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# Polymeric raspberry-like particles via template-assisted polymerisation<sup>†</sup>

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There is growing interest in the preparation of raspberry-like particles in the field of colloid science on account of their unique morphology and properties. In this study, we report polymeric raspberry-like particles with internal nanosized domains prepared using template-assisted polymerisation. In this method, polystyrene (PS) particles are employed as templates and 'reaction-vessels' inside which methyl methacrylate (MMA) and divinylbenzene (DVB) are absorbed and subsequently polymerised. PMMA raspberry-like particles are subsequently obtained after removal of the PS templates. The monodisperse PMMA raspberry-like particles can self-assemble into optical materials with high dispersion stability in salty aqueous environments.

## 1 Introduction

Raspberry-like particles exhibit a complex structure consisting of a large core decorated by smaller corona particles. They are attracting growing attention on account of their unique rough morphology and diverse applications on biomimetic superhydrophobic surfaces.<sup>1–19</sup> A traditional and straight-forward synthetic route towards raspberry-like particles is grafting pre-formed corona particles onto core particles *via* physical absorption,<sup>3,4</sup> supramolecular interactions<sup>17,20,21</sup> and/or chemical bonding.<sup>18,19</sup> Delicate functional raspberry-like particles have been obtained in this manner. However, the interactions between the corona particles and the core are generally weak, resulting in difficulties in further handling and application of such prepared raspberry-like particles.<sup>17</sup> Moreover, this synthetic method is highly dependent on a complicated interplay of experimental design and processes to control the size and to prevent particle coagulation during the formation of raspberry-like particles, which drastically impede their application in industry.

Template-assisted polymerisation is a powerful and scalable technique to prepare uniform polymeric particles with advanced structures. In this method, polymeric particles are usually employed as templates and reaction vessels inside which organic (such as polymers) or inorganic (such as silica) materials are formed, resulting in particles with advanced structures. This technique has been widely applied to prepare polymeric core-shell particles,<sup>22</sup> hollow colloids,<sup>23</sup> yolk-shell microspheres<sup>24</sup> and anisotropic Janus particles.<sup>25–27</sup> One intriguing example is

the preparation of polymeric Janus particles where crosslinked polystyrene (PS) microspheres are utilised as a template that was swollen with monomers. Subsequent polymerisation of the monomers inside the template results in asymmetric dumbbell particles on account of phase separation and elastic restriction of the crosslinked template network.<sup>25</sup>

In this study, we present the synthesis of raspberry-like particles using a template-assisted polymerisation method. As shown in Fig. 1a, PS particles (non-crosslinked) are employed as templates and reaction vessels for the polymerisation of methyl methacrylate (MMA) and the crosslinking agent divinylbenzene (DVB). Crosslinked polymethyl methacrylate (PMMA) nano-domains are then formed inside the reaction vessels. Subsequently, the non-crosslinked PS templates are removed by simple solvent etching, resulting in PMMA raspberry-like particles. To the best of our knowledge, we demonstrate for the first time that polymeric raspberry-like particles can also be prepared using a template-assisted polymerisation method. Our synthesis method delivers PMMA raspberry-like particles with uniform size as the monodisperse reaction vessels also serve as templates to regulate the size of the final raspberry-like particles. Moreover, the PMMA raspberry-like particles consist of integrated nano domains as the components are simultaneously formed and undergo phase-separation inside the PS reaction vessels. In addition, template-assisted emulsion polymerisation enables the generation of highly uniform raspberry-like particles in large scale, giving rise to potential applications in industry such as optical materials.

## 2 Experimental

### Materials and general methods

Chemicals were purchased from Alfa Aesar and Sigma Aldrich and used as received unless stated otherwise. <sup>1</sup>H NMR (400 MHz)

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spectra were recorded using a Bruker Avance QNP 400. ATR FT-IR spectroscopy was performed using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with a universal ATR sampling accessory. Transmission electron microscopy (TEM) characterisation was carried out by a FEI Philips Tecnai 20 TEM under an accelerating voltage of 200 kV. Samples were prepared by applying one drop of the dispersion onto a Holey R carbon coated copper TEM grid (400 mesh) drying overnight. Dynamic light scattering (DLS) and zeta potential (ZP) measurements were performed on Malvern Zeta-sizer NS90 instrument.

### Preparation of PS template particles

2,2-Azobis(2-methylpropionamidine) dihydrochloride (AIBA, 560.0 mg, 2.0 mmol) and DI water (300 mL) were added to a 500 mL round-bottle flask. The flask was then degassed and recharged with nitrogen five times to remove the oxygen. Subsequently, the flask was heated to 80 °C. After 5 min, styrene (St, 15.6 g, 150.0 mmol) was added while stirring at 1000 rpm. The mixture was stirred at 80 °C for 24 h. Finally, the obtained particles were purified by centrifugation and washed with DI water. The purified particles were dispersed in 300 mL DI water.

### Polymerisation inside the PS template particles

**Polymerisation of MMA and DVB.** To a 100 mL round-bottom flask, the PS template particles (30 mL) and water (30 mL) were added. The mixture was then degassed and refilled with nitrogen five times. Subsequently, a mixture of MMA (1.0 g, 10.0 mmol) and DVB (52.0 mg, 0.40 mmol) were added dropwise in 30 min while stirring at room temperature. The mixture was then stirred at 80 °C for 5 min before the addition of AIBA (1.0 mL, 50.0 mM) in an aqueous solution. The reaction was stopped after 24 h. The product was purified by centrifugation and the purified particles were dispersed in 60 mL DI water.

**Polymerisation of MMA, DVB and StMV.** To a 100 mL round-bottom flask, the PS template particles (30 mL), 1-methyl-1'-(4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-dium chloride iodide<sup>28</sup> (StMV, 45.0 mg, 0.10 mmol) and water (30 mL) were added. The mixture was then degassed and refilled with nitrogen five times. Subsequently, a mixture of MMA (1.0 g, 10.0 mmol) and DVB (52.0 mg, 0.40 mmol) were added dropwise in 30 min while stirring at room temperature. The mixture was then stirred at 80 °C for 5 min before the addition of AIBA (1.0 mL, 50.0 mM) in an aqueous solution. The reaction was stopped after 24 h. The product was purified by centrifugation and the purified particles were dispersed in 60 mL DI water.

### Preparation of raspberry-like particles

The composite particles (20 mL) were washed with dimethylformamide (DMF, 40 mL) and left stirring in DMF for 24 h. The washing procedure was exhaustively repeated five times. The final product was transferred into DI water (20 mL).

### Quantification of MV groups

Cucurbit[8]uril (CB[8]) can bind with perylene bis(diimide) (PDI) and another guests such as MV simultaneously, leading to strong ternary complexes of CB[8]/PDI/MV.<sup>29</sup>

A dispersion consisting of 10.0 mL PDI/CB[8] (PDI:CB[8] = 1:1, 20 μM) and 10.0 μL PMMA-MV raspberry-like particles was added into 9.99 mL H<sub>2</sub>O and stirred at room temperature for 5 min. The resultant dispersion was then filtered against dialysis tubing (MWCO 12400). The concentration of PDI/CB[8] in the filtrate was obtained from fitting the UV/vis to a calibration curve (ESI, Figure S3). The density of accessible MV on the PMMA-MV raspberry-like particles was determined to be 0.26 MV molecules per nm<sup>2</sup> calculated by the equation below:

$$d_{MV} = \frac{n_{MV} \times N_A}{4\pi r^2 \times N}, N = \frac{m_o}{\frac{4}{3}\pi r^3 \times \rho}$$

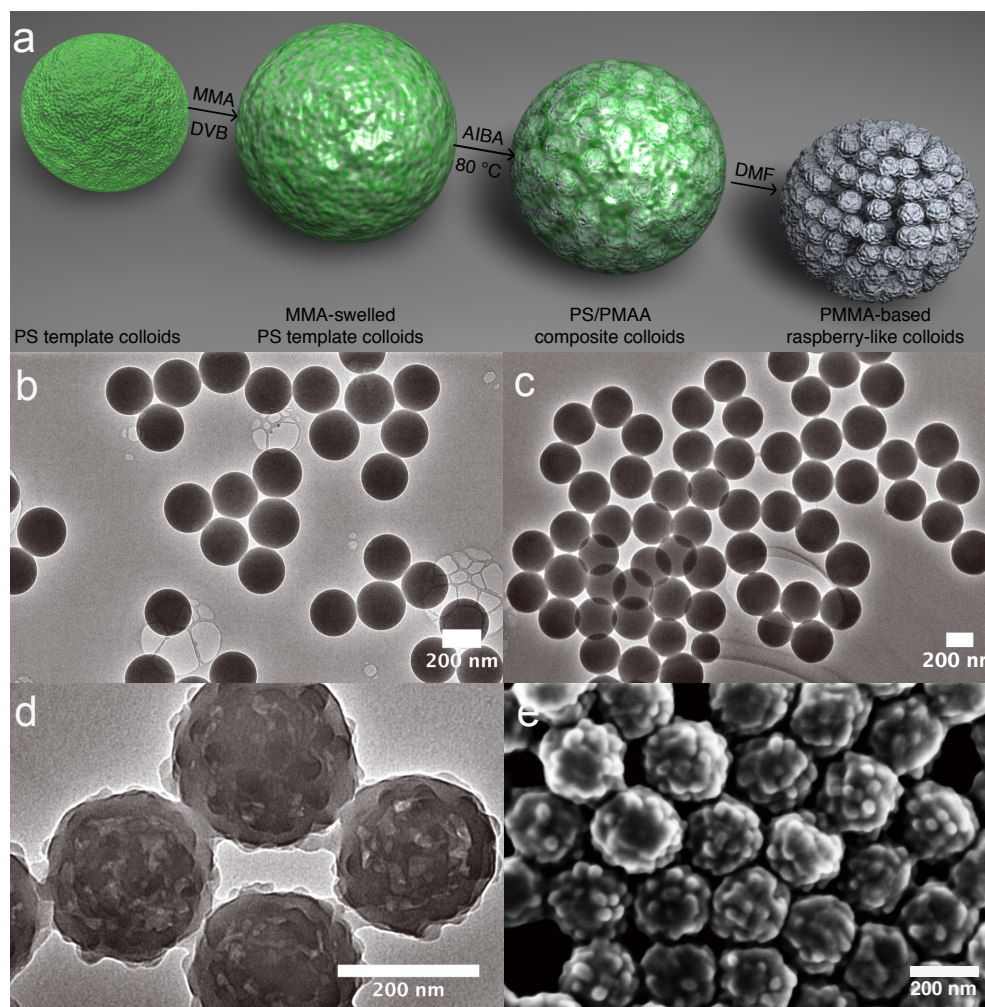
$d_{MV}$ : the density of MV on the PMMA-MV raspberry-like particles;  $n_{MV}$ : moles of accessible MV groups on PMMA-MV raspberry-like particles;  $N_A$ : Avogadro constant;  $r$ : average radius of PMMA-MV raspberry-like particles from TEM images;  $N$ : number of PMMA-MV raspberry-like particles;  $m_o$ : weight of PMMA-MV raspberry-like particles;  $\rho$ : density of PMMA-MV raspberry-like particles. Assuming that PMMA-MV raspberry-like particles is an ideal sphere, and  $\rho = 1 \text{ g/cm}^3$ .

## 3 Results and discussion

### Synthesis of PMMA raspberry-like particles

The PMMA raspberry-like particles are prepared in three steps as shown in Figure 1a. Initially, non-crosslinked PS particles with an average diameter of 250 nm ( $D_{TEM}$ , obtained from TEM images, Table 1, Entry 1) are prepared and employed as templates and reaction vessels. The advantage of using non-crosslinked PS particles as the reaction vessel is that they can be readily prepared on a large scale via soap-free emulsion polymerisation (SFEP) with controllable size and polydispersity.<sup>30</sup> The uniform morphology of the PS template particles, which exhibit a smooth surface are confirmed by TEM (Fig. 1b). The average hydrodynamic diameter ( $D_h$ ) of the PS template particles measured by dynamic light scattering (DLS) is 290 nm with a low polydispersity (PDI) of 0.01 (Table 1, Entry 1). The small difference between  $D_h$  and  $D_{TEM}$  results from solvation in water.

Subsequently, a monomer mixture of MMA and DVB is loaded into the PS template particles by mixing and stirring at 80 °C in water for 5 min (Fig. 1a).<sup>25,31</sup> Polymerisation of MMA and DVB inside the PS template particles is then initiated by adding an aqueous solution of initiator of 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AIBA), leading to the formation of PS/PMMA composite particles. Figure 1c shows the TEM image of the PS/PMMA composite particles. The  $D_{TEM}$  of the PS/PMMA composite particles measured from TEM is 320 nm, which is 70 nm larger than that of PS template particles (Table 1, Entry 1 and 2). The TEM image also shows that the PS/PMMA



**Fig. 1** a, Template-assisted polymerisation method for the preparation of PMMA-based raspberry-like particles. b-d, TEM images of PS template particles (b), PS/PMMA composite particles (c) and PMMA-based raspberry-like particles (d). e, SEM image of PMMA-based raspberry-like particles.

composite particles are spherical particles with smooth surfaces, indicating that the polymerisation of MMA and DVB was carried out inside the PS template. In other words, PS template particles serve as reaction vessels for the polymerisation of MMA and DVB. The  $D_h$  of the PS/PMMA composite particles is 360 nm (PDI=0.03), which is also 70 nm larger than that of PS template particles, consistent with the  $D_{TEM}$  results (Table 1, Entry 1 and 2).

**Table 1** Size summary of particles from TEM and DLS.

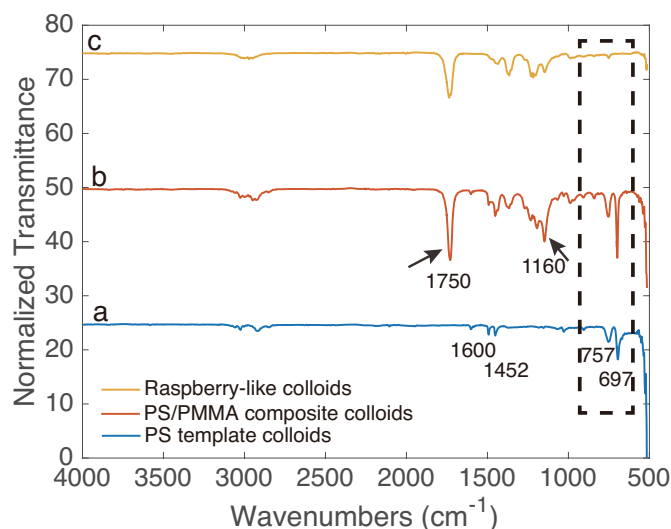
Entry	Samples	$D_{TEM}(\text{nm})^a$	$D_h(\text{nm})^b$	PDI <sup>b</sup>
1	PS template particles	250	290	0.01
2	PS/PMMA composite particles	320	360	0.03
3	PMMA raspberry-like particles	250	340	0.13

<sup>a</sup>Average diameter measured from TEM images; <sup>b</sup>Average hydrodynamic diameter measured by DLS.

Finally, the PS/PMMA composite particles are treated with DMF, a good solvent for non-crosslinked PS at room temperature. Only the non-crosslinked PS template is extracted from the PS/PMMA composite particle by DMF because the PMMA formed within the PS template particles is crosslinked, leading to the for-

mation of PMMA raspberry-like particles (Fig. 1a). The raspberry-like structure was confirmed by both TEM and SEM images. Fig. 1d shows the TEM image where monodisperse raspberry-like particles can be observed. Compared to the core-corona structure of raspberry-like particles fabricated using traditional grafting-on methods,<sup>3,4,17–19</sup> the PMMA raspberry-like particles prepared here are structurally different in that they show a novel raspberry-like structure with internal nano domains. These nano domains are integrated throughout the PMMA raspberry-like particles, which look like supraparticles assembled from nanosized PMMA particles. The surface roughness is confirmed by SEM images (Fig 1e) where monodisperse raspberry-like particles with nanosized coronas can be observed. The  $D_{TEM}$  of the PMMA raspberry-like particles is 250 nm, which is 70 nm smaller than that of PS/PMMA composite particles (Table 1, Entry 2 and 3). Interestingly, the PMMA raspberry-like particles are about the same size as the original PS template particles (Table 1, Entry 1 and 3). These results indicate that the PS template particles may be able to control the sizes of the PMMA raspberry-like particles. Moreover, the  $D_h$  of the PMMA raspberry-like particles is 340 nm (PDI=0.13), which is only 20 nm smaller than that of PS/PMMA

composite particles, yet 50 nm larger than that of the PS template particles (Table 1, Entry 1-3). Given that the PMMA raspberry-like particles are measured in the dry state for TEM and in an aqueous environment for DLS, it suggests that the PMMA raspberry-like particles were slightly compressed (by 20 nm) in water after extraction of the polystyrene by DMF. Moreover, they can further shrink to 250 nm after removal of water during TEM sample preparation.



**Fig. 2** FTIR spectra of PS template particles (a), PS/PMMA composite particles (b), PMMA-based raspberry-like particles (c).

### Characterisation of PMMA raspberry-like particles.

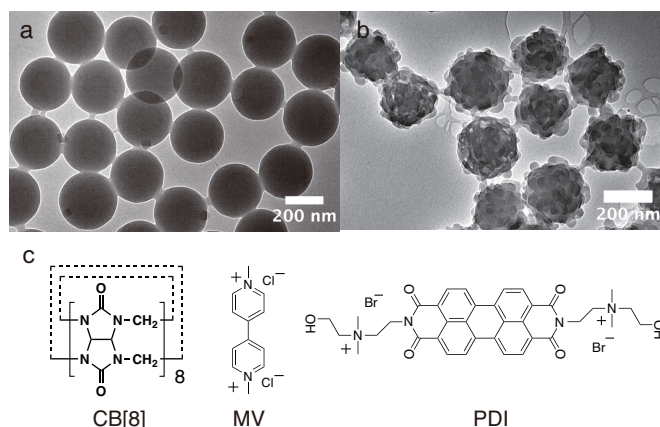
The formation of PMMA raspberry-like particles *via* template-assisted polymerisation was also monitored by Fourier transform infrared spectroscopy (FTIR). Fig. 2a shows the FTIR spectra of PS template particles, wherein the characteristic absorption peaks at 1600, 1493, 1452, 757 and 697  $\text{cm}^{-1}$ , respectively, confirms the composition of the template particles to be solely that of PS. Fig. 2b depicts the spectra of the PS/PMMA composite particles with two new strongly absorbing peaks at 1750 and 1160  $\text{cm}^{-1}$  (indicated by the black arrows). This can be ascribed to the stretching of the carbonyl groups and the vibration of the carbon-oxygen bond in PMMA, confirming the formation of PS/PMMA composite particles. Fig. 2c shows the FTIR spectrum of the raspberry-like particles after treatment with DMF. Here, only the characteristic absorption peaks of PMMA (1750 and 1160  $\text{cm}^{-1}$ ) remain. Additionally, the significantly weakened absorption at 757 and 697  $\text{cm}^{-1}$  indicates removal of PS from the composite particles (see the area highlighted by the black rectangle in Fig. 2).

### Discussion on the formation mechanism of PMMA raspberry-like particles.

A possible mechanism for the formation of raspberry-like particles *via* template-assisted polymerisation is discussed based on the results obtained here and previous studies in the literature.<sup>25–27,32</sup> The hydrophobic monomer mixture of MMA and DVB are readily absorbed into the network of non-crosslinked PS

template particles due to hydrophobic-hydrophobic interactions. The PS template particles then serve as reaction vessels for the polymerisation of MMA and DVB after addition of the initiator. The PMMA strands formed inside the PS template particles have very low miscibility with the local PS strands on account of the high Flory-Huggins interaction parameter between these two polymers.<sup>32</sup> Thus, polymerisation-induced phase separation results in the formation of PS/PMMA composite particles within which nanosized PMMA domains are covalently connected in the presence of DVB crosslinker. Interestingly, PS/PMMA composite particles with smooth surfaces are obtained using this template-assisted polymerisation method, while previous reports on template-assisted polymerisation using similar chemicals and reaction conditions produced anisotropic Janus particles.<sup>25</sup> This is likely due to the non-crosslinked nature of the PS template particles used in this study, which exhibits less elastic restriction than crosslinked PS particles and allows easier internal rearrangement of the newly formed PMMA polymers.<sup>25</sup> After extraction by DMF, the non-crosslinked PS is removed, resulting in PMMA raspberry-like particles with an integrated structure of connected nanosized PMMA particles (Fig. 1). It is worth noting the importance of premixing the MMA and DVB monomers and their complete absorption into the PS template particles prior to the addition of initiator at 80 °C in order to prepare the raspberry-like colloids. Otherwise, core-shell colloids would be formed if the MMA and DVB monomer mixture is added after the initiator.<sup>23</sup>

### Synthesis of PMMA-MV functional raspberry-like particles.



**Fig. 3** TEM images of (a) PS/PMMA-MV composite particles and (b) PMMA-MV raspberry-like particles. c) Chemical structure of cucurbit[8]uril (CB[8]), methyl viologen (MV) and perylene bisdiimide (PDI).

The template-assisted polymerisation method was extended to prepare raspberry-like particles with functional moieties. Functional groups can be readily introduced together with MMA and DVB. Using the same PS template particles, PS/PMMA composite particles bearing methyl viologen (MV) groups (PS/PMMA-MV composite particles, Fig. 3a) are fabricated *via* the template-assisted polymerisation of MMA, DVB and 1-methyl-1'-(-4-vinylbenzyl)-[4,4'-bipyridine]-1,1'-diium chlo-

ride iodide (StMV). Viologen derivatives have been used as antibacterial and electrochromic materials as well as in herbicide formulations.<sup>33</sup> Similar to PS/PMMA composite particles, the PS/PMMA-MV composite particles are also spherical particles with smooth surfaces as shown in Fig. 3a. The  $D_{TEM}$  of the PS/PMMA-MV composite particles is 290 nm. Fig. 3b shows the TEM image of the raspberry-like particles with MV groups (PMMA-MV raspberry-like particles) obtained after the removal of PS template particles, where monodisperse particles with clear raspberry-like structures can be distinguished. The  $D_{TEM}$  of the PMMA-MV raspberry-like particles is 250 nm. The presence of MV groups is confirmed by their complexation with cucurbit[8]uril (CB[8]) and perylene bis(diimide) (PDI) (Fig. 3C).<sup>29</sup> The concentration of accessible MV groups on each PMMA-MV raspberry-like particle is 0.26 MV molecules per nm<sup>2</sup>.

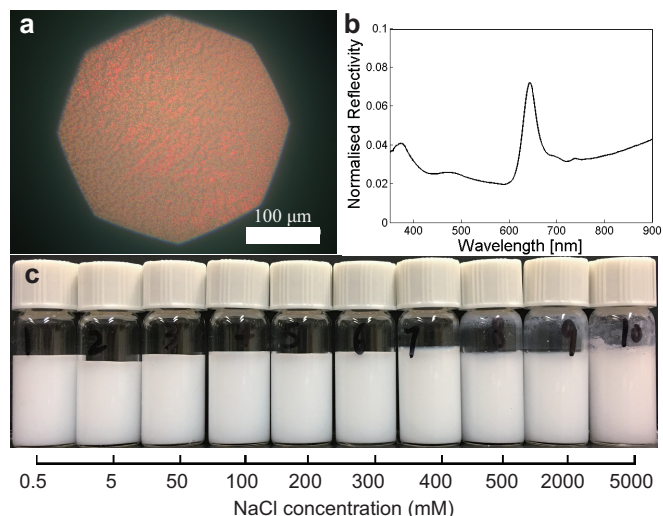
### Optical property and dispersion stability of PMMA raspberry-like particles.

Raspberry-like particles prepared using the template-assisted polymerisation are uniform in size and thus can spontaneously self-assemble into lattice structures (Fig. 1e), exhibiting unique optical properties (Fig. 4). A drop of a dispersion (4 wt%) of the PMMA raspberry-like particles was deposited onto a glass substrate. Upon evaporation, a red film resulted from Bragg reflections of a periodic structure of raspberry-like particles, which formed on the glass substrate (Fig. 4a), its reflection spectrum has a peak centred at 645 nm (Fig. 4b).

The applicability of colloidal dispersions in research or industry highly depends on their stability in the dispersion. Recently, we have shown that raspberry-like particles exhibit unprecedented stability against salt-induced aggregation over large variations of salt concentrations on account of their unique morphology.<sup>34</sup> In this study, we also find that the PMMA raspberry-like particles show incredibly high resistance to salt-induced aggregation (Fig. 4c). The dispersions of PMMA raspberry-like particles are stable and no coagulation of particles is observed even when 2000 mM sodium chloride (NaCl) is added. Small aggregates of PMMA raspberry-like particles are observed in water only when the concentration of NaCl is as high as 5000 mM (about 10 times higher than the salt concentration in seawater).

## 4 Conclusions

In summary, raspberry-like particles with internally-connected nano domains has been prepared *via* template-assisted polymerisation. Non-crosslinked polystyrene (PS) particles are employed as reaction vessels and templates within which methyl methacrylate (MMA) and divinylbenzene (DVB) are polymerised. On account of phase separation and proper elastic restriction from the PS template, monodisperse PMMA raspberry-like particles are obtained after removal of the PS template. Functional PMMA raspberry-like particles bearing methyl viologen groups can also be prepared using the template-assisted polymerisation method. The PMMA raspberry-like particles are uniform in size, and can self-assemble into optical materials with structural colour. In addition, the dispersion of PMMA raspberry-like particles shows in-



**Fig. 4** a, Optical microscopy image taken in reflective mode of a dried film of PMMA raspberry-like particles and b, the corresponding reflectivity curve. c, Photograph of dispersions of PMMA raspberry-like particles (1 wt%) with different added NaCl concentrations.

credible stability against salt-induced aggregation.

### Conflicts of interest

There are no conflicts to declare.

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