Supporting Information

## **Bright Structural Coloration from Organic Polymeric Photonic Crystal with Robust Heat-Resistance**

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**Fig. S1** Typical large-scale SEM image of TPF spheres synthesized using 0.225 g of 4,4'-Thiodiphenol, 0.225 mL of formaldehyde, 0.05 g of F127, and 0.3 mL of TEA, 20 mL of ethanol, 50 mL of water and undergoing 150 °C of hydrothermal process for 12 h.

Sample	Thiodiphenol	Formaldehyde	TEA	Size (nm)			$ZP^4$
	(g)	(mL)	(mL)	Da <sup>1</sup>	Dh <sup>2</sup>	- PDI <sup>3</sup>	(mV)
1	0.125	0.125	0.3	142	161.7	0.002	-34.9
2	0.175	0.175	0.3	168	196.1	0.017	-35.4
3	0.225	0.225	0.3	231	256.5	0.003	-33.5
4	0.275	0.275	0.3	285	313.0	0.021	-34.1
5	0.300	0.300	0.3	337	361.2	0.029	-31.8

 Table S1
 Synthesis parameters and corresponding properties of TPF microspheres

 synthesized at different monomer concentration.

1 Da: Average particle diameter calculated on the base of counting 200 individual particles in the SEM images. 2 Dh: Hydrodynamic particle size of corresponding TPF spheres measured by DLS. 3 PDI: Particle size distribution index. 4 ZP: Zeta potential. Other parameters: 50 mL water, 20 mL ethanol, 0.05 g F-127.



**Fig. S2** Digital photographs of red, orange and green structural color flms self-assembled from TPF microspheres with different particle sizes: a) 278 nm, b) 265 nm, and c) 231 nm.



**Fig. S3** Digital photographs of the red TPF structural color films heat-treated at different temperature and time.



**Fig. S4** Digital photographs of the orange TPF structural color films heat-treated at different temperature and time.



**Fig. S5** Digital photographs of the green TPF structural color films heat-treated at different temperature and time.



**Fig. S6** a)-c) Reflectance spectra of three TPF structural color films heat-treated at 300 °C for different time: a) red b) orange and c) green; d) Peak position curve as a founction of the heat-treatment time.



Fig. S7 a) TGA curve of the TPF microspheres sample, b) Corresponding DTG curve.