac.th](mailto:nisanart.t@chula.ac.th) (N. Traiphol), [rakchart.tra@mahidol.ac.th](mailto:rakchart.tra@mahidol.ac.th) (R. Traiphol).

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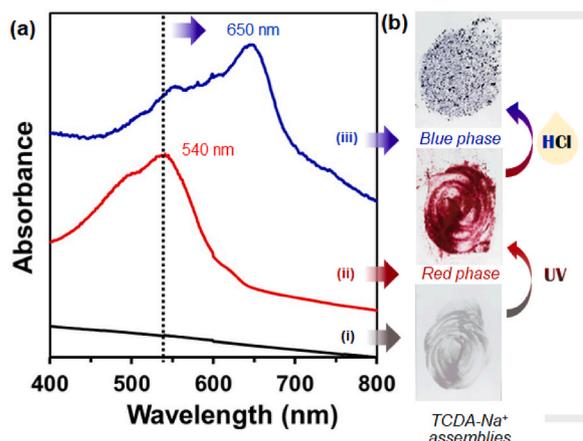
**Fig. 1.** (a) Absorption spectra and (b) photographs of 1 mM poly (TCDA- $\text{Na}^+$ ) assemblies prepared with various NaOH concentrations from  $1 \times 10^{-5}$  to 5 M.

properties allow for colorimetric sensing of temperature [8–13], UV light [5,6], pressure [7], friction force [14,15], acid/base [16–21], organic solvents [22], surfactants [23,24], and polymers [25,26].

A commercially available 10,12-tricosadiynoic acid (TCDA) monomer can be photopolymerized into poly (TCDA) assemblies with an irreversible blue-to-red thermochromism [27,28]. Since the side chain of poly (TCDA) constitutes carboxylic (-COOH) headgroup, it also responds to bases such as sodium hydroxide and alkylamines [27–29]. However, no color transition is observed with addition of acid to the poly (TCDA) system [29]. To utilize the PDA as acid sensors, scientists have synthesized new types of DA monomers with various functional headgroups such as amine, amide, imidazole and triazole [27,30–34]. For example, Jeon and coworkers showed that newly synthesized PDA with trimethyl amine headgroup responded to HCl gas by changing color from blue to red and exhibiting fluorescence [32]. Similarly, PDAs with amide and tertiary amine moieties, fabricated into various forms such as PDA-embedded PVC film, PDA-embedded PS film, and PDA-printed on paper, showed acid-responsive property [34]. However, the syntheses of new PDAs often involve complicated and time-consuming processes that may present obstacles for industrial-scale applications.

Intercalation of metal cations into PDA interlayer has the potential for enhancing the PDA formations and/or creating unique stimuli-responsive properties [8,13,17,35–43]. For example,  $\text{Zn}^{2+}$  ion intercalated with PDA bilayers results in a reversible thermochromism [8,13,37,39,40].  $\text{Li}^+$  ion addition leads to the increase of sensitivity to UV light [41]. The co-assembly of PDA with  $\text{Cs}^+$  ion yields new materials that exhibit colorimetric response to water [42,43]. Recently, our group introduced poly (HDDA- $\text{Na}^+$ ) nanoribbons, synthesized via co-assembly of 5,7-hexadecadiynoic acid (HDDA) and excess sodium hydroxide (NaOH), for colorimetric sensing of HCl gas [17]. The system exhibited fast color transition from red to orange at 400 ppm HCl gas. However, water also induced the color changing of poly (HDDA- $\text{Na}^+$ ) nanoribbons, limiting the utilization for colorimetric detection of acid in an aqueous phase.

In this study, we have found that the co-assembly of TCDA monomer and excess NaOH, followed by low-temperature incubation and then photopolymerization, produces red-phase poly (TCDA- $\text{Na}^+$ ) assemblies. This system exhibits an unusual red-to-blue color change when exposed to HCl acid in both aqueous and gaseous phases. The colorimetric response to HCl of poly (TCDA- $\text{Na}^+$ ) and poly



**Fig. 2.** (a) Absorption spectra and (b) the colorimetric response of 1 mM poly (TCDA-Na<sup>+</sup>) assemblies to HCl acid. Sample was prepared using 1 M NaOH. (i) Colorless TCDA-Na<sup>+</sup> assemblies before polymerization. Poly (TCDA-Na<sup>+</sup>) assemblies (ii) before and (iii) after the addition of 50  $\mu$ L of 1 M HCl aqueous solution.

(HDDA-Na<sup>+</sup>) systems are rather different. Furthermore, the PDA with red-to-blue color transition is quite rare [44,45]. The PDA alkyl chain length also affects the responsive properties of PDA-Na<sup>+</sup> assemblies. This fundamental knowledge is useful for developing acid-responsive PDA materials for colorimetric detection of acid.

## 2. Experimental

TCDA monomer was commercially available from Sigma-Aldrich as well as NaOH and HCl in AR grade. The preparation of poly (TCDA-Na<sup>+</sup>) assemblies was adopted from our previous study [17]. Briefly, a TCDA solution in ethanol was slowly dried at 60  $^{\circ}$ C. NaOH aqueous solution (10 mL) was added to the dried TCDA film, then, ultrasonicated at  $\sim$ 80  $^{\circ}$ C for 90 min. In the first experiment, the TCDA concentration was fixed at 1 mM while the NaOH concentrations were 0–5 M. The (TCDA:NaOH) molar ratios in these samples were (1:0), (1:0.01), (1:0.1), (1:1), (1:10), (1:100), (1:1000), (1:2000), (1:3000), (1:4000) and (1:5000). In the second experiment, the NaOH concentration was fixed at 1 M while the TCDA concentration was increased from 1 mM to 100 mM. The samples were allowed for co-assembly overnight at 4  $^{\circ}$ C, then UV irradiated (10 W,  $\lambda$   $\sim$ 254 nm) for 2 min, yielding blue or red suspensions.

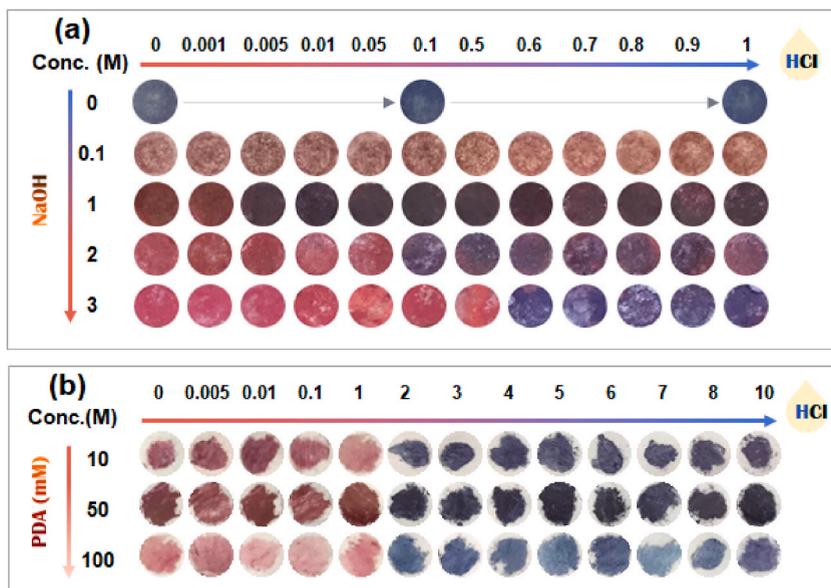
Absorption spectra of solution and solid phase samples were measured using UV–VIS spectrophotometry (LABTECH, Blue Star B). Morphologies were explored by field emission scanning electron microscopy (FE-SEM, FEI Nova Nano SEM 450) using samples cast on glass slides. Thermal property was measured by differential scanning calorimeter (DSC, TA Instruments Q200) in nitrogen atmosphere at 5  $^{\circ}$ C/min heating/cooling rate. Fourier-transformed infrared spectrometer (FT-IR, Thermo Scientific Nicolet 6700) with attenuated total reflectance (ATR) mode and Raman microscope (Horiba, XploRA Plus, excitation wavelength 785 nm) were employed for studying local interactions using samples cast on glass slides. X-ray diffraction patterns of samples cast on a silicon wafer (111) were acquired by X-ray diffractometer (Bruker AXS Model D8 Discover) under ambient conditions.

To prepare poly (TCDA-Na<sup>+</sup>) thin films, suspensions were cast on filter papers (1 cm  $\times$  1 cm), dried at room temperature, and UV irradiated for 2 min. The resulting red-phase poly (TCDA-Na<sup>+</sup>) paper-based sensors were exposed to a 50  $\mu$ L drop of HCl solution with various concentrations for  $\sim$ 5 min before photographing. Colorimetric detection of HCl gas was described in our previous report [17].

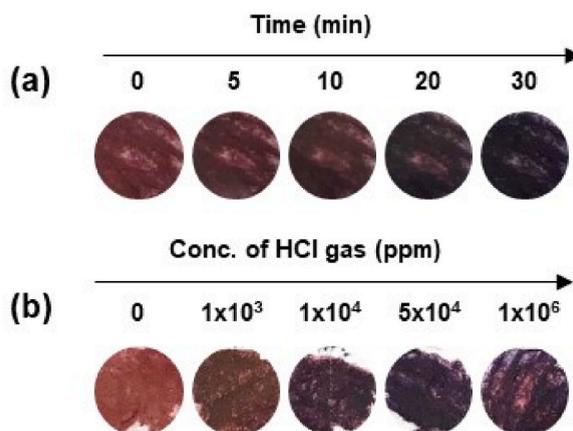
## 3. Results and discussion

### 3.1. Red-to-blue colorimetric response to acid

In the first part, the effects of NaOH concentrations on self-assembly and optical properties of poly (TCDA) were studied. Fig. 1a illustrates the absorption spectra of 1 mM poly (TCDA-Na<sup>+</sup>) assemblies synthesized by increasing NaOH concentrations from  $1 \times 10^{-5}$  to 5 M. The spectra of 1 mM poly (TCDA) assemblies with 0.01 and 0.1 mM NaOH exhibit a characteristic blue-phase peak at  $\sim$ 645 nm. Further increasing the concentration of NaOH to 1 mM causes a new peak to appear at  $\sim$ 540 nm indicating the red phase formation. The original blue-phase peak is still observed. When increasing the NaOH concentration to 10 mM, the suspension shows an intense red color (Fig. 1b). Since the NaOH concentration is 10 times higher than the TCDA concentration, all –COOH headgroups of TCDA are expected to react with NaOH, converting them to –COO<sup>−</sup>Na<sup>+</sup> groups. The local interactions at the headgroup alter, influencing segmental arrangements within the assemblies, and resulting in the red phase poly (TCDA-Na<sup>+</sup>) [44–46]. At high NaOH concentration (1–5 M), large aggregates are observed. The large excess of NaOH (1–5 M) increases the ionic strength of the aqueous medium, and, then, affects the growth and morphologies of poly (TCDA-Na<sup>+</sup>) assemblies. This hypothesis is parallel to our recent study showing that the change of physicochemical properties of solvent media drastically affects the self-assembly of PDAs [22]. The increase of TCDA concentration to 100 mM while fixing NaOH concentration at 1 M causes the increase of viscosity (Fig. S1, supporting information).



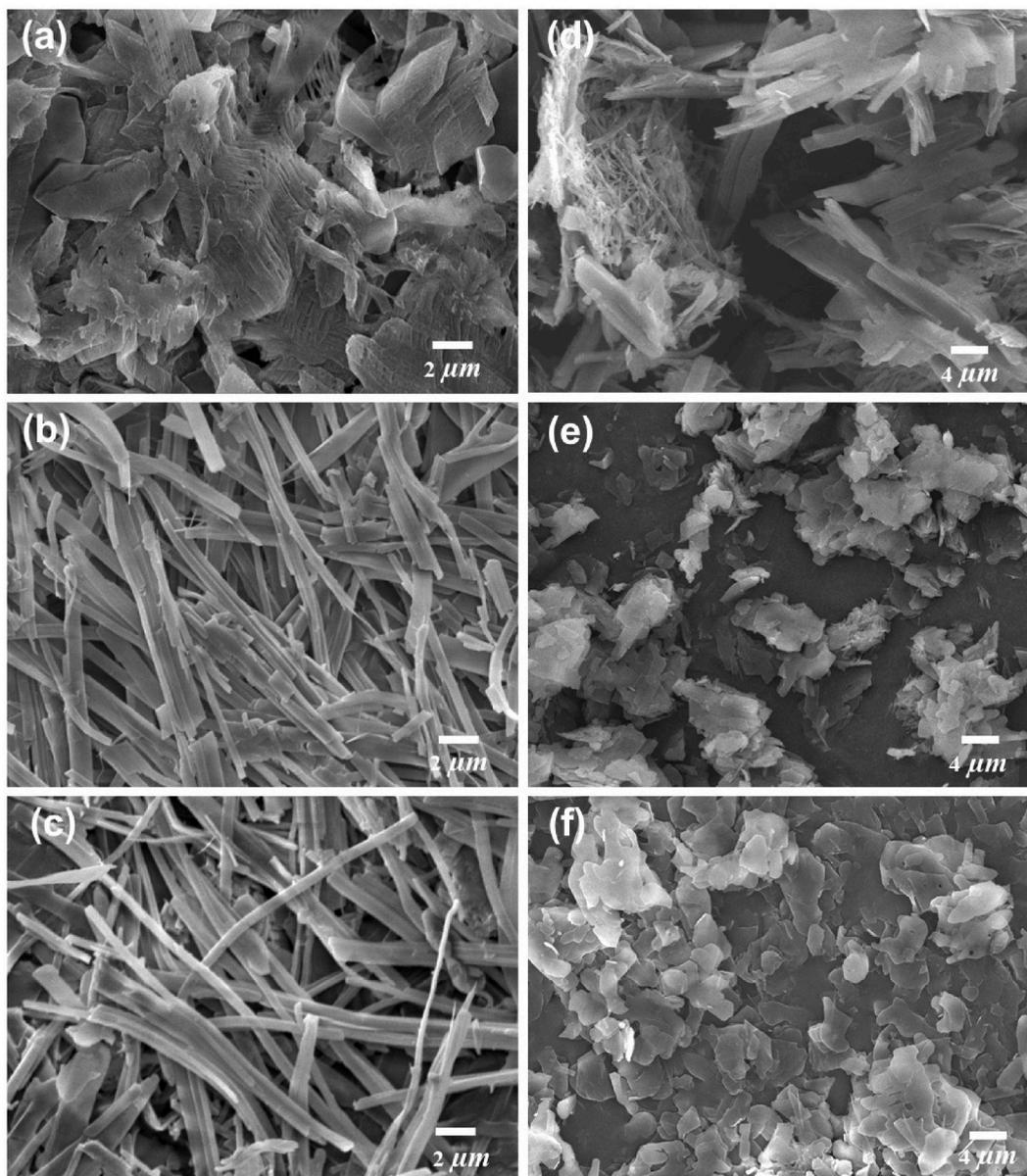
**Fig. 3.** Photographs showing color transition of poly (TCDA- $\text{Na}^+$ ) assemblies upon addition of HCl aqueous solutions with various concentrations. (a) The poly (TCDA- $\text{Na}^+$ ) assemblies were prepared using NaOH concentrations at 0, 0.1, 1, 2, and 3 M with 1 mM TCDA concentration. (b) The poly (TCDA- $\text{Na}^+$ ) assemblies were prepared by increasing TCDA concentrations to 10, 50, and 100 mM with fixed NaOH concentration at 1 M. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 4.** Photographs of poly (TCDA- $\text{Na}^+$ ) films (1 mM TCDA and 1 M NaOH). (a) The film was exposed to  $1 \times 10^6$  ppm of HCl gas. Pictures were taken upon increasing the exposure time from 0 to 30 min. (b) The poly (TCDA- $\text{Na}^+$ ) films were exposed to HCl gas with different concentrations. Pictures were taken at 30 min of exposure time.

However, the poly (TCDA- $\text{Na}^+$ ) assemblies do not form a gel phase at room temperature unlike the system of poly (HDDA- $\text{Na}^+$ ) assemblies [17]. This observation suggests that the alkyl chain length of DA monomers affects the physical gelation. We are currently exploring this topic in our laboratory.

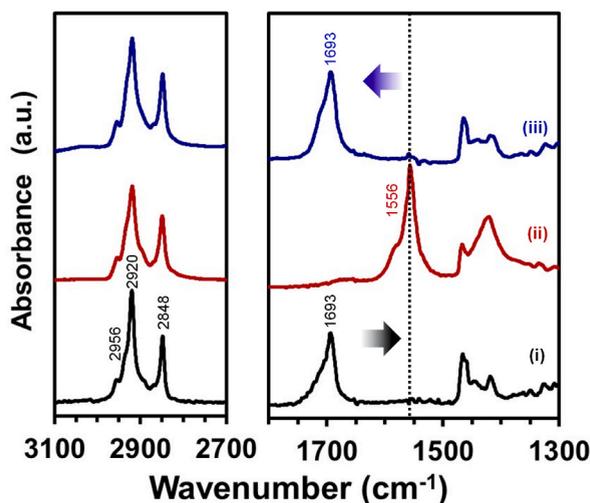
When PDA materials are subjected to external stimuli, the common color transition is blue-to-red [1,2,4,27,28]. However, there are reports of different color transitions i.e., blue-to-purple, purple-to-red, red-to-orange, blue-to-orange, and blue-to-yellow, depending on their molecular architectures and/or chemical stimuli [11,12,17,23–25]. The color transition generally involves conformational changes of alkyl side chain and PDA backbone [44–46]. In this study, we detect an unusual color transition from red to blue of the poly (TCDA- $\text{Na}^+$ ) assemblies when subjected to HCl acid. Fig. 2 displays the absorption spectra and the colorimetric response of poly (TCDA- $\text{Na}^+$ ) films (prepared from 1 mM TCDA and 1 M NaOH). After polymerization by UV-light, the colorless TCDA- $\text{Na}^+$  assemblies change to red phase, governing with the absorption peak at  $\sim 540$  nm (Fig. 2(ii)). The red phase was also observed in previous studies with other DA monomers, including HDDA, 5,7-octadecadiynoic acid (ODDA), and 10,12-pentacosadiynoic acid (PCDA) [17,44,45, 47]. Comprehensive study of PCDA- $\text{Na}^+$  assemblies showed that  $\text{Na}^+$  ions and carboxylate headgroups form strong electrostatic interaction that prohibited the molecular rearrangement during the topotactic polymerization [44]. Therefore, the conjugated



**Fig. 5.** SEM images of poly (TCDA- $\text{Na}^+$ ) assemblies (a) 1 mM TCDA, 0.1 M NaOH, (b) 1 mM TCDA, 1 M NaOH, (c) 1 mM TCDA, 2 M NaOH, (d) 10 mM TCDA, 1 M NaOH, (e) 50 mM TCDA, 1 M NaOH, and (f) 100 mM TCDA, 1 M NaOH.

backbone of resultant poly (PCDA- $\text{Na}^+$ ) exhibited relatively short conjugation length (i.e., red phase). We have found that the red poly (TCDA- $\text{Na}^+$ ) film in this study changes color to blue upon exposure to 1 M HCl aqueous solution. The absorption spectrum exhibits the shift of  $\lambda_{\text{max}}$  from  $\sim 540$  nm to  $\sim 640$  nm indicating the longer conjugation length of poly (TCDA- $\text{Na}^+$ ) assemblies (Fig. 2(iii)). This is opposite to the common blue-to-red color transition detected in many PDAs [1,27,28]. The origins of this phenomenon will be further discussed in the following section. The red-to-blue color transition was also detected for the poly (PCDA- $\text{Na}^+$ ) system [44]. However, the color transition occurred when the sample was annealed near the melting temperature of PCDA monomer.

The colorimetric response of poly (TCDA- $\text{Na}^+$ ) assemblies can be controlled by increasing the concentrations of NaOH and TCDA during the synthesis. Fig. 3 illustrates the colorimetric response of poly (TCDA- $\text{Na}^+$ ) films coated on filter papers upon exposure to HCl of various concentrations. The blue films of pristine poly (TCDA) with  $-\text{COOH}$  headgroup do not show any response to HCl acid. The red films of poly (TCDA- $\text{Na}^+$ ) assemblies prepared from 0.1 M NaOH hardly show any colorimetric response upon increasing the HCl concentration up to 1 M. In a solution phase, however, we observe a slight change to purple color at  $\sim 4$  M HCl (Fig. S2, supporting information). A small growth of blue-phase peak at  $\sim 640$  nm can be observed. Further increasing NaOH concentration to 1, 2, and 3 M provides the red poly (TCDA- $\text{Na}^+$ ) assemblies that change color to purple/blue at  $\sim 0.005$ ,  $\sim 0.1$ , and  $\sim 0.6$  M HCl, respectively (Fig. 3a). This result suggests that this class of PDAs could be utilized for semiquantitative analysis of HCl acid based on their



**Fig. 6.** FT-IR spectra of (i) pure poly (TCDA), and poly (TCDA-Na<sup>+</sup>) assemblies (ii) before (red phase) and (iii) after (blue phase) exposing to 1 M HCl aqueous solution. The poly (TCDA-Na<sup>+</sup>) assemblies were prepared at 1 mM TCDA and 1 M NaOH. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

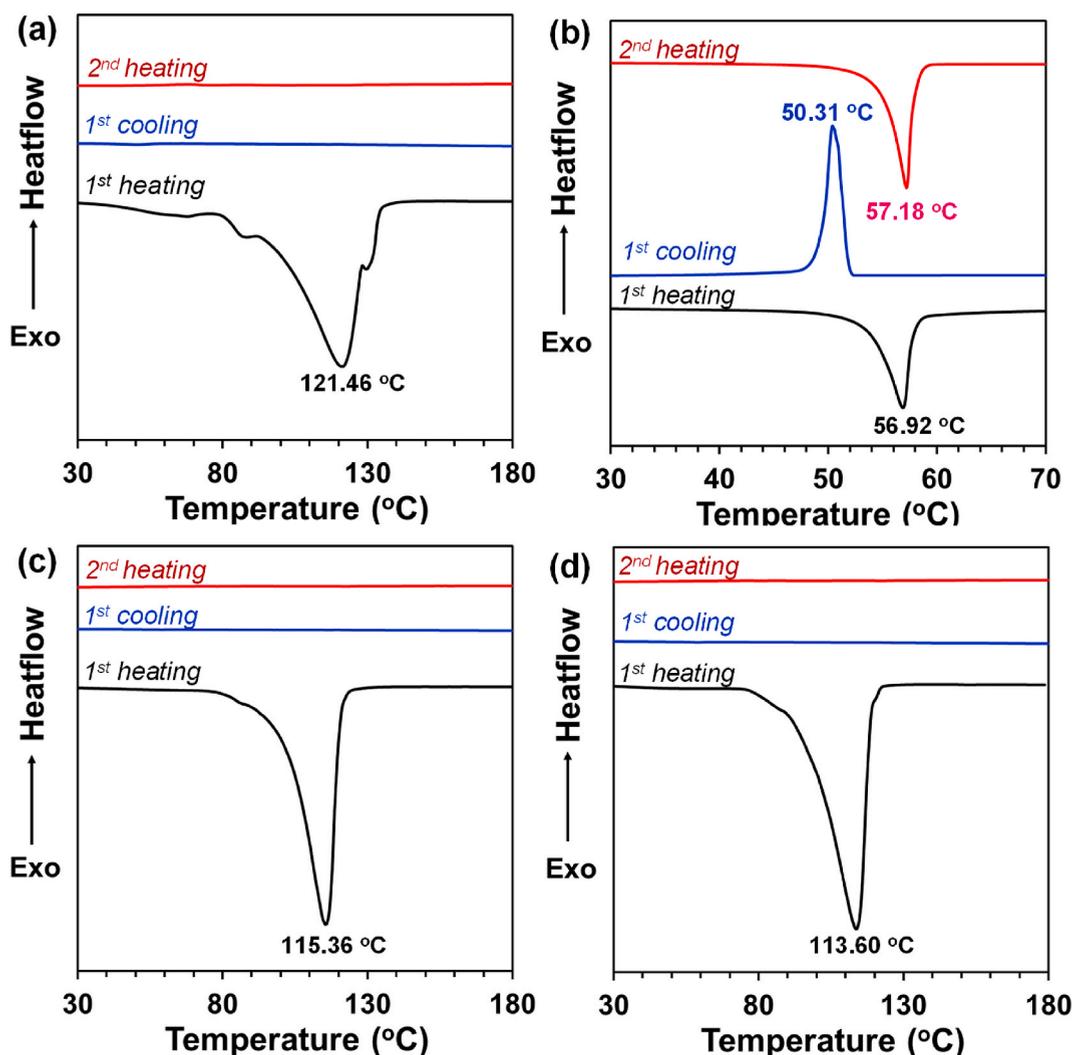
colorimetric responses. We believe that the residual NaOH affects the sensitivity of poly (TCDA-Na<sup>+</sup>) sensors. The added HCl solution reacts with both poly (TCDA-Na<sup>+</sup>) assemblies and the residual NaOH within the films. Therefore, the HCl concentration required for neutralizing the residual NaOH increases with the NaOH concentration used for synthesizing the poly (TCDA-Na<sup>+</sup>) assemblies. The poly (TCDA-Na<sup>+</sup>) sensors fabricated at fixed NaOH concentration (1 M) while varying the TCDA concentrations (10, 50, and 100 mM) exhibit a similar color-transition behavior as shown in Fig. 3b. All sensors exhibit the red-to-blue color transition at ~2 M HCl. We point out that these systems change color at higher HCl concentration compared to the sensors prepared with 1 mM TCDA. This is due to the higher concentrations of poly (TCDA-Na<sup>+</sup>) assemblies. The change in morphologies may also affect sensitivity. The mechanism of color transition will be further discussed in the next section.

Our previous study showed that the poly (HDDA-Na<sup>+</sup>) sensors exhibited color transition from red to orange within 60 s when exposed to HCl gas at 1300 ppm [17]. Fig. 4 shows that the poly (TCDA-Na<sup>+</sup>) can also detect HCl gas. At  $1 \times 10^6$  ppm HCl, the red poly (TCDA-Na<sup>+</sup>) sensor prepared from 1 M NaOH changes to blue at ~30 min of exposure time. When the exposure time is fixed at 30 min, the sensors change from red to blue at  $\sim 1 \times 10^4$  ppm HCl. Compared to the poly (HDDA-Na<sup>+</sup>), the poly (TCDA-Na<sup>+</sup>) sensor changes color with HCl at longer exposure time and higher HCl gas concentration. It has been known that hydrogen bond and Van der Waals force stabilize the PDA structure [27,28]. The poly (TCDA-Na<sup>+</sup>) assemblies with longer alkyl side chain exhibit stronger intrachain interaction i.e., Van der Waals force, within the assemblies compared to the poly (HDDA-Na<sup>+</sup>). Therefore, the sensitivity to HCl gas of poly (TCDA-Na<sup>+</sup>) is lower than that of the poly (HDDA-Na<sup>+</sup>) sensor. It is noted that water can also cause the color transition (red-to-orange) in poly (HDDA-Na<sup>+</sup>) sensors [17]. However, the red color of poly (TCDA-Na<sup>+</sup>) sensor remains unchanged upon exposure to water.

### 3.2. Morphologies, local interactions, conformations, and packing structures

Fig. 5 shows the morphologies of poly (TCDA-Na<sup>+</sup>) assemblies explored by SEM. The poly (TCDA-Na<sup>+</sup>) assemblies (0.1 M NaOH) exhibit a sheet-like structure (Fig. 5a). Some well-organized nanoribbons (width ~50–100 nm) are detected within the sheets. Upon increasing NaOH concentration to 1 M, the morphologies change to a ribbon-like structure with ~100 nm–150 nm in width and >20 μm in length. Further increasing NaOH concentration to 2 M results in the increase of ribbon width (~150–200 nm) (Fig. 5c). At 3 M NaOH, the ribbon width increases to a micron size (Fig. S3, supporting information). We suggest that the increase of excess NaOH concentration (i.e., increasing in ionic strength) enhances the hydrophobic interaction between the TCDA alkyl tail and the aqueous medium. The solubility of TCDA decreases at high NaOH concentrations, affecting the self-assembly, and leading to different morphologies. The influences of solvent properties on the self-assembly and morphology of PDAs were discussed in our previous report [22]. The poly (TCDA-Na<sup>+</sup>) assemblies prepared at relatively high TCDA concentrations also exhibit different morphologies. When NaOH is fixed 1 M, the TCDA concentration increased from 1 to 10 mM still yields the ribbon-like structure (Fig. 5d). However, the ribbon width significantly increases. When TCDA concentrations increase to 50 and 100 mM, the formation of micron-size sheet-like aggregates occurs (Fig. 5e and f). We do not observe the ribbon-like structure under these conditions. SEM images show that the poly (TCDA-Na<sup>+</sup>) morphologies vary with the NaOH and TCDA concentrations. We suggest that the change in morphologies may also affect their colorimetric responses to HCl acid.

FT-IR spectroscopy reveals the local interactions of poly (TCDA-Na<sup>+</sup>) assemblies before and after subjected to HCl acid (Fig. 6). The pure poly (TCDA) spectrum constitutes peaks of  $\nu_s$  (CH<sub>2</sub>),  $\nu_{as}$  (CH<sub>2</sub>), and  $\nu_{as}$  (CH<sub>3</sub>) at 2848, 2920, and 2956 cm<sup>-1</sup>, respectively [37,45]. A broad peak at 1693 cm<sup>-1</sup> is due to hydrogen-bonded carbonyl stretching of -COOH headgroup [28,37]. The peak at 1693 cm<sup>-1</sup>

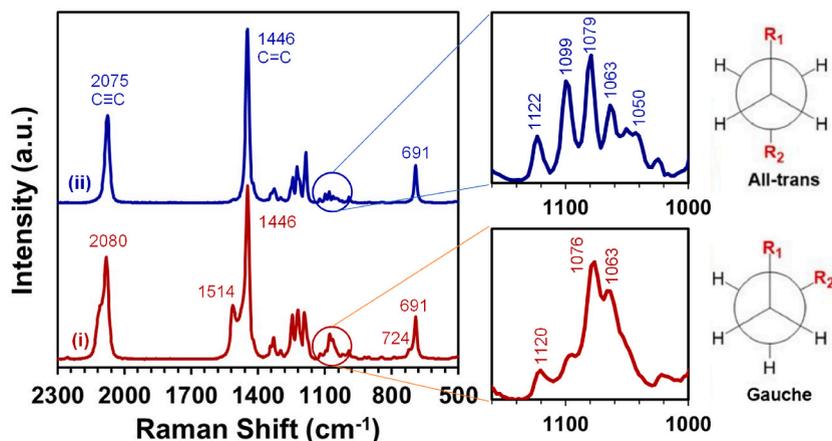


**Fig. 7.** DSC thermograms of red-phase poly (TCDA- $\text{Na}^+$ ) assemblies (a) 1 mM TCDA, 1 M NaOH, (c) 1 mM TCDA, 2 M NaOH, and (d) 1 mM TCDA, 3 M NaOH. (b) DSC thermogram of blue-phase poly (TCDA- $\text{Na}^+$ ) assemblies (prepared from 1 M NaOH) obtained by adding 50  $\mu\text{L}$  of 1 M HCl acid. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

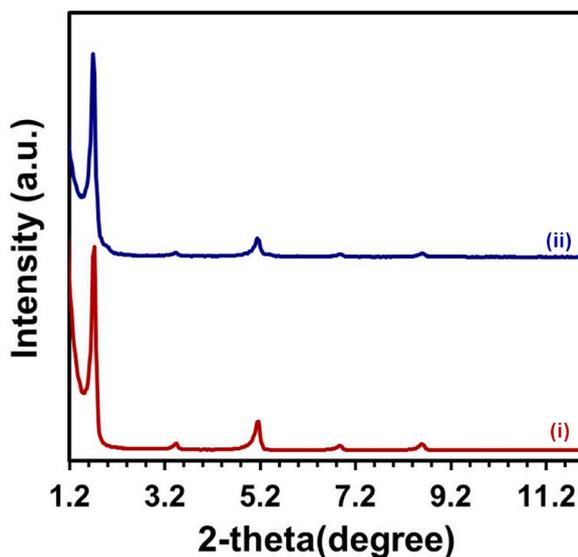
disappears in the red-phase poly (TCDA- $\text{Na}^+$ ) spectrum while a peak at  $1556\text{ cm}^{-1}$  is detected, indicating sodium carboxylate ( $-\text{COO}^-\text{Na}^+$ ) [45,46]. At 1 M HCl, the poly (TCDA- $\text{Na}^+$ ) assemblies change to blue phase. The  $-\text{COO}^-\text{Na}^+$  groups are protonated by  $\text{H}^+$  ions, forming  $-\text{COOH}$  headgroups. The re-appearance of carbonyl peak at  $1693\text{ cm}^{-1}$  indicates the H-bond between the  $-\text{COOH}$  headgroups. FT-IR measurements of the poly (TCDA- $\text{Na}^+$ ) assemblies prepared by using (TCDA:NaOH) molar ratios of (1:10), (1:100) and (1:1000) are also examined (Fig. S4, supporting information). The spectra of all samples show the characteristic peak of  $-\text{COO}^-\text{Na}^+$  group at  $1556\text{ cm}^{-1}$ , indicating the same local interaction.

DSC measurement of the red-phase poly (TCDA- $\text{Na}^+$ ) assemblies (1 mM TCDA, 1 M NaOH) exhibits a broad melting peak at  $\sim 121\text{ }^\circ\text{C}$  in the 1<sup>st</sup> heating cycle (Fig. 7). Our previous study reported the melting point of the pure poly (TCDA) at  $\sim 52\text{ }^\circ\text{C}$  [48]. We suggest that the higher melting point of poly (TCDA- $\text{Na}^+$ ) assemblies arises from the strong local interaction between  $-\text{COO}^-$  group and  $\text{Na}^+$  ion. Upon the 1<sup>st</sup> cooling from  $200\text{ }^\circ\text{C}$ , the poly (TCDA- $\text{Na}^+$ ) assemblies become amorphous. The 2<sup>nd</sup> heating cycle does not detect any melting peak. The poly (TCDA- $\text{Na}^+$ ) assemblies prepared from 2 M to 3 M NaOH show similar thermal behaviors. The red-to-blue color transition occurs when the poly (TCDA- $\text{Na}^+$ ) assemblies are exposed to 1 M HCl aqueous solution. Interestingly, the 1<sup>st</sup> heating cycle of blue-phase poly (TCDA- $\text{Na}^+$ ) assemblies shows melting temperature at  $\sim 57\text{ }^\circ\text{C}$ , comparable to that of the pure poly (TCDA) assemblies. The 1<sup>st</sup> cooling cycle also detects recrystallization temperature at  $\sim 50\text{ }^\circ\text{C}$ . The 2<sup>nd</sup> heating cycle observes the melting point at a slightly higher temperature. This observation is in agreement with the FT-IR result where the poly (TCDA- $\text{Na}^+$ ) assemblies with H-bonded carboxylic headgroup form in the blue phase. Therefore, the thermal properties of blue-phase poly (TCDA- $\text{Na}^+$ ) assemblies are similar to those of the pure poly (TCDA) assemblies.

Raman spectroscopy was employed to study conjugated backbone and alkyl side chain conformations. Fig. 8 shows that the red-



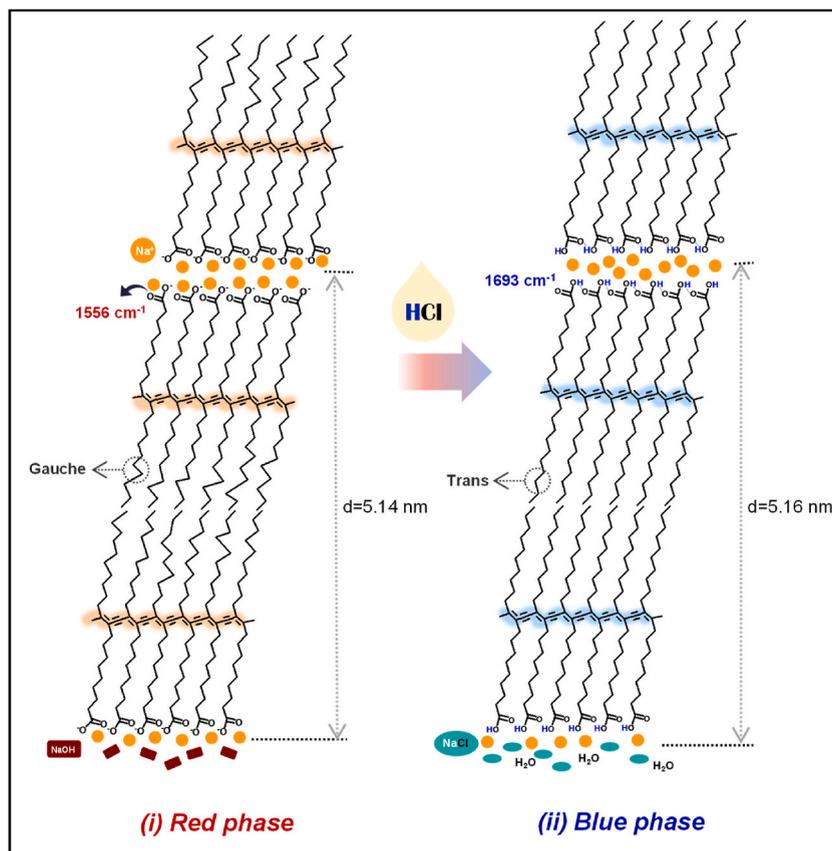
**Fig. 8.** Raman spectra of poly (TCDA-Na<sup>+</sup>) assemblies (i) before (red phase) and (ii) after (blue phase) exposing to 1 M HCl aqueous solution. The poly (TCDA-Na<sup>+</sup>) assemblies were prepared at 1 mM TCDA and 1 M NaOH. The all-trans and gauche conformations of alkyl side chains are shown on the right side of spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 9.** XRD profiles of poly (TCDA-Na<sup>+</sup>) assemblies (i) before (red phase) and (ii) after (blue phase) exposing to 1 M HCl aqueous solution. The poly (TCDA-Na<sup>+</sup>) assemblies were prepared at 1 mM TCDA and 1 M NaOH. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

phase poly (TCDA-Na<sup>+</sup>) assemblies exhibits two strong peaks of the C≡C and C=C stretching modes of the conjugated backbone at 2080 cm<sup>-1</sup> and 1446 cm<sup>-1</sup> [5,6,8,46,47]. The spectrum also constitutes small peaks at ~2100 cm<sup>-1</sup> and 1514 cm<sup>-1</sup>, indicating that a small fraction of poly (TCDA) backbone exists in different local environments. Upon exposure to HCl aqueous solution, the C≡C peak shifts to 2075 cm<sup>-1</sup> while the C=C bond shows a single peak at 1446 cm<sup>-1</sup>. The local interaction changes are suggested to induce segmental rearrangements, causing the red-to-blue color transition of poly (TCDA-Na<sup>+</sup>) assemblies. The broad bands in the region of 1150–1000 cm<sup>-1</sup> become sharp peaks in the blue phase, indicating the conformational change from gauche to trans of the alkyl side chain [6,12,25,46]. The peak at 691 cm<sup>-1</sup> corresponds to the C–C bending mode of poly (TCDA) conjugated backbone [8,49–52]. In the red phase, there are two peaks at 724 cm<sup>-1</sup> and 691 cm<sup>-1</sup>. These peaks merge into one peak at 691 cm<sup>-1</sup> in blue phase, confirming the rearrangement of poly (TCDA) backbone.

The molecular packing structure of poly (TCDA-Na<sup>+</sup>) assemblies was studied (Fig. 9). The XRD pattern of red-phase poly (TCDA-Na<sup>+</sup>) assemblies contains five peaks at 2θ = 1.7° (001), 3.4° (002), 5.2° (003), 6.8° (004) and 8.6° (005), corresponding to a lamellar structure with a d-spacing of 5.14 nm [8,46,53,54]. The d-spacing value of poly (TCDA-Na<sup>+</sup>) is much higher than that of the pure poly (TCDA) assemblies (d = 4.16 nm) [28,54]. Our observation suggests the intercalation of Na<sup>+</sup> ions with the poly (TCDA) bilayers. The XRD pattern of blue-phase poly (TCDA-Na<sup>+</sup>) assemblies also illustrates the lamellar structure with slightly larger d-spacing (d = 5.16



**Fig. 10.** Schematic model represents structural change of poly (TCDA- $\text{Na}^+$ ) when red-to-blue color transition occurred. (i) Before (red phase) and (ii) after (blue phase) exposing to 1 M HCl aqueous solution. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

nm). We point out that the interlayer d-spacing value of the blue phase hardly changes compared to that of the red phase. This result suggests that the  $\text{Na}^+$  ions remain in the interlayer space of poly (TCDA) bilayer.

From these results, a schematic model of structural change during the red-to-blue color transition is proposed in Fig. 10. The red-phase poly (TCDA- $\text{Na}^+$ ) assemblies exhibit  $\text{Na}^+$ -intercalated bilayer structure where some segments of the alkyl side chains adopt a gauche conformation. There is residual NaOH in the poly (TCDA- $\text{Na}^+$ ) film. The added HCl acid protonates the  $-\text{COO}^-\text{Na}^+$  headgroups and reacts with the residual NaOH. The change of local interactions induces conformational changes of conjugated backbones and alkyl side chains, resulting in the red-to-blue color transition. The sensitivity to acid varies with the concentrations of residual NaOH and poly (TCDA- $\text{Na}^+$ ). It is worthwhile to note that the red phase of poly (TCDA- $\text{Na}^+$ ) assemblies has different crystal structure compared to the red phase of pure poly (TCDA). We believe that the presence of strong interaction between  $-\text{COO}^-$  headgroup and  $\text{Na}^+$  ion restricts the segmental rearrangements during topotactic polymerization, yielding the metastable red phase [44]. The perturbation by HCl acid weakens the local interaction, allowing the segmental rearrangement to the more stable blue phase.

#### 4. Conclusion

Our study demonstrates a facile route for synthesizing acid-responsive poly (TCDA- $\text{Na}^+$ ) assemblies that exhibit a unique red-to-blue color transition. The color transition mechanism involves the protonation of  $-\text{COO}^-\text{Na}^+$  headgroups, leading to the conformational changes of conjugated backbone and alkyl side chains. The sensitivity of this system can be controlled by adjusting experimental conditions such as NaOH and TCDA concentrations during the synthesis. These properties allow for naked eye detection of HCl acid at different concentration ranges. This research offers an alternative development path of PDA-based materials for colorimetric sensing of acids.

#### Data availability statement

Data will be made available on request.

## CRediT authorship contribution statement

**Rungarune Saymung:** Writing – original draft, Visualization, Methodology, Investigation. **Ruttayapon Potai:** Investigation. **Christine M. Papadakis:** Formal analysis. **Nisanart Traiphol:** Writing – review & editing, Funding acquisition, Formal analysis, Conceptualization. **Rakchart Traiphol:** Writing – review & editing, Funding acquisition, Formal analysis, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e27574>.

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