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PAPER

Molecular assembly of a squaraine dye with cationic surfactant and nucleotides: its impact on aggregation and fluorescence response†

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A novel fluorescent system has been assembled by using ATP, surfactant, and a squaraine dye in an aqueous buffer solution. In the system, a cationic surfactant such as cetyl trimethyl ammonium bromide (CTAB) forms a sphere-like micelle, whose positive charge at the surface of the micelle attracts the negatively charged ATP to form a unique organized nanostructure. Such an organized system is shown to interact with the squaraine dye (**SQ**) to perturb its aggregate structure, thereby generating the optical response. The nanostructure of the assembly has been characterized by dynamic light-scattering (DLS) and atomic force microscopy (AFM). The unique feature of the developed sensing system is that the analytes ATP form part of the assembly structure. The system utilizes forces such as electrostatic interaction and π–π stacking of the aromatic segment of ATP and **SQ** to achieve the selective detection of ATP.

Introduction

The design and construction of chemical sensors that selectively recognize anions has received ever-increasing attention in recent years, because anions are ubiquitous in biological systems.[1] Among various anions, detection of phosphates, pyrophosphate (PPi), and nucleotides is of special interest.[2] As a multifunctional nucleotide, adenosine triphosphate (ATP) functions as an energy shuttle to power nearly all forms of cellular work, from the generation of light by fireflies to the movement of muscle cells. It also provides an energy source for biosynthetic reaction, consumption of many enzymes and cell division.[3] Adenosine diphosphate (ADP) is another nucleotide, which is the product of ATP dephosphorylation by ATPases and can be converted back to ATP by ATP synthases. The conversion of these two molecules plays a critical role in supplying energy for many processes of life.[4] Thus, selective detection of ATP from ATP/ADP in aqueous media has emerged as an important area of research. Although several studies have employed colorimetric and fluorescent probes, electrostatic and hydrogen bonding interactions to recognize ATP,[5] it remains a challenge to find new approaches to simplify ATP detection while keeping higher selectivity over other nucleoside triphosphates such as GTP. Fluorescent probes as a conventional and highly sensitive analytical method have been used to detect ATP, however, few of these sensors show turn-on emission upon ATP binding in aqueous medium over PPi.[5e–g]

Squaraines form a class of novel dyes possessing sharp and intense absorption and fluorescence in the red to near-infrared region.[6] In the solution, squaraine dyes can be spontaneously assembled with chromophores in a parallel-oriented fashion (H-aggregates), or in a head-to-tail arrangement (J-aggregates) by varying the solvents or adding ionic species. The J-aggregates give red-shifted absorption bands (as compared with monomer absorption), and H-aggregates give blue shifted absorption bands. The different form of the aggregate also affects the emission properties, with H-aggregates usually being poor emitters while J-aggregates often give efficient luminescence.[7,8] The distinction in optical characteristics between J- and H-aggregates can be used as an effective means to monitor the molecular assembly. Although ATP has been demonstrated to be a building block to aid the H-aggregate formation of a cyanine dye,[9] no study has been found utilizing the electrostatic interaction (between the negatively charged ATP and positively charged squaraine dye) to influence the aggregate structures of squaraine dye (**SQ**) in aqueous solution. An interesting question is whether such an aggregate structure change, if induced, could lead to a useful spectroscopic response to detect ATP.

Molecular self-assembly offers an excellent tool to construct, *via* a "bottom-up" approach, diverse supermolecular architectures in which the organization of individual molecules can be controlled by proper selection of different self-assembling components.[10] For example, surfactants are well known to self-assemble in aqueous solutions to give organized nanostructures (*e.g.*, micelles and vesicles).[11] Utilization of surfactants in the chemical sensor ensemble has led to detection of several transition-metal cations,[12] proteins[13] and other analytes such as Cl^-, pH, Ba^{2+} and

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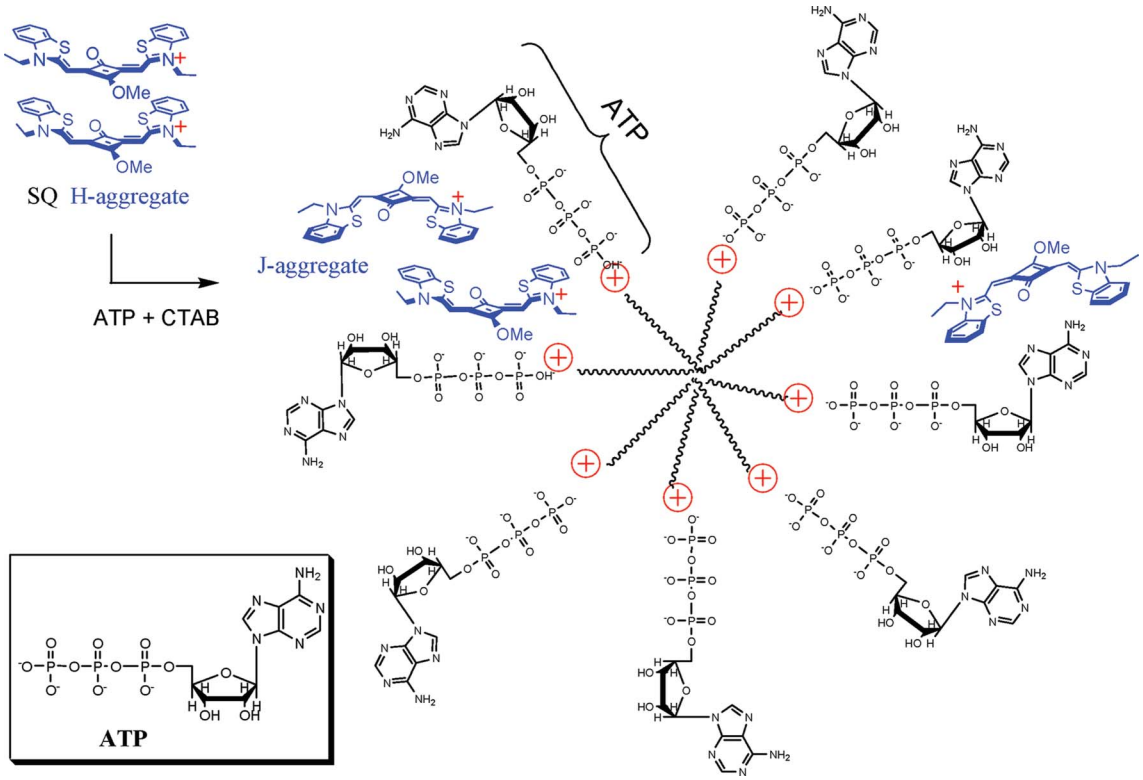

Scheme 1 Structures of **SQ**, ATP and schematic illustration of the working micellar system. In the **SQ** structure, the counter ion $CF_3SO_3^-$ is not shown for clarity.

lipophilicity.[14] The current strategy is limited to encapsulating a fluorophore in the micelle, whose fluorescence is then quenched by an analyte (*e.g.*, by using heavy atom effect or electron transfer).

The well-defined nanostructure of the surfactant micelle raises the possibility that it can be used as an assembly building block. To demonstrate its feasibility, we have examined a ternary system that consists of ATP, squaraine dye, and cationic surfactant (cetyl trimethyl ammonium bromide (CTAB)) as illustrated in Scheme 1. The basis for our hypothesis is as follows: in the system, CTAB can form a sphere-like micelle,[15] whose positive charge at the surface of the sphere attracts the ATP to form a unique organized nanostructure through electrostatic interaction. It is known that squaraine dye tends to form dimers or H-aggregates through π–π stacking, owing to its poor solubility in aqueous media.[7] Upon interaction with ATP at the outer surface of the nanostructured sphere, the squaraine dyes in the H-aggregate form are found to be changed to the J-aggregate form (head-to-tail arrangement), as a consequence of electrostatic interaction between the squaraine and the phosphate group of ATP.[16] In this study, we report the formation of a nanostructured assembly by using CTAB, ATP and squaraine **SQ**. The optical responses of **SQ**, induced by the assembly structure, exhibit potential for desirable ATP detection in aqueous solution.

Results and discussion

The **SQ** dye was synthesized as reported previously.[17] UV–vis absorption spectra of **SQ** in various organic solvents gives one band at about 635 nm with similar absorbance, attributed to the monomeric form (Fig. 1). Solvent polarity only slightly affects the absorption peak, with λ_{max} = 646 nm in the nonpolar toluene and λ_{max} = 631 nm in methanol. To assess the feasibility of detecting ATP at physiological pH values, the sensing ability of **SQ** toward ATP was examined in an aqueous solution containing phosphate buffer (10 mM, pH 7.20) and 1% EtOH. Poor water solubility requires us to first dissolve **SQ** dye in EtOH, which was then diluted in water.

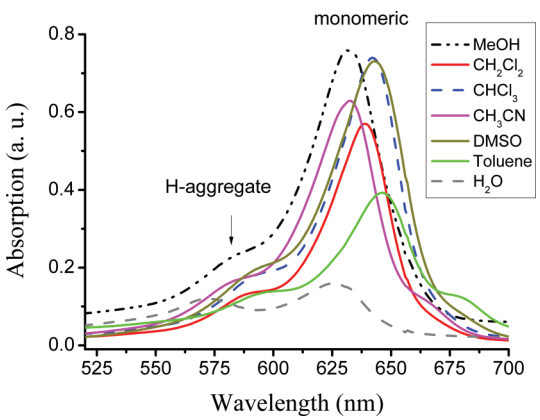

Fig. 1 UV–vis absorption spectra of **SQ** (5 μM) in different solvents.

In the aqueous buffer solution, **SQ** showed characteristic absorption maxima at 547, 569 and 627 nm (Fig. 2a). The absorption band at 627 nm was assigned to the monomeric species. On the basis of the observed spectral blue shift, the bands at 547 and 569 nm were attributed to the H-aggregates (in the dimer

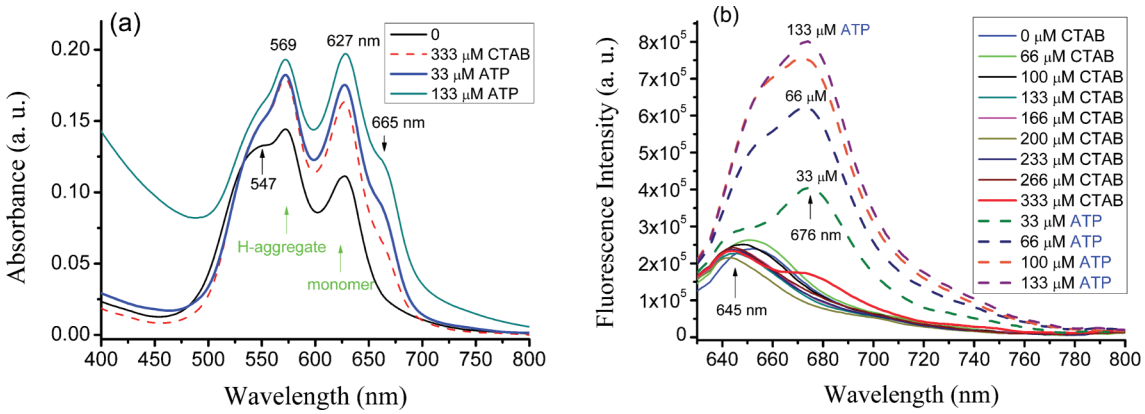

Fig. 2 Absorption change (a) and fluorescence response (b) of **SQ** (5 μM) in phosphate buffer (10 mM, pH 7.2) upon addition of CTAB (0–333 μM), followed by ATP (0–133 μM). The emission spectra were acquired when the solutions were excited at 620 nm.

or oligomeric form).[7,8] The absorption intensity of these three peaks increased slightly with increasing CTAB concentration (Fig. S2, ESI†). After the CTAB concentration in the solution reached 0.33 mM, ATP was added. When the ATP concentration was increased, the aggregate absorption peaks at 547 and 569 nm weakened, while the monomeric absorption at 627 nm went up. No change in the absorption spectra was observed upon addition of other ions, including AMP, PPi, phosphate, adenosine, CO_3^{2-}, AcO^-, SO_4^{2-}, NO_3^-, Cl^-, Br^-, I^-, Na^+, K^+, Ca^{2+}, Mg^{2+}. The specific optical response from ATP, which was visible (Fig. 3), indicated that the **SQ** could be used as colorimetric probe for ATP in aqueous buffer solution. Addition of ATP also induced a shoulder at ~665 nm, suggesting the formation of a new chemical species-"**SQ**-surfactant" complex,[18] although formation of J-aggregate remained a possibility.

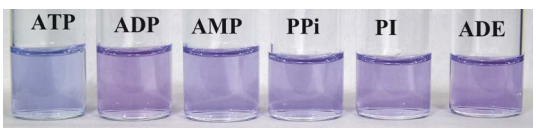

Fig. 3 Color changes induced in **SQ** (5 μM) in the presence of CTAB (333 μM) in 3 mL phosphate buffer (10 mM, pH 7.2) upon addition of different anions and adenosine (0.2 mM).

In order to understand the sensing process, the percentage change of each species (dimer and higher H-aggregate, and monomer) was correlated with the addition of CTAB, followed by ATP. As seen in Fig. 4, the critical micellar concentration (CMC) of CTAB can be obtained at 133.3 μM.[19] In the micellar solution (CTAB concentration = 133–333 μM), ATP created a favorable environment to transfer squaraine dye from H-aggregates to monomer to some extent. Since CTAB could disperse squaraine aggregates like other surfactants (Fig. S6, ESI†),[20] CTAB concentration in the solution was controlled below 0.33 mM.

SQ exhibited a fluorescence maximum at ~650 nm in aqueous buffer solution, which can be attributed to the monomer since squaraine dye typically has a small Stokes' shift (about 10–30 nm). Although the anionic phosphate ATP could be associated with the cationic **SQ** species, addition of ATP (up to 2 mM) to the **SQ** solution induced nearly no fluorescence response in the absence of CTAB (Fig. 5 and Fig. S7†). The control experiment clearly

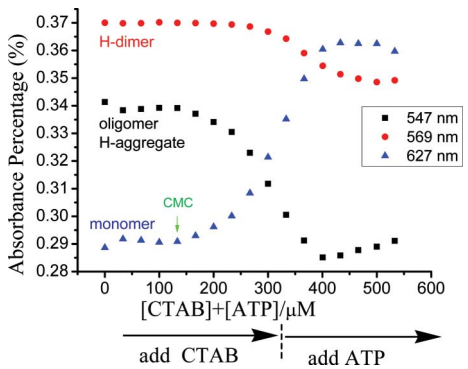

Fig. 4 Percentage change of **SQ** (5 μM) in phosphate buffer (10 mM, pH 7.2) upon addition of CTAB (0–333 μM), followed by ATP (0–200 μM). Since the concentration of each **SQ** species is proportional to the corresponding absorbance A_i, the percentage change is calculated to be $A_i/(A_{547} + A_{569} + A_{627})$. Here, the absorption at 547, 569, and 627 nm was used to approximate the enriched H-dimer, oligomer H-aggregate, and monomer, respectively.

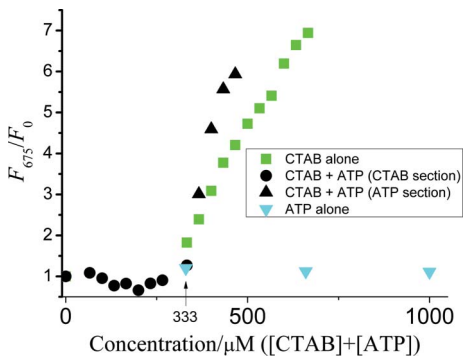

Fig. 5 Comparison of the fluorescence response of **SQ** (5 μM) in phosphate buffer (10 mM, pH 7.2) upon addition of various concentrations of CTAB and ATP.

indicated that an adequate amount of CTAB was necessary for the assembly to work. As illustrated in Fig. 2b, CTAB had a negligible effect on the fluorescence spectra of **SQ** when CTAB concentration was low (<0.33 mM). Subsequent addition of ATP to the **SQ** solution containing CTAB (0.33 mM concentration), however, resulted in a new fluorescence peak at 676 nm (Fig. 2b).

The current assembly design utilized 333 μ M CTAB to form just sufficient micelles, which were used as the building blocks for further assembly with the ATP and **SQ**. In other words, the strategy provided the optimum condition to incorporate the ATP and **SQ** into the desirable assembly, while avoiding the interruption of the **SQ** aggregate structure by excessive CTAB.

Excitation spectra obtained by monitoring the emission at 645 and 676 nm revealed maxima at 630 and 643 nm (Fig. 6), respectively. In the excitation spectra, a shoulder at ~585 nm was also visible, which was attributed to the H-aggregate (in consistency with its absorption at 569 nm). The emission band at the longer wavelength (676 nm), therefore, indicated the formation of a new species, which was likely to be the J-aggregate from **SQ** on the basis of the spectral red-shift.[21] Although the control experiment by using excess CTAB also exhibited an emission at 676 nm, a similar signal intensity at ~676 nm required the use of a higher concentration of CTAB (in comparison with ATP) (Fig. 5). In summary, the fluorescence at 645 nm was attributed to **SQ** monomer and the emission at 676 nm to its J-aggregate.

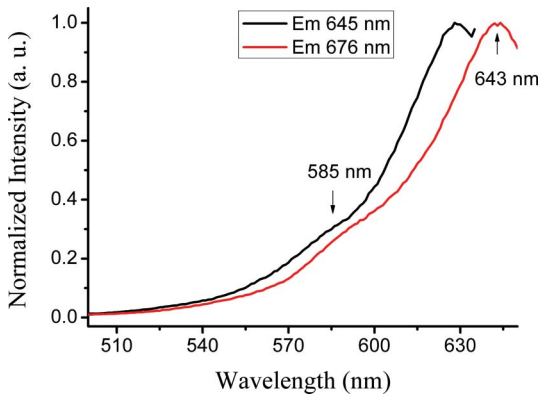

Fig. 6 Excitation spectra of **SQ** (5 μM) in the presence of CTAB (333 μM) and ATP (133 μM).

Dynamic light scattering (DLS) techniques were employed to probe the size of the self-assembled structures in solution quantitatively. CTAB (333 μM) exhibited average solvodynamic diameters of 220 nm, corresponding to its micelle formation (Fig. 7). The solution of **SQ** (5 μM) revealed a broad distribution of species (with average size of about 430 nm), attributed to H- and J-aggregates of various sizes. The solution of CTAB and **SQ** revealed a species at ~400 nm (similar to the aggregate of **SQ** alone),

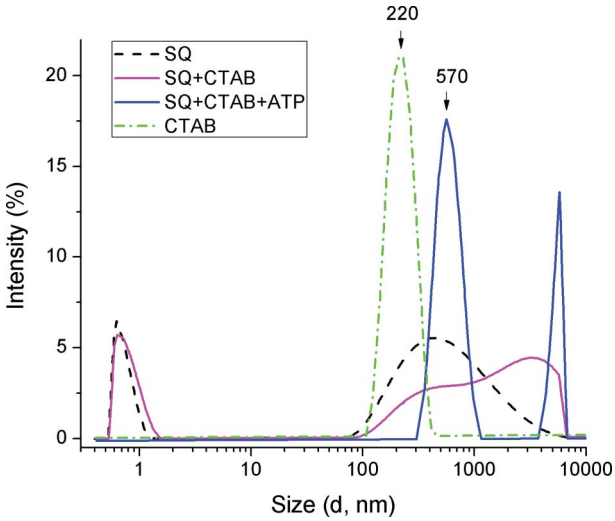

Fig. 7 Solvodynamic diameters of CTAB (333 μM) aggregates, CTAB with **SQ**, and CTAB with **SQ** and ATP in water determined by dynamic light scattering.

in addition to a significantly larger particle at ~3000 nm. Lack of characteristic sizes from either **SQ** or **SQ**–CTAB in solutions suggested that the well-defined assembly was not occurring in the absence of ATP. Interestingly, addition of ATP (to the solution including CTAB and **SQ**) led to a defined nanostructure with a diameter of about 570 nm, clearly indicating that a self-assembly process took place in the solution. A significant increase in the dimension of the CTAB–**SQ**–ATP assembly (570 nm), in comparison with that of CTAB micelle (~220 nm), supported the assumption that the ATP and **SQ** were interacting with CTAB micelle at its outer perimeter. Light scattering data also revealed a second species (size at ~5200 nm) for CTAB–**SQ**–ATP assembly, suggesting that the **SQ** molecule could link multiple CTAB micelles during the assembly process.

Atomic force microscopy (AMF) further confirmed the interaction pattern. The CTAB micelle was detected to be slightly less than 0.1 μm (Fig. 8). Addition of **SQ** to CTAB did not alter the micelle size. From the CTAB+**SQ**+ATP sample, however, two distinctive sizes were observed. One species had a dimension of about 0.1–0.15 nm, in consistency with the proposed assembly pattern. A second species with significant larger size (~0.4–1 nm) was also observed, in agreement with the two distinct species

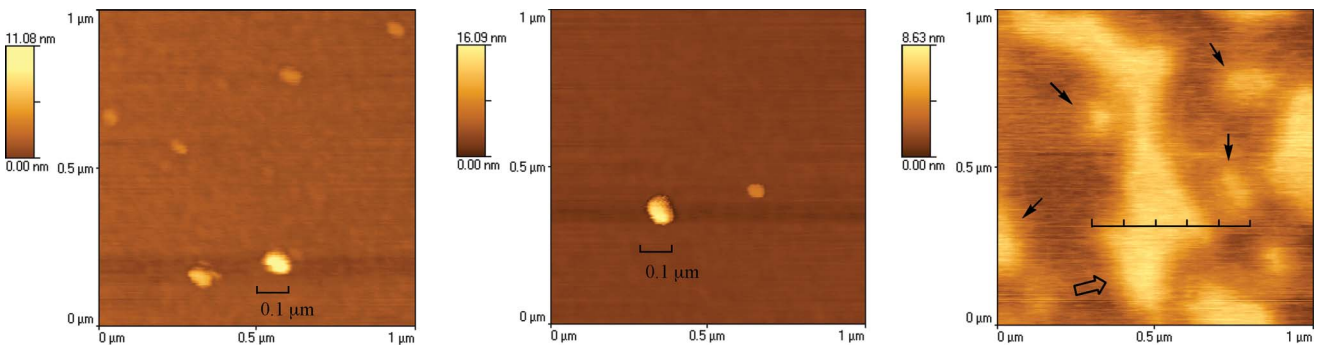

Fig. 8 AFM images of films spin-cast from the CTAB, CTAB+**SQ**, and CTAB+**SQ**+ATP solutions. The image of CTAB+**SQ**+ATP contains the single species of dimension ~0.1 μm (small arrow) and connected species (thick arrow).

detected in the light scattering experiment. The consistent trend, which was revealed from both light scattering and AFM images, supports the assumption that the ATP was assembled on the surface of CTAB micelles, resulting in increased particle sizes (Scheme 1). It should be noted that the particle sizes from AFM are different from those detected from DLS. This is because DLS is measured in solution where solvation results in the larger sizes, while AFM measures the sizes of dried particles which are laid on the AFM grid surface. Correlation of AFM and DLS data (Fig. 7 & 8) showed that the CTAB alone existed as spheric micelles in solution, with an average size of 220 nm. The predominant particle size in the solution of "**SQ**+CTAB+ATP" assembly was about twice as large (~570 nm), and had similar size distribution to CTAB. The results pointed to the fact that the particles in the "**SQ**+CTAB+ATP" solution were likely to be spherical. Both DLS and AFM data also showed a larger species that existed as a minor component (Fig. 7).

To validate the specificity of the system toward the anionic guests in practice, the fluorescence response of **SQ** in aqueous buffer solution was examined upon addition of various biologically important anions and cations. No apparent fluorescence enhancement was observed for AMP, PPi, phosphate, adenosine, CO_3^{2-}, AcO^-, SO_4^{2-}, NO_3^-, Cl^-, Br^-, I^-, Na^+, K^+, Ca^{2+}, Mg^{2+} (Fig. 9, Fig. S11, ESI†). The ratio of I_{670}/I_0 (herein I_0 is the fluorescence intensity of free **SQ** at 670 nm; I_{670} represents the fluorescence intensity at 670 nm upon addition of different ions) is plotted against the concentration of various ions (Fig. 9). The I_{670}/I_0 value for ATP reached up to 3.1-fold, in sharp contrast to I_{670}/I_0 < 1.1-fold for other ions. Therefore, this system could be used as a selective sensor for ATP. A good linear correlation was observed between the relative fluorescence intensity and ATP concentration (0–140 μM) (Fig. 10), and the detection limit was in the order of 10^{-6} M when the ratio of signal to noise was 3. The Hill's plot gave a Hill coefficient of 0.78 (Fig. S1†), which indicates negative cooperative interaction.[22]

The selective fluorescence response to ATP appeared to be associated with the electrostatic interaction between **SQ** and ATP. As illustrated in Scheme 1, a cationic surfactant was necessary to form the spherical micelle core with a positive charged surface. When the cationic surfactant CTAB was replaced by an anionic surfactant such as SDS (sodium dodecyl sulfate) or Triton X-100 (isooctylphenolicpolyglycol ether), the resulting system showed no fluorescence response to ATP. The assembly of the ordered system (Scheme 1) appeared to favor addition in the following sequence: CTAB, then ATP to the **SQ** solution. If the addition sequence is reversed (*i.e.* ATP first, then CTAB), the resulting system exhibited a much weaker fluorescence response (Fig. S10, ESI†) than that observed in Fig. 2. If no CTAB existed in the solution, there was no response to ATP (Fig. 5). Therefore, formation of spherical micelles with a positively charged surface was a necessary step. The result clearly pointed to the fact that an assembly with an ordered structure might play an important role in the observed fluorescence response. The results also support the assumption that, in the second step, electrostatic interaction guided the phosphate terminals of ATP to the positively charged surface of the spherical micelle.

Based on the design, the concentration of the squaraine reporter is expected to affect the performance of the sensor assembly. Screening of the dye concentration (between 1–20 μM, Fig. S17†)

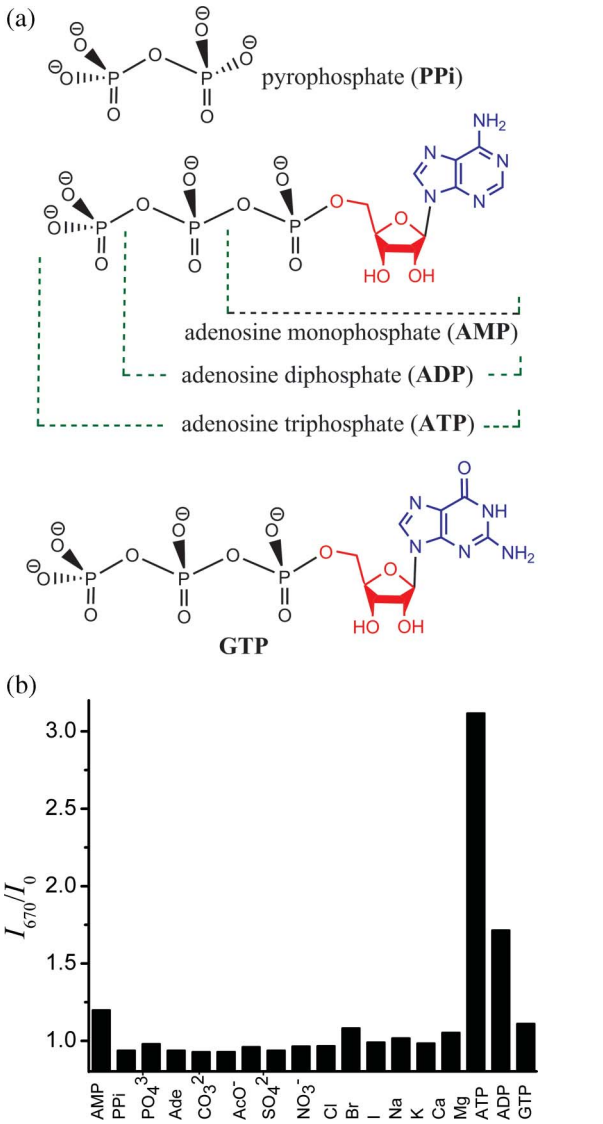

Fig. 9 (a) Structure of phosphates. (b) Relative fluorescence ratio (I_{670}/I_0) of **SQ** (5 μM) in the presence of CTAB (333 μM) in phosphate buffer (10 mM, pH 7.2) upon addition of different ions (0.2 mM).

showed that **SQ** gave the optimum fluorescence response at a concentration of 5 μM. Higher **SQ** concentration resulted in decreased fluorescence response, possibly attributing to a higher degree of aggregation.

The experimental data were consistent with the proposed model for the assembly of the ordered system from CTAB, **SQ** and ATP (Scheme 1). Driven by the assembly forces, part of the **SQ** was changed from the H-aggregate to the more fluorescent monomer and J-aggregate form, resulting in a spectral red-shift and fluorescence enhancement. In the absence of ATP, the surfactant CTAB initially formed the micelles, which also allowed the **SQ** to be partially dissolved in the hydrophobic cavity of the micelles as monomeric or aggregated form (Fig. 11, assemblies **I** and **II**). CTAB concentration in the solution was thus controlled to below 0.33 mM, thereby creating a favorable environment for the CTAB–**SQ**–ATP assembly **III** while avoiding excessive solubilization of **SQ** by CTAB surfactant. Formation of assembly **III** was energetically more favorable, which was enhanced by the

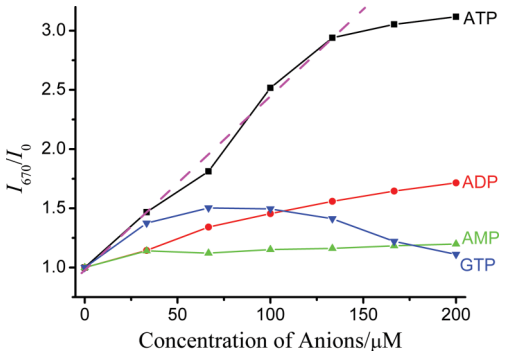

Fig. 10 Relative fluorescence ratio (I_{670}/I_0) of **SQ** (5 μM) in the presence of CTAB (333 μM) in phosphate buffer (10 mM, pH 7.2) upon addition of different ions (0–0.2 mM). The broken line on the ATP curve shows the linear correlation between the fluorescence response and ATP concentration (0–140 μM).

electrostatic interaction between the oppositely-charged species CTAB–ATP and ATP–**SQ**, in contrast to the assemblies **I** and **II** that involved the interaction of two positively charged species. Excessive CTAB could turn on the fluorescence of **SQ** (Fig. 5), since the increasing micelle concentration makes the formation of **I** and **II** a more competitive process.

It was assumed that the **SQ** was attracted to the phosphate group of ATP through electrostatic interaction. In this step, the two phosphate groups appeared to be necessary (one attaching to positively charged surface of the spherical micelle, the other to **SQ**) for the assembly. This was likely to be the reason for the selective recognition of ATP over AMP, adenosine, phosphate and other anions. The π–π stacking interaction between **SQ** backbone and the aromatic segment of ATP could also play an important role in the stability of the **SQ**–ATP–micelle assembly,[23] which accounted for the selective recognition of ATP over PPi. The different response between the nucleotide triphosphates ATP and GTP (Fig. 9 and 10) further pointed to the fact that the π–π stacking interaction could be used to differentiate different triphosphates. Owing to steric hindrance, **SQ** molecules had a tendency to exist in J-aggregate form rather than H-aggregate form in the cavity of the **SQ**–ATP–micelle assembly (Scheme 1). Observation of a new band, 664 nm in absorption and 676 nm in fluorescence, is consistent with the proposed ternary structure. The moderate selectivity between ATP and ADP was associated with the length of phosphates, as the triphosphate provided more space to accommodate the **SQ** aggregates, which can simultaneously interact with the phosphate (electrostatic interaction) and adenosine segments (π–π interaction).

To detect ATP in the biological system, it is necessary to assess the selectivity in the presence of alkali and alkali-earth metal cations. It is known that ATP can bind cations Mg^{2+} (at 9554 M^{-1}), Ca^{2+} (at 3722 M^{-1}), Na^+ (at 13 M^{-1}) and K^+ (at 8 M^{-1}).[24] The influence of various cations on the fluorescence of **SQ** was examined by addition of Na^+, K^+, Ca^{2+} and Mg^{2+} (Fig. S12, ESI†). In the presence of 0.2 mM of various cations, Na^+ and K^+ exhibit little influence on the fluorescence enhancement, whereas the presence of Ca^{2+} and Mg^{2+} suppressed the fluorescence increase to some extent. However, these results do not interfere with the sensing process.

Conclusions

In summary, we have demonstrated a new ternary system, which incorporates ATP and **SQ** into an ordered molecular self-assembly to induce fluorescence turn-on. The molecular assembly is driven by a balanced electrostatic interaction and π–π stacking of the aromatic segment of ATP and **SQ**. The sensor operates by attenuating the aggregate structure of squaraine dyes (from H- to monomer and J-aggregates) under physiological pH conditions. The study provides a simple approach for the detection of ATP. Due to the specific requirements for the *analyte* to enter the nano-structured molecular assembly, the ternary system exhibits good selectivity to sense ATP. The new sensor system provides an additional example

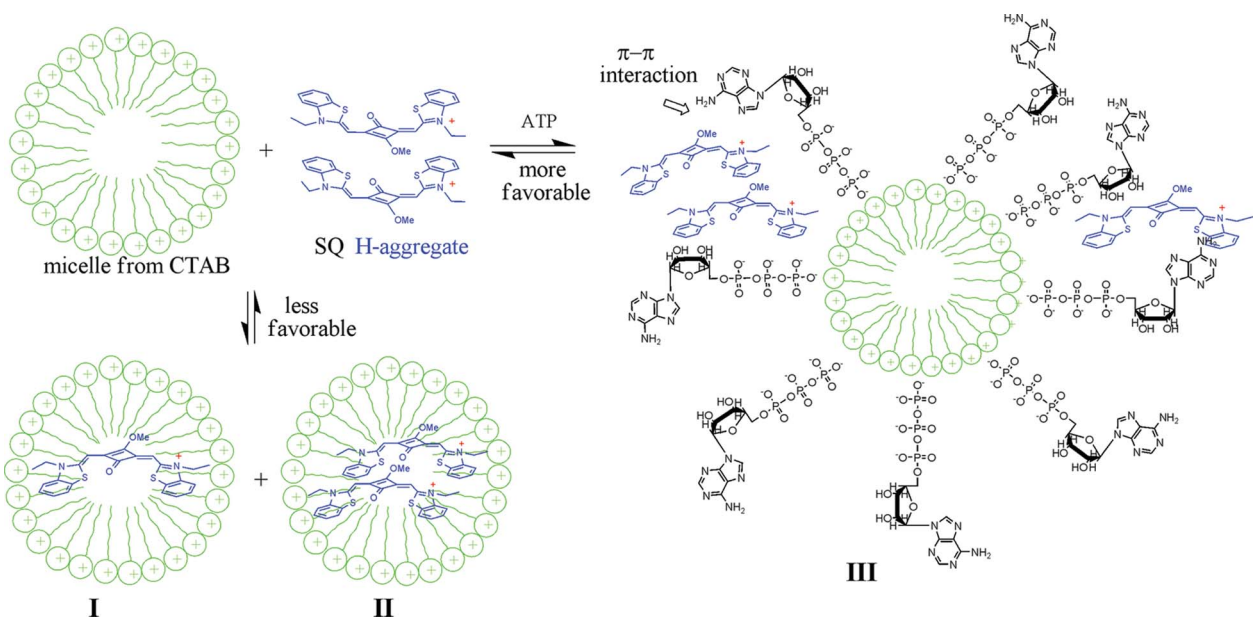

Fig. 11 Micelle-based equilibrium to redistribute the H-aggregate **SQ** into monomeric and aggregate form.

that operates by recognizing a *specific* pattern transformation (*i.e.* here from H- to J-aggregate) that has the advantage of simpler molecular design in comparison with typical sensors.[25] This is because the synthesis of a classical fluorescent sensor often involves a lengthy synthetic procedure. Supramolecular assembly using easily accessible components, therefore, could provide a cost-effective solution.

Acknowledgements

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