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## Perylene diimide derivative via ionic self-assembly: helical

## supramolecular structure and selective detection of ATP

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#### Abstract

A novel perylene diimide material (perylene diimide tetracid- dihexadecyldimethylammonium bromide, PDTA-DHAB) with unique hierarchical structure was designed and prepared by ionic self-assembly (ISA) method. The self-assembly behavior and aggregated structure of the complex were then studied by a variety of techniques such as UV-Vis absorption spectra, differential scanning calorimetry, and two-dimensional X-ray diffraction. With the presence of a rigid linkage, the complex can self-assemble into highly ordered helical columns which further pack into a monoclinic crystalline lattice with dimensions of a = 4.02 nm, b = 3.40 nm, c = 2.90 nm,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 92^{\circ}$ . During heating, the helical supramolecular structure was destroyed and transformed to a lamellar liquid crystalline phase. Furthermore, the complex solution upon addition of ATP showed a remarkable absorption and fluorescence intensity decrease compared with other anions. These results will provide insight into the rational design of functional materials with helical supramolecular structure through ISA method.

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### 1. Introduction

Perylene diimides (PDIs), as an important class of fluorophores, have been intensively studied owing to their excellent properties, such as high thermal and photochemical stability,<sup>1</sup> extraordinary spectroscopical and electrochemical property.<sup>2-4</sup> The dyes and their derivatives have a wide range of practical applications in organic photovoltaic cells,<sup>5</sup> organic field-effect transistors,<sup>6,7</sup> liquid-crystal displays<sup>8</sup> and fluorescent chemosensors.<sup>9,10</sup> In order to further optimize the properties of PDIs, the introduction of substituent groups at the imide position or bay region of the perylene core is an effective strategy. In the past decade, many researches have been working on enhancing the performance of PDI materials by purposeful molecular designing.<sup>11-14</sup> For example, we and other laboratories have reported that the bulky nanoparticle substituents connected to perylene cores can restrain their strong self-assembly by the spatially steric hindrance, which consistently improve the solubility and the fluorescence quantum yield both in solution and in solid state.<sup>15-18</sup> The chemical modification of PDIs would modulate their physical and chemical properties, which further offers more possibilities for the applications in different fields. However, most of the chemical methods require harsh synthesis conditions, and often the yield is relatively low.

Ionic self-assembly (ISA) is a simple non-covalent strategy to construct novel functional materials based on the combination of charged functional species with opposite charged surfactants.<sup>19-23</sup> This synthetic method has been widely used to fabricate PDI materials with diverse supramolecular structures owing to its advantages of feasibility, green, and high yield.<sup>19</sup> The ISA process utilizes electrostatic interactions between charged PDIs and oppositely charged surfactants as the primary interaction to drive structure formation. Other noncovalent interactions such as  $\pi$ - $\pi$  interactions, hydrogen bonding, and geometric factor can be used as secondary driving force to further promote and stabilize the organization of the assemblies.<sup>20</sup> By careful selection of both components involved in complex formation, functional PDI materials that are endowed with a variety of

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supramolecular structures have been prepared.<sup>24-27</sup> For example, non-chiral surfactants tethered PDI connected with a flexible alkyl linkage, named as PDIC-DOAB (Fig. S1), has been reported in our previous work.<sup>28</sup> The PDIC-DOAB possesses interesting multiple thermally-induced phase structures. However, it cannot exhibit helical supramolecular structures.

In most cases, PDI materials with helical supramolecular structure are produced by complexing PDI with chiral surfactants.<sup>29-35</sup> The chiral surfactants often exert steric demands on the possible arrangement of PDI complex, which promote the construction of helical supramolecular structures. However, to the best of our knowledge, the helical stacking ISA PDI material without guidance of chiral surfactants has not been reported yet. Compared to chiral surfactant, non-chiral surfactant can be more commercially available and conveniently incorporated into PDI systems. It is of great interest to investigate whether it is possible to develop PDI material with helical supramolecular structure by complexing PDI with non-chiral surfactants. Moreover, it has been demonstrated that the flexible or rigid linkages have a great influence on the molecular packing behavior and then finally tune the material structure and properties. <sup>16,36,37</sup> Thus, it should be possible to fabricate ISA PDI compound capable of forming helical supramolecular structure by the rigid linkage between the PDI core and non-chiral surfactant.

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Furthermore, the advantage of the ionic compound, and the strong absorption and high solution fluorescence quantum yield of the PDI compound can also play important roles in the fluorescence detection. ATP (adenosine triphosphate), as the primary energy currency, plays an important role in various physiological and pathological processes of cells. The changes in ATP levels can affect cell function and reflect the normal state of the cell.<sup>38-45</sup> Therefore, the accurate and sensitive detection of ATP is important for biochemical studies and clinical diagnosis. However, most of the methods of detecting ATP need multiple operations for detection, such as form copper complex before responding to ATP.<sup>46,47</sup> Therefore, it is necessary to develop the PDI compound to directly detect ATP with high selectivity.

In this article, as part of our continuing research in PDI materials, a novel complex with non-chiral surfactants attached to PDI via a rigid phenylene linkage (PDTA-DHAB) was prepared by ISA method. Due to the steric requirement of the rigid linkage, the PDTA-DHAB molecules can rotationally stack and self-assemble into highly ordered helical columns which further pack into a monoclinic crystalline lattice. During heating, this helical crystalline structure transformed to a lamellar liquid crystalline structure. Furthermore, the PDTA-DHAB system realize the sensitivity and selectivity detection to ATP and the changes of the detection solution color can be clearly observed by naked eye in sunlight or in UV light.

#### 2. Experimental Section

#### 2.1. Instruments

<sup>1</sup>H NMR spectra were employed on a Bruker 400 HMz NMR spectrometer at room temperature using tetramethylsilane (TMS) as the internal standard. Pressed KBr disks of samples were employed on FT-IR measurements, and the FT-IR spectra were obtained on a Perkin-Elmer FTIR-100 spectrometer. UV-Vis absorption spectra were performed on an Agilent Technologies Cary 300 UV-Vis spectrophotometer. Fluorescence quantum yield was measured using a Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus\_QY. The dynamic light scattering (DLS) experiments were performed on zetasizer by utilizing Malvern Nano ZS instrument. The absorbance for MTT analysis was recorded on microplate reader (Thermofisher, USA) at a wavelength of 450 nm.

Thermogravimetric analysis (TGA, TA SDTQ-600 controller) and differential scanning calorimetry (DSC, TA Q100 controller) were used to study the thermal stability and phase transition of the complex. Two-dimensional X-ray diffraction (2D XRD) patterns of the oriented sample were recorded by employing a Bruker D8 Discover diffractometer with a Vantec500 detector. The oriented sample prepared by mechanical shearing was mounted on the sample stage equipped with a temperature control unit. The 2D XRD patterns were obtained through a transmission mode, with the X-ray incident beam aligned perpendicular to the shearing direction.

#### 2.2. Chemicals

Perylene-3,4,9,10-tetracarboxylic acid dianhydride (PDA), 5-aminoisophthalic acid and dihexadecyldimethylammonium bromide (DHAB) were bought from HWRK Chem Co. Ltd. The adenosine triphosphate (ATP), adenosine diphosphate (ADP), adenosine monophosphate (AMP), glucose, cyclic adenosine monophosphate (cAMP) and guanosine triphosphate (GTP) were purchased from Beijing Solarbio Science & Technology Co., Ltd. All the other materials were bought from Jiangtian Chemical Technology Co. Ltd. and used directly without further purification.

#### 2.3. Synthesis

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Under nitrogen atmosphere, PDA (1g, 2.55 mmol), 5-aminoisophthalic acid (1.15 g, 6.37 mmol) and imidazole (20 g) were heated at 130 °C for 6 h. Then 100 mL of ethanol was added into the hot mixture and refluxed for 6 h. The precipitate was filtered and washed with ethanol. After dried under vacuum, PDTA was obtained as deep red powder (yield: 82%). <sup>1</sup>H NMR (D<sub>2</sub>O, 400 MHz), δ (TMS, ppm): 7.15 (m, 8 H), 8.11 (s, 4 H), 8.43 (s, 2 H). Then, 143.6 mg (0.2 mmol) PDTA was added in 40 mL KOH aqueous solution with stir for 2 h to get potassium salt (PDTK) at 50 °C. The DHAB solution was obtained by dissolving 460 mg (0.8 mmol) DHAB in 40 mL mixed solution of water and ethanol (v:v = 2:1) at 50 °C for 2 h. After completely dissolved, PDTK solution was dropwise added into DHAB solution. The mixture was stirred overnight at room temperature and a charge stoichiometric precipitated complex was formed. The precipitate was purified by filtrating, washing with mixed water and ethanol solution to remove any remaining excess surfactants or inorganic salt. The PDTA-DHAB was dried under vacuum and obtained as red powder (yield: 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz), δ (TMS, ppm): 0.90 (t, 24 H), 1.28 (m, 208 H), 1.66 (m, 16 H), 3.04 (s, 24 H), 3.30 (m, 16 H), 8.05 (m, 8 H), 8.38 (s, 4 H), 8.74 (s, 2 H). FI-IR (KBr, cm<sup>-1</sup>): 3025, 2955, 2918, 2852, 1664, 1590, 1468, 1347, 1241, 1099, 995, 801, 780, 717.

#### 3.1. Molecular Design and Synthesis

The supramolecular organization of PDIs can be modified by the introduction of diverse functional substituents. A non-chiral surfactants-tethered PDI connected with a flexible alkyl linkage (PDIC-DOAB) has been reported recently (Fig. S1).<sup>28</sup> The complex possesses multiple thermally-induced phase structures, while exhibits non-helical supramolecular structure. It is interesting to study the influence of the linkage between PDI and surfactants on the optical property and phase structure. In order to explore the effect of rigid linkage on the supramolecular structure of the ISA PDI complex, the phenylene linkage was chosen to connect PDI and non-chiral surfactants in this study. It is expected that the change of linkage from flexible alkyl to rigid phenylene will endow the complex with novel supramolecular structure.

In order to introduce phenylene linkage between PDI core and surfactants, compound PDTA was conveniently synthesized in one step from 5-aminoisophthalic acid and PDA according to the reported procedure (Fig. S2).<sup>42</sup> Then the potassium salt was prepared from a simple treatment of PDTA with aqueous potassium hydroxide. Adding DHAB aqueous solutions dropwise to PDTK aqueous solution immediately yielded the charge-stoichiometric precipitates. The formed complex was obtained with high yield at room temperature, named as PDTA-DHAB. The synthetic procedure in detail is showed in Scheme 1. The target complex was characterized by <sup>1</sup>H NMR and FT-IR measurements, which confirmed the successful preparation of PDTA-DHAB (Figs. S3-S4).



(a) Aminoisophthalic acid, imidazole, 6 h, 130 °C

(b) KOH (excess),  $H_2O$ , 50 °C

(c) Dihexadecyldimethylammonium bromide (DHAB), C<sub>2</sub>H<sub>5</sub>OH/H<sub>2</sub>O, RT

Scheme 1. Synthesis process and chemical formula of PDTA-DHAB complex.

#### 3.2. Self-Assembly Behavior in Solution and Film State

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It is well known that the PDI derivative exhibits different self-assembly behavior in different polar solvents. In order to investigate the aggregation behavior, the solubility of PDTA-DHAB was tested in various solvents. PDTA-DHAB shows high solubility in a wide range of common organic solvents such as ethanol, tetrahydrofuran and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), but exhibits poor solubility in toluene. Thus, the concentration-dependent UV-Vis spectra of PDTA-DHAB were studied in CH<sub>2</sub>Cl<sub>2</sub> and toluene to investigate the dynamic process of aggregation behaviors, respectively.

In Fig. 1, the spectra of PDTA-DHAB show well-resolved vibronic absorption bands from 450-600 nm in CH<sub>2</sub>Cl<sub>2</sub> solution, which is characteristic of PDI chromophores. The absorption maxima occur at around 525, 489, and 457 nm, corresponding to the  $S_{0-0}$ ,  $S_{0-1}$ , and  $S_{0-2}$  vibronic transitions, respectively. Based on the reported literatures,<sup>49, 50</sup> the ratio of the absorption intensity of 0–0 and 0–1 transitions (A<sub>0-0</sub>/A<sub>0-1</sub>) can be utilized to analyze the degree of aggregation in solution. As shown in Table S1, the A<sub>0-0</sub>/A<sub>0-1</sub> ratios of PDTA-DHAB in CH<sub>2</sub>Cl<sub>2</sub> solution are very close to the literature value of  $1.6^{35,49}$ , indicating that the complex was in monomeric state throughout the investigated concentration range.



Fig. 1. UV-Vis spectra of PDTA-DHAB in CH<sub>2</sub>Cl<sub>2</sub> with different concentration.

In contrast, PDTA-DHAB shows low solubility in toluene and then will exhibit different selfassembly behavior. As displayed in Fig. 2, the absorption spectra of PDTA-DHAB exhibit a broad structured feature from 450 nm to 550 nm in toluene. Compared to the fine vibrational profiles in  $CH_2Cl_2$ , the spectra become less structured, indicating a predominant aggregated state of PDTA-DHAB in toluene. There are only two distinct absorption bands at around 530 nm and 500 nm of the spectra, and the absorption maximum with high concentration now represents for the  $S_{0-1}$  transition instead of the  $S_{0-0}$ . The  $A_{0-0}/A_{0-1}$  ratios reveal that PDTA-DHAB exhibits increased tendency for aggregation behavior in the all experimental concentrations (Table S1). The blue shift of the absorption maximum in toluene is characteristic of the formation of aggregated PDTA-DHAB in which the central perylene units are stacked cofacially.



Fig. 2. UV-Vis spectra of PDTA-DHAB in toluene with different concentration.

To obtain further information about the self-assembly behavior of PDTA-DHAB, UV-Vis spectroscopy was recorded in solid state at room temperature. The PDTA-DHAB film was prepared by heating the solution-cast film to 70 °C followed by cooling to ice-water mixture and then annealed at room temperature for 2 days. As shown in Fig. 3, the solid-state absorption spectrum appears broadened and the vibronic structure becomes much less defined. Moreover, the spectral feature is similar to that of

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PDI compound with bulky substituent group, which is highly indicative of parallel and rotary packing

arrangement of perylene units.51



Fig. 3. UV-Vis spectrum of PDTA-DHAB in thin film.

#### **3.3. Thermal Properties and Structural Evolution**

The complex was subjected to thermal analysis to determine its stability and phase behavior. TGA result in Fig. S5 reveals that the complex has a comparably good thermal stability. Fig. 4 shows the DSC diagram of PDTA-DHAB obtained during cooling and subsequent heating at a rate of 10 °C/min. Two thermal transition processes are clearly observed before the onset of degradation, and the endothermic peaks during heating progress are at 24 and 48 °C, respectively. The DSC trace suggests three phases: first phase (at lower temperature); second phase (at room temperature); third phase (at higher temperature). Although DSC experiment is sensitive to heat absorption and release events, it cannot provide direct information about structural change and molecular packing behavior. Therefore, 2D XRD experiments of the oriented sample were utilized to identify the corresponding structural evolutions. Since the temperature of the first phase is relatively low, we focus on the second phase and the third phase in following content.



**Fig. 4.** A set of DSC cooling and subsequent heating thermal diagrams of PDTA-DHAB at a rate of 10 °C/min.

#### 3.4. Structure Identification and Molecular Packing Behavior

A 2D XRD pattern for PDTA-DHAB, from a sample sheared at 70 °C followed by cooling to icewater mixture and then annealed at room temperature for 2 days, is shown in Fig. 5. The pattern was taken at room temperature with the X-ray incident beam perpendicular to the shear direction which is along the meridian. It shows diffractions not only on the equator and meridian but also in the quadrants, indicating an ordered crystalline phase. In particular, several diffractions between 0.37 and 0.48 nm can be detected in the high-angle region, which indicates the ordered arrangement of the alkyl chains.<sup>52, 53</sup> As indicated in this figure, the  $a^*$ - and  $b^*$ - axes are assigned to the equator, and the  $c^*$ - axis is along the meridian. On the equator, the locations of the first two strong diffraction arcs in low-angle region can be identified at  $2\theta = 2.20^{\circ}$  (d = 4.02 nm) and  $2.60^{\circ}$  (d = 3.40 nm), which can be indexed as (100) and (010), respectively. When the diffraction arc in the low-angle quadrants (indexed as (-111)) is projected onto the equator, the location of the diffraction arc on the equator can be identified at  $2\theta = 3.35^{\circ}$  (d = 2.64nm), which can be assigned to be (-110) according to the triangulation method of building a 2D  $a^*b^*$ lattice of the unit cell.<sup>54-57</sup> Consequently, an oblique lattice of the (hk0) diffractions on the equator direction can be constructed as: a = 4.02 nm, b = 3.40 nm and  $\gamma = 92^{\circ}$ , and all of the (*hk*0) diffractions can be indexed based on this triangle.

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**Fig. 5.** 2D XRD pattern of sheared PDTA-DHAB recorded at 25 °C. The shear direction is on the meridian and the X-ray beam is perpendicular to the shear direction.

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On the meridian, there is a pair of strong diffractions with *d*-spacing of 0.36 nm in the high-angle region. Seeing that this is the typical spacing of  $\pi$ - $\pi$  stacking of the PDI cores, this set of culminant arcs reveals that the PDI cores may stack parallel to each other. However, the diffraction arc (-111) in the quadrant should not be overlooked. When this diffraction arc is projected onto the meridian, the location of the extinct diffraction arc on the meridian can be identified at  $2\theta = 3.05^{\circ}$ , which can be assigned to be the (001). Note that the meridianal arc of 0.36 nm is in fact located on the eighth layer of the diffractions, and thus should be indexed as the (008), identifying that the structure of PDTA-DHAB possesses a large c parameter of 2.90 nm. Such a large c parameter is quite remarkable, which indicates that the molecules are rotationally stacked and helically assembled in the supramolecular column, giving an 8-fold helix (Fig. 6). This new complex helical column differs from that reported previously for non-helical column composed of PDIC-DOAB without rigid linkage.<sup>28</sup> As pointed out by Würthner,<sup>51</sup> the two phenylene rings at imide positions are not co-planar with the PDI core. Owing to the bulkiness of the phenylene linkage, a rotation displacement is required for the close  $\pi$ - $\pi$  stacking of PDTA-DHAB. As a result, a rotationally stacked and helically supramolecular structure with large c parameter has been detected from the 2D XRD pattern. Then, these helical columns further pack into a lattice irrespective of the helical sense, so the circular dichroism spectra of the PDIC-DOAB film showed no Cotton effect at the

absorption band of the complex. Using the standard refinement procedure,<sup>54-57</sup> the unit cell of the crystalline structure is finally calculated to be a monoclinic one with dimensions of a = 4.02 nm, b = 3.40 nm, c = 2.90 nm,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 92^{\circ}$ . The experimental and calculated *d*-spacing values and diffraction angles of the crystal lattice are listed in Table 1. The calculated crystallographic density is 0.91 g/cm<sup>3</sup>, in agreement with the experimental result of 0.90 g/cm<sup>3</sup>.



**Fig. 6.** Model of the helical column in the monoclinic lattice of PDTA-DHAB. For clarity, peripheral alkyl chains are not shown and the benzene rings are drawn in different colors.

	$2\theta$ (deg)		d-spacing (nm)		Intensity
(hkl)	expt <sup>a</sup>	calcd <sup>b</sup>	expt <sup>a</sup>	calcd <sup>b</sup>	expt <sup>c</sup>
100	2.20	2.20	4.02	4.02	S
010	2.60	2.60	3.40	3.40	VS
-110	3.35	3.35	2.64	2.64	VW
200	4.45	4.40	1.99	2.01	W
020	5.20	5.20	1.70	1.70	m
220	6.95	6.93	1.27	1.28	VW
-320	8.10	8.26	1.09	1.07	W
440	13.90	13.89	0.64	0.64	W
450	16.10	16.00	0.55	0.55	W
-111	4.55	4.53	1.94	1.95	W
008	24.60	24.58	0.36	0.36	m

Table 1. Crystallographic parameters of the monoclinic crystalline phase of PDTA-DHAB.

<sup>*a*</sup> Experimental values observed in Fig. 5. <sup>*b*</sup> Calculated values based on the monoclinic unit cell of a = 4.02 nm, b = 3.40 nm, c = 2.90 nm,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 92^{\circ}$ . <sup>*c*</sup> The experimental intensities in Fig. 5 are semiquantitatively estimated via a microdesitometer and classified as very strong (vs), strong (s), medium (m), weak (w), and very weak (vw).

When the oriented sample was heated to 70 °C, the 2D XRD pattern (Fig. 7a) shows fewer and diffused diffraction arcs in comparison with Fig. 5, suggesting the formation of liquid crystalline phase. The original diffractions between 0.37 and 0.48 nm in the quadrants degenerate into a diffuse ring, indicating that the crystalline ordering of side-chains has been destroyed. Simultaneously, the original diffraction arc indexed as the (-111) in the low-angle quadrant disappears, indicating that helically assembled structure was disturbed. However, the three diffractions on the equator are found to possess q ratio of 1:2:3 with corresponding *d*-spacings of 3.33, 1.67, and 1.11 nm, respectively. This indicates that PDTA-DHAB still forms ordered lamellar structure due to the separation between the aromatic PDI core and peripheral aliphatic chains (Fig. 7b).



**Fig. 7.** (a) 2D XRD pattern of sheared PDTA-DHAB recorded at 70 °C. The shear direction is on the meridian and the X-ray beam is perpendicular to the shear direction. (b) Molecular packing model of PDTA-DHAB in lamellar liquid crystalline phase.

#### 3.5. The Sensitivity and Selectivity Responses to ATP

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Considering the PDTA-DHAB material has many characteristics: self-assembly characteristic, the presence of ionic bonds, strong absorption (molar absorptivity:  $5 \times 10^4$  L•mol<sup>-1</sup>•cm<sup>-1</sup>) and moderately high fluorescence quantum yield in EtOH: H<sub>2</sub>O (1:1) solution (fluorescent quantum yield: 56%), we

would like to further study the potential application of PDTA-DHAB as detection sensor. In order to evaluate the detection ability of PDTA-DHAB toward ATP, the absorption spectroscopy in an aqueous solution was carried out. As showed in Fig. 8a, the absorption bands at 492 nm and 528 nm of PDTA-DHAB decrease gradually and a new broad shoulder at 459 nm is appeared with increasing ATP concentrations. The changes of spectra indicate that ATP can interact with PDTA-DHAB in aqueous solution and the degree of aggregation has significantly increased in the new system. More interesting, the color of the solution has also undergone obvious changes that can be observed by the naked eye before and after the addition of ATP. Notably, there exists liner relationship between absorbance and ATP concentration in the range of 0-28  $\mu$ M (R<sup>2</sup> = 0.996), indicating that this method is applicable for quantitative detection of ATP (Fig. S6). Furthermore, the selectivity of PDTA-DHAB to ATP over other ions or similar chemicals was also studied (Fig. 8b). Only after the addition of ATP, it displays a significant change in the shape of the spectra. It finds that ADP can also reduce the absorbance intensity to some extent. The absorption decrease could be because that ADP has two phosphate species, so ADP will also exhibit a certain electrostatic interaction with PDTA-DHAB as that of ATP. However, no bathochromic shift or hypsochromic shift can be observed for ADP, while the more serious intensity decrease and the distinct hypsochromic shift can be detected for ATP. And the addition of other ions did not cause a significant change in the spectra. These results show that the approach has good selectivity and can be applied to ATP detection directly in aqueous solution.



Fig. 8. (a) Absorption spectra of PDTA-DHAB (10  $\mu$ M) in EtOH:H<sub>2</sub>O (1:1) solution by increasing the amount of ATP (0-4 equiv.). Inset: images of PDTA-DHAB solution with 0 and 4 equiv. ATP in

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sunlight. (b) Absorption spectra change of PDTA-DHAB (10  $\mu$ M) upon the addition of various anions (4 equiv.).

The sensitivity and selectivity of PDTA-DHAB to ATP was further investigated by fluorescence spectra. With the addition of ATP, the fluorescence intensity of the solution was gradually decreased. As displayed in Fig. 9a, the solution color under UV light from bright yellow emission to fluorescence quenching shows remarked change before and after the ATP addition. In addition, no significant changes in the fluorescence spectra were observed after the addition of other anions only the ATP exhibits a decrease of the emission intensity (Fig. 9b). And the addition of ATP at the same concentration will decrease obviously, indicating that ATP can be detected selectively. These results imply that the PDTA-DHAB system can realize the sensitivity and selectivity responses to ATP.



**Fig. 9.** (a) Fluorescence spectra of PDTA-DHAB (10  $\mu$ M) in EtOH:H<sub>2</sub>O (1:1) solution by increasing the amount of ATP (0-4 equiv.). Inset: emission images of PDTA-DHAB solution with 0 and 4 equiv. ATP under UV light. (b) Fluorescence spectra change of PDTA-DHAB (10  $\mu$ M) upon the addition of various anions (4 equiv.).

To further study the mechanism of ATP binding to the PDTA-DHAB, the dynamic light scattering (DLS) experiment were employed (Fig. 10). Before the addition of ATP, the average particle size of the sample in the EtOH: H<sub>2</sub>O (1:1) solution was 346 nm. After the addition of ATP, the particle size increases to 1109 nm. And then the aggregates are further enlarged to 1518 nm after 30 minutes. While with the addition of other anions (ADP, AMP, Br) to system, the average particle size of the solution respectively was 533 nm, 378 nm, 346 nm (Fig. S7). Due to the ATP has three phosphate species, it shows the stronger electrostatic binding ability with PDTA-DHAB, leading to the maximum particle

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size of the solution system. Furthermore, cytotoxicity study was performed using the MTT method to evaluate the biocompatibility of the PDTA-DHAB to living cells (Fig. S8). At low concentrations, PDTA-DHAB has little effect on cell viability. While the concentration at 10  $\mu$ M, the average of cell viability decreases to 91%. This result means that PDTA-DHAB has lower cytotoxicity at moderate concentrations and can be used in biological applications.



**Fig. 10.** (a) Particle size distribution of PDTA-DHAB (10  $\mu$ M) in the EtOH: H<sub>2</sub>O (1:1) solution. (b) Particle size distribution of PDTA-DHAB (10  $\mu$ M) upon the addition of ATP (4 equiv.). (c) Particle size distribution of PDTA-DHAB (10  $\mu$ M) upon the addition of ATP (4 equiv.) after 30min.

#### 4. Conclusions

In summary, a novel functional material PDTA-DHAB with non-chiral surfactants attached to PDI core via a phenylene linkage was designed and prepared by ISA method. Different to the reported PDI complex with flexible linkage, the PDTA-DHAB molecules with rigid linkage can be rotationally stacked and helically assembled in the supramolecular column. The unit cell of crystalline phase at room temperature was determined to be monoclinic with dimensions of a = 4.02 nm, b = 3.40 nm, c = 2.90 nm,  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 92^{\circ}$ . With increasing temperature, the helical supramolecular structure was destroyed, and the crystalline phase transformed to a lamellar liquid crystalline phase. In addition, PDTA-DHAB system can realize the sensitivity and selectivity responses to ATP. The unique supramolecular structure and the detection of ATP are significant for the field of ionic self-assembly and for the molecular design of supramolecular electronics.

#### **Conflicts of interest**

There are no conflicts of interest to declare.

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The novel PDI complex can be self-assembled into helical supramolecular structure. Moreover, the solution of complex can also realize the visual detection on ATP.

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