ELECTRONIC SUPPLEMENTARY INFORMATION

Customizing Polyelectrolyte Complex Shape through Photolithographic Directed Assembly

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A. Photopatterning Chamber Constructed inside a Petri Dish

To prepare free-standing custom-shaped PECs via photoirradiation through a photomask, a 2.5 cm × 2.5 cm × 0.1 cm chamber was prepared inside a petri dish using 1-mm-thick gasket tape (see Fig. S1). The rectangular region inside the four tape strips was then filled with precursor PAH/AA/IC solution and covered with a coverslip and photomask.

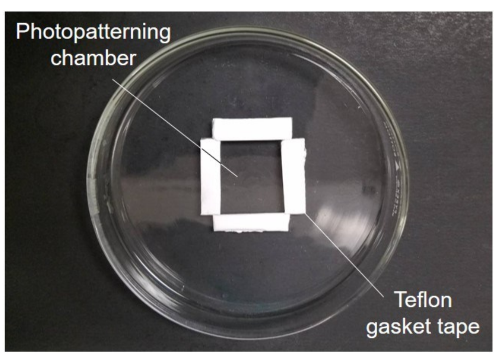

Fig. S1. Digital photograph of photopatterning chamber prepared in a petri dish using Teflon gasket tape.

B. Removal of Residual Photoinitiator and Monomer

To explore whether residual photoinitiator and monomer could be removed from the photopatterned PECs, flower-shaped PECs (see Fig. 8) were washed in 300 ml of gently stirred 5 mM NaCl solution for 3 d with the media replaced daily. After this wash, the PECs were dissolved in 3 ml of 100 mM NaOH solution to release the IC photoinitiator and acrylate monomer remaining inside the PEC. The IC and acrylate content in the NaOH solution was then probed by UV-vis spectroscopy using a Varian Cary 50 (Sparta, NJ) spectrophotometer and BRAND® Ultra-micro UV cuvettes, and compared with that obtained using unwashed flower-shaped PECs (which were dissolved in 3 ml of 100 mM NaOH solution immediately upon preparation). The unwashed PECs yielded strong absorbance at λ = 277 nm and around 220 nm (see Fig. S2), which matched the peaks detected from the IC photoinitiator and AA monomer, respectively (data not shown). When the PECs were washed in 5 mM NaCl solution, however, the peak at 277 nm entirely vanished (indicating near-complete removal of the initiator) and the peak near 220 nm also sharply diminished. This drastic reduction in UV signal indicates that, though further optimization of the washing procedure should be pursued in the future, most of the unreacted initiator and monomer was successfully removed.

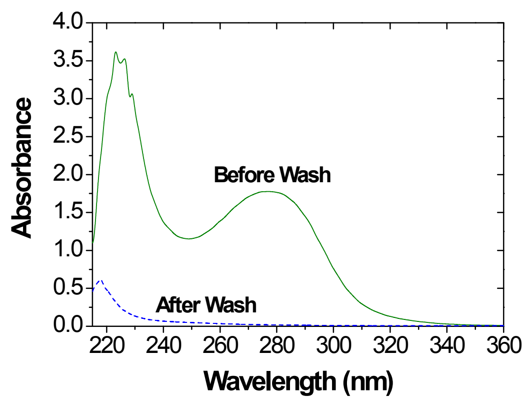

Fig. S2. UV-vis spectra obtained upon dissolving a flower-shaped PEC (see Fig. 2a) in 3 ml of 100 mM NaOH solution (—) immediately after forming the PECs and (- - -) after washing the PECs for 3 d in 5 mM NaCl solution.

C. Aggregation States of Photopatterned PECs

The aggregation states of photopatterned PAH/PAA PECs depended on the compositions of the precursor PAH/AA solutions and were evident from visual observation (see Fig. S3). When the photopatterned PECs were continuous they maintained their shape and could hold their own weight. Conversely, when the PECs were discontinuous, they dispersed when the coverslip was removed.

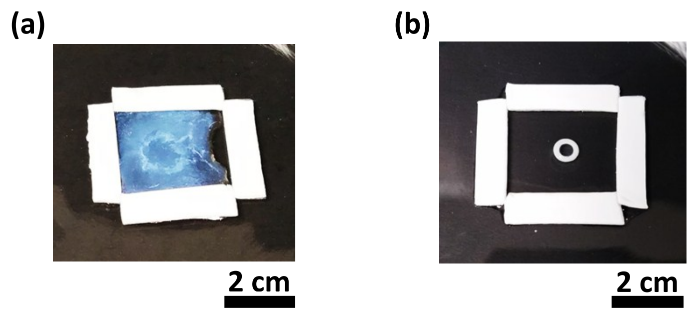

Fig. S3. Photographs of toroidal PECs with (a) dispersed and (b) continuous aggregation states. The PEC in (a) was prepared using 2.0 M PAH and 1.5 M AA,while that in (b) was prepared using 1.0 M PAH and 1.0 M AA.

D. Nonuniformity in Photopatterned PEC Flowers

The nonuniformity of flower-shaped PECs was investigated by preparing them from precursor solutions with 1:1 PAH:AA molar ratios and either 1 or 2 M PAH and AA concentrations. These flowers were then carefully cut with a sharp razor blade to separate their top and bottom halves (which had roughly similar weights and where the top half was the side of the flower exposed to the incident light). These sections were then washed in 200 ml of 50 mM NaCl for 24 h (to remove the unreacted AA monomers), whereupon they were separately dissolved in 5 ml of pH 1.5 water and titrated with 20 µl aliquots of 1 M NaOH to determine their buffering capacity. The pH evolution during the titration was measured using a Mettler-Toledo pH meter (Columbus, OH) fitted with an InLab Expert Pro electrode.

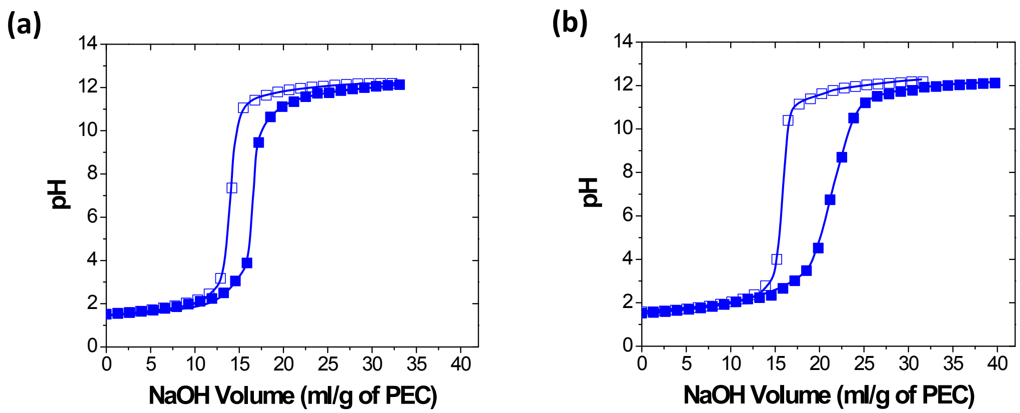

Fig. S4. Titration curves for PAH/PAA mixtures prepared by dissolving the (closed symbols) top and (open symbols) bottom sections of PEC flowers prepared from stoichiometric PAH/AA precursor solutions that were either (a) 1 M or (b) 2 M in each monomer. The lines are a guide to the eye.

Regardless of the precursor solution, the buffering capacity of the top section of the PEC (which was closest to the irradiation source) exceeded that of the bottom section (see Fig. S4, open and closed squares), indicating a higher concentration of carboxylic acid and primary amine groups. This difference stemmed from the complexation gradient developed during photoirradiation, where more polymerization-based polyelectrolyte complexation occurred on the top side of the flower. The buffering capacity was further enhanced by increasing the PAH and AA concentrations from 1 to 2 M (see Fig. S4a and b). This enhancement in buffering also coincided with a larger difference in buffering between the top and bottom PEC layers. This change in buffering difference may have reflected a greater complexation non-uniformity in PECs formed from more-concentrated precursor solutions.

The nonuniformity within these PECs was further investigated by gravimetrically measuring their swelling in gently stirred pH 7.0 water (without any added salt) after being washed for 24 h in 200 ml of 50 mM NaCl solution. Here the normalized degree of swelling was calculated as:

$$Q_{swelling} = \frac{W_t - W_i}{W_i} \tag{S1}$$

where, W_t was the weight of the PEC at time, t, and W_i was the initial PEC weight. The swelling of the top section of the PEC flower (the portion nearest to the irradiation source) was much less than that of the bottom section (see Fig. S5a and b). This swelling difference stemmed from the nonuniformity in complexation within the PECs, which led to their self-folding. Moreover, when the PAH and AA concentrations were increased from 1 to 2 M, the swelling became both faster and more extensive, likely due to an increased osmotic pressure difference between the PEC and the surrounding solution (Fig. S5a and b).

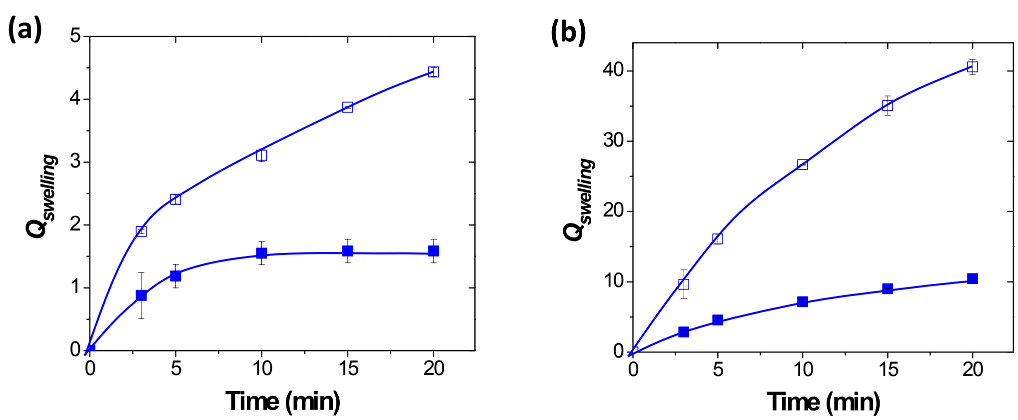

Fig. S5. Swelling behavior of (closed symbols) top and (open symbols) bottom PEC sections at PAH/AA concentrations of (a) 1 M and (b) 2 M. The lines are a guide to the eyes and the error bars are standard deviations.

E. Swelling Properties of PEC Flowers

In addition to having variable structural nonuniformity, the flower-shaped PECs prepared at different PAH and AA concentrations varied significantly in their final extents of swelling. As seen from the final/plateau $Q_{swelling}$ values in Table S1 (obtained as described in Section 4.7), flowers prepared using higher PAH/AA concentrations swelled much more than those prepared at lower PAH/AA concentrations.

Table S1. Effect of PAH/AA concentration on the final/plateau degree of swelling of the folding PEC flowers in Figs. 8 and 9.

[AA] (M)	*[PAH] (M)*	$Q_{swelling}$
1.0	1.0	2.16 ± 0.70
1.5	1.5	9.31 ± 1.00
2.0	2.0	25.36 ± 0.29