

Photoluminescent sulfur quantum dots stabilized by pillar[5]arenes containing amide and amino groups

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INTRODUCTION & AIM

Sulfur quantum dots (SQDs) are semiconductor nanocrystals that have gained significant attention due to their tunable photoluminescence, high photostability, and low toxicity, offering an eco-friendly alternative to heavy-metal-based QDs.

However, their application as independent sensory platforms is limited by the absence of intrinsic receptor groups.

A solution to this problem can be achieved through the surface modification of SQDs with amido- and aminofunctionalized pillar[5]arenes (AP[5]A).

Thus, the **aim of this work** is to develop a method for the synthesis of SQDs using decasubstituted amido- and aminofunctionalized pillar[5]arenes, which addresses three key challenges. **First**, AP[5]A act as efficient surface passivation agents. The high density of electron-donating amino groups ensures their stable anchoring on the SQD surface, suppressing defect formation and aggregation. **Second**, these amino groups create the alkaline medium necessary for sulfur dissolution and nanoparticle formation, eliminating the need for traditionally used NaOH in SQDs synthesis, thereby reducing the number of reagents. **Finally**, AP[5]A are capable of forming “host-guest” inclusion complexes, imparting molecular recognition functionality to the SQDs.

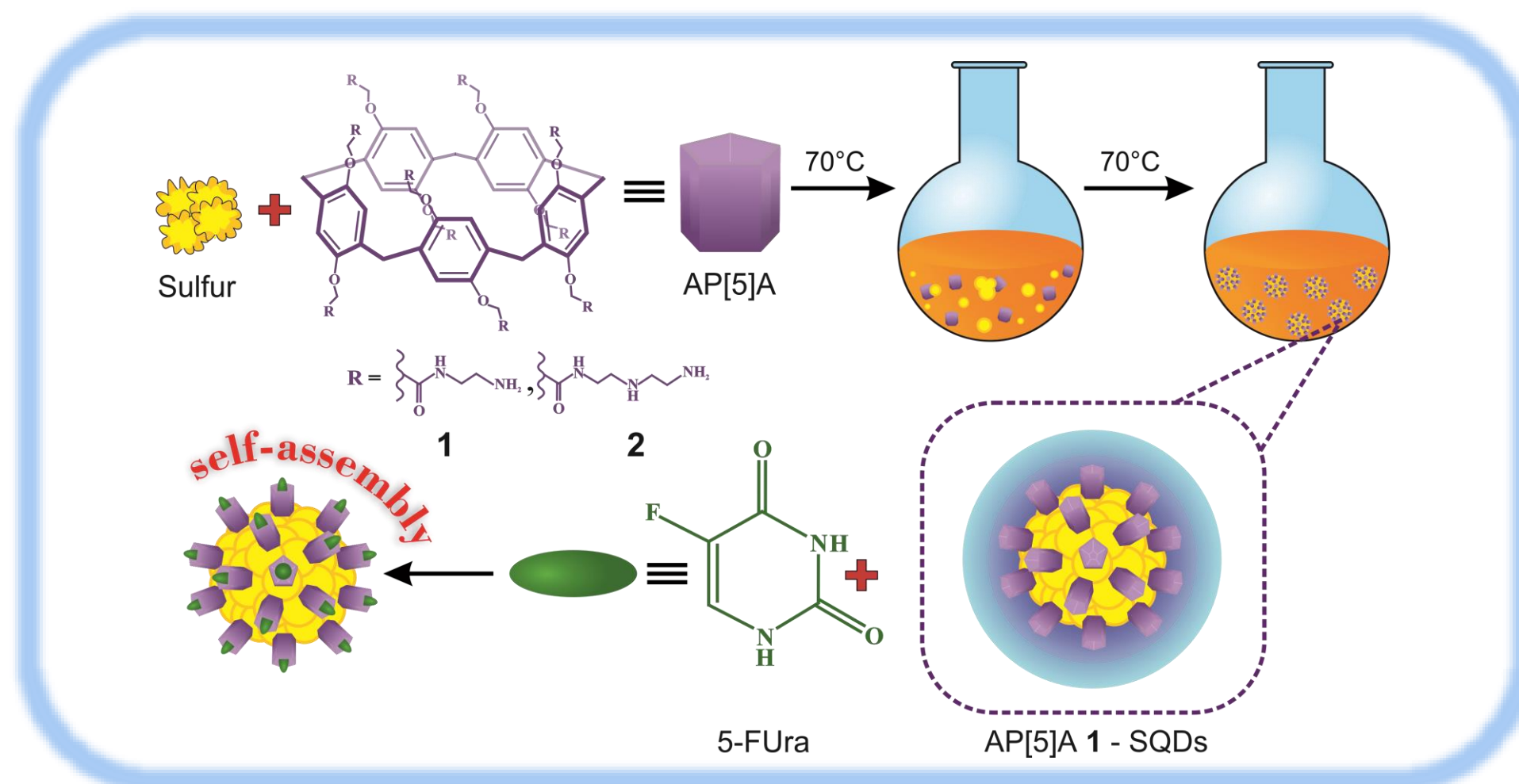
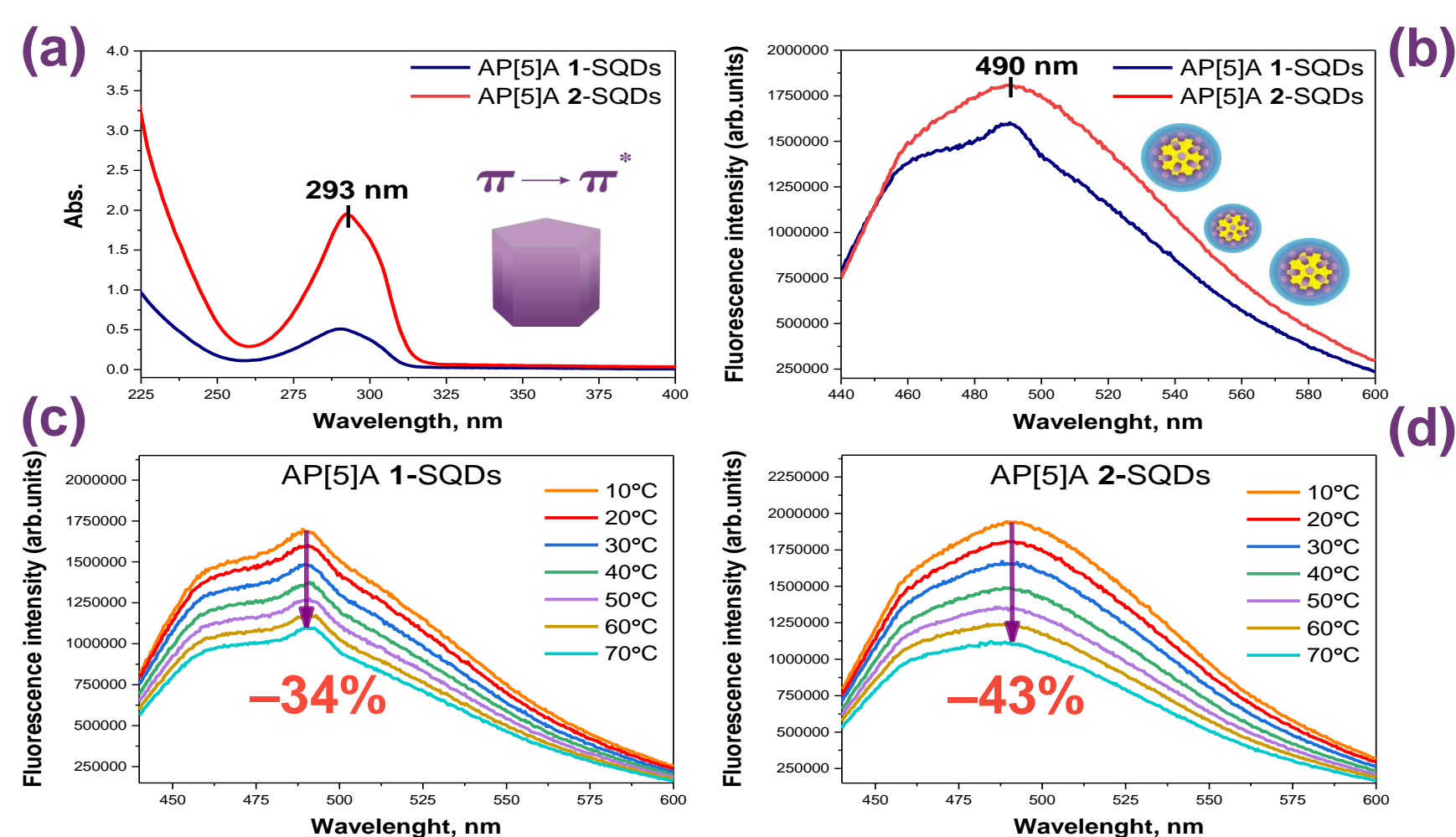


Fig. 1. Synthesis of SQDs using AP[5]A and fluorescent detection of 5-fluorouracil (5-FUra)

RESULTS & DISCUSSION



QY of AP[5]A 1 – SQDs = 8.0%

QY of AP[5]A 2 – SQDs = 3.2%

Fig. 2. Spectral properties of AP[5]A 1/2 – SQDs: (a) absorption spectra; (b) fluorescence spectra; (c), (d) temperature dependence of fluorescence

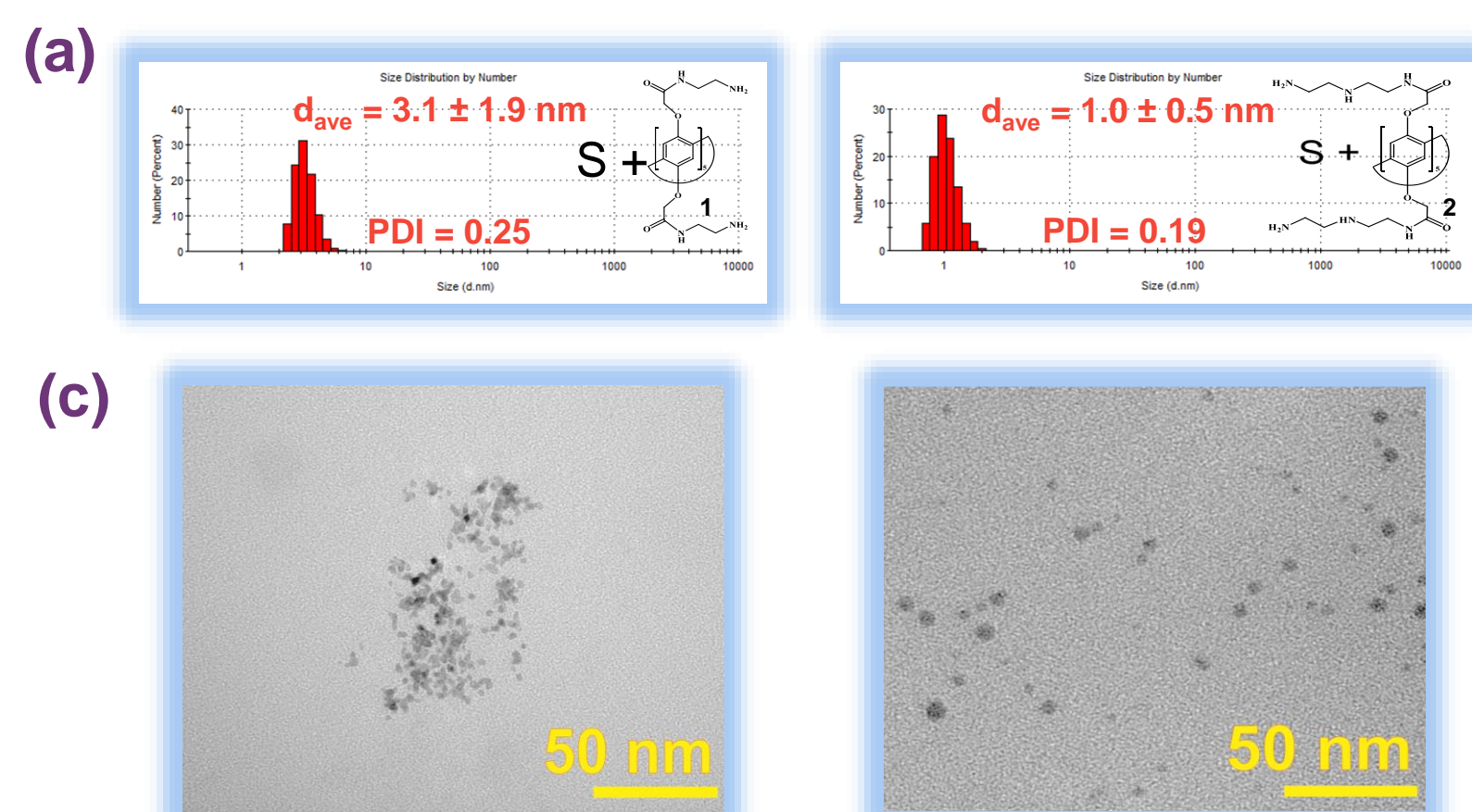


Fig. 3. Size distribution by number: (a) AP[5]A 1 – SQDs; (b) AP[5]A 2 – SQDs; and TEM images: (c) AP[5]A 1 – SQDs; (d) AP[5]A 2 – SQDs

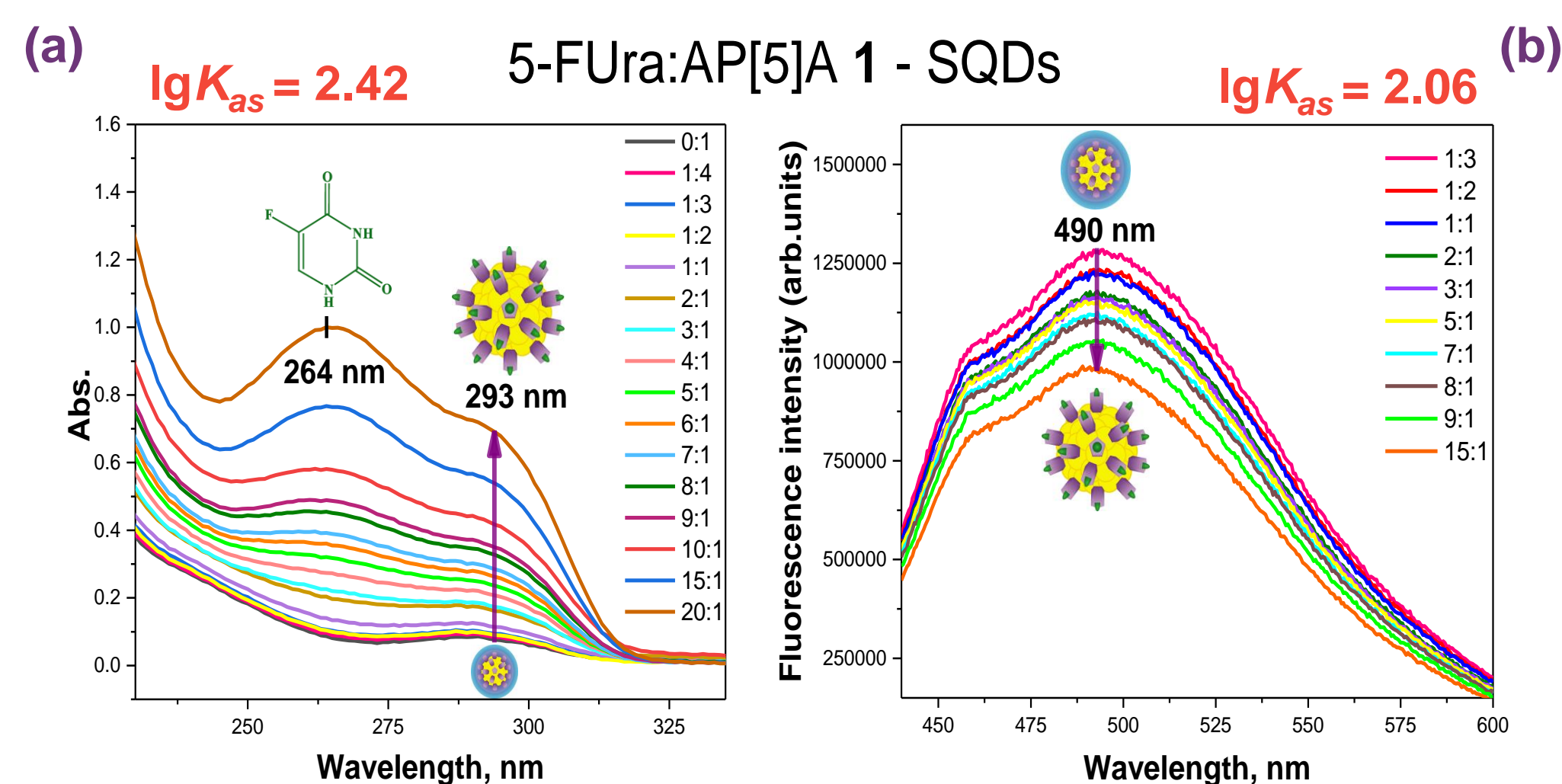


Fig. 4. (a) Spectrophotometric titration of AP[5]A 1 – SQDs with 5-FUra; (b) Fluorescence titration of AP[5]A 1 – SQDs with 5-FUra

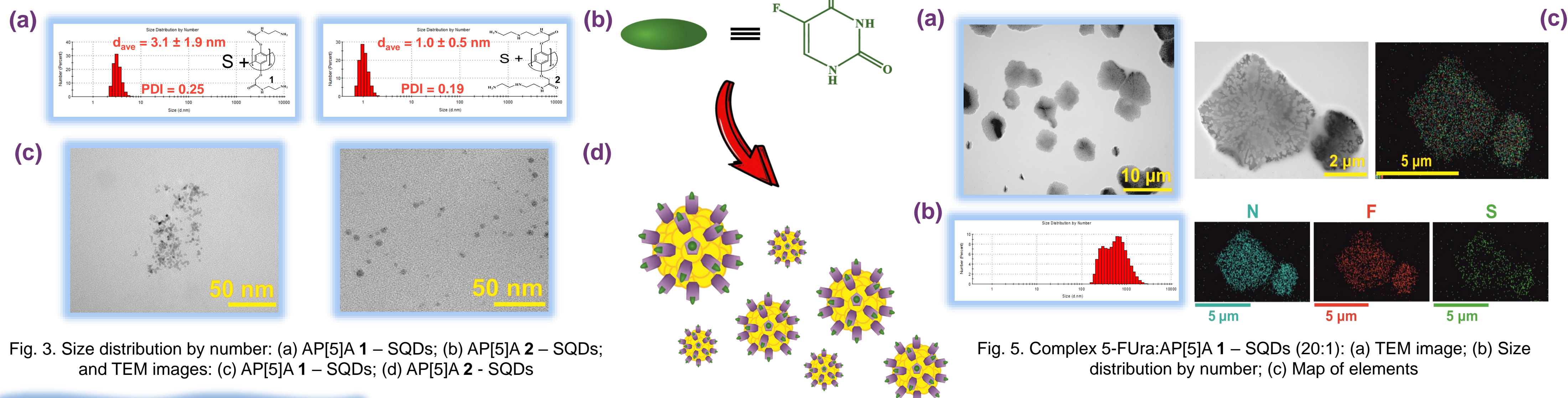


Fig. 5. Complex 5-FUra:AP[5]A 1 – SQDs (20:1): (a) TEM image; (b) Size distribution by number; (c) Map of elements

CONCLUSION

1. For the first time, SQDs were synthesized in the presence of AP[5]A serving as both surface passivation agents and alkaline medium providers;

2. Using UV-vis and fluorescence spectroscopy, the spectral characteristics of AP[5]A 1/2 – SQDs were studied ($\lambda_{\text{abs}} = 293 \text{ nm}$, $\lambda_{\text{em}} = 490 \text{ nm}$ ($\lambda_{\text{ex}} = 420 \text{ nm}$), the quantum yield (QY) for the AP[5]A 1 – SQDs and AP[5]A 2 – SQDs samples was QY = 8.0% and QY = 3.2%, respectively);

3. Using DLS and TEM, the size characteristics and morphology of AP[5]A 1/2 – SQDs were studied (the average diameters for the AP[5]A 1 – SQDs and AP[5]A 2 – SQDs samples were $d_{\text{ave}} = 3.1 \pm 1.9 \text{ nm}$ (PDI = 0.25) and $d_{\text{ave}} = 1.0 \pm 0.5 \text{ nm}$ (PDI = 0.19), respectively; AP[5]A 1/2 – SQDs have a spherical morphology);

4. Using UV-vis and fluorescence spectroscopy, the ability of 5-FUra to bind to AP[5]A 1 – SQDs was demonstrated. The decimal logarithms of the binding constants obtained from spectrophotometric and fluorescence titration for the 5-FUra:AP[5]A 1 – SQDs system were $\lg K_{\text{as}} = 2.42$ and $\lg K_{\text{as}} = 2.06$, respectively, with a 1:1 complex stoichiometry. The $\lg K_{\text{a}}$ values are within the same order of magnitude. **The obtained results open up promising possibilities for the development of sensors based on SQDs, in particular for the detection of specific bioactive molecules such as 5-FUra.**