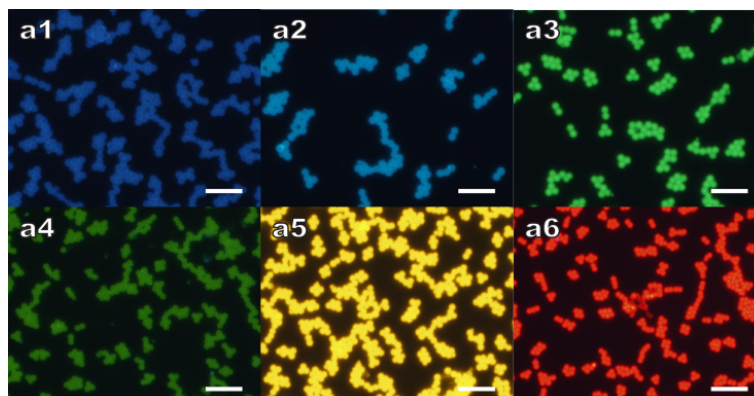## Supporting Information

Figure S1. Fluorescence microscopic images of dye doped microsphere samples under UV excitation. From a1 to a6: samples doped with AMC, ANS, Flu, Rh 110, Rh B and SRh 101 dyes.
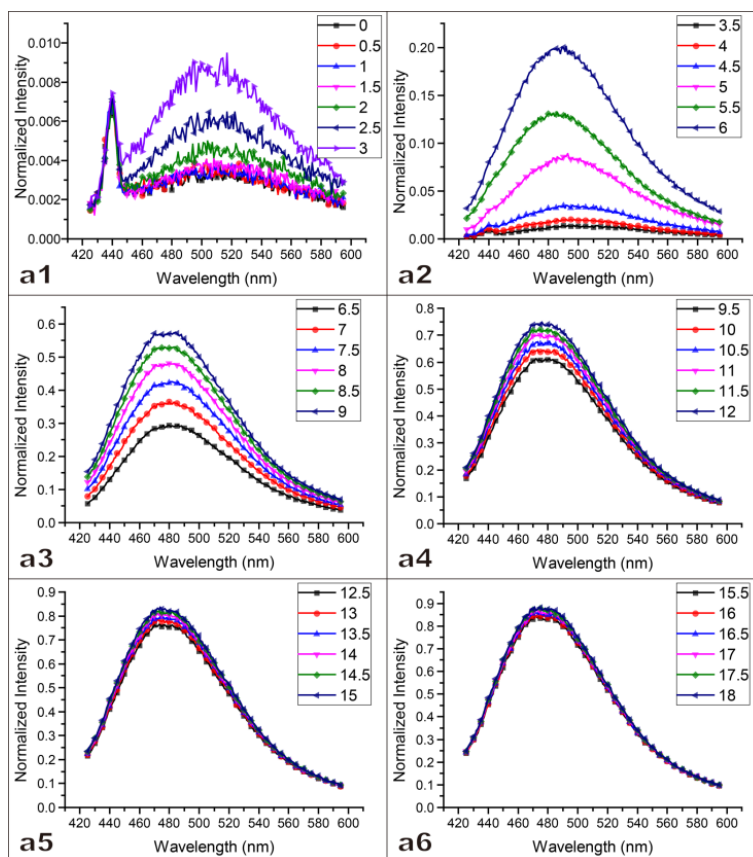
Figure S2. Emission spectra of the reaction system during the organic sol-gel process in 0 to 18 minutes, with excitation of 380nm. From a1 to a6: spectra recorded in 0-3 minutes, 3-6 minutes, 6-9 minutes, 9-12 minutes, 12-15 minutes and 15-18 minutes, respectively, with time intervals of 30 seconds.
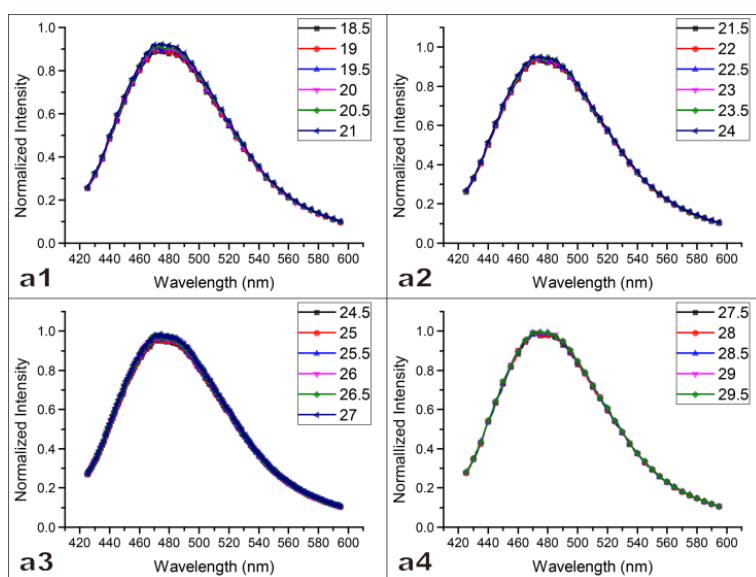
Figure S3. Emission spectra of the reaction system during the organic sol-gel process in 18 to 30 minutes, with excitation of 380nm. From a1 to a4: spectra recorded in 18-21 minutes, 21-24 minutes, 24-27 minutes and 27-29.5 minutes, respectively, with time intervals of 30 seconds.
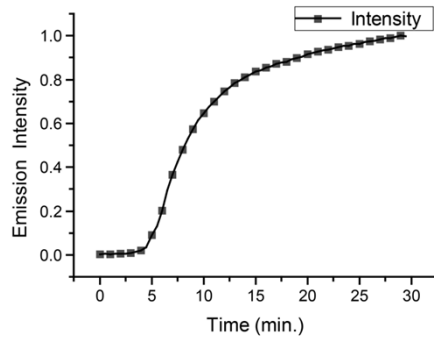
Figure S4. Maximum emission intensity changes of the system during the organic sol-gel process in 30 minutes, with excitation of 380nm.
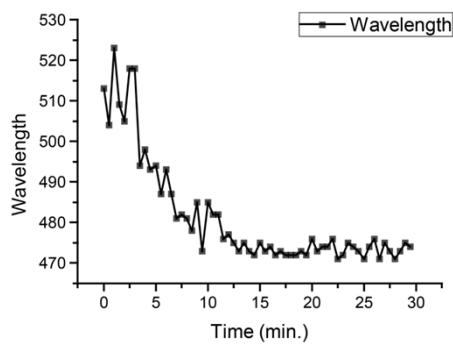

Figure S5. Maximum emission wavelength changes of the system during the organic sol-gel process in 30 minutes, with excitation of 380nm.
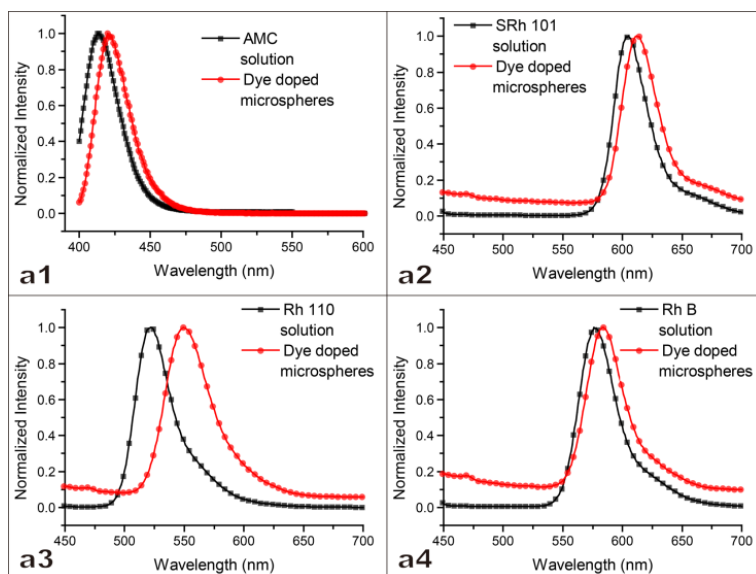
Figure S6. Representative emission spectra of the dye solution and dye doped microspheres samples. From a1 to a4: emission spectra of AMC, SRh 101, Rh 110 and Rh B dye solution and dye doped microspheres, with excitation of 360nm for AMC and 380nm for other three dyes.
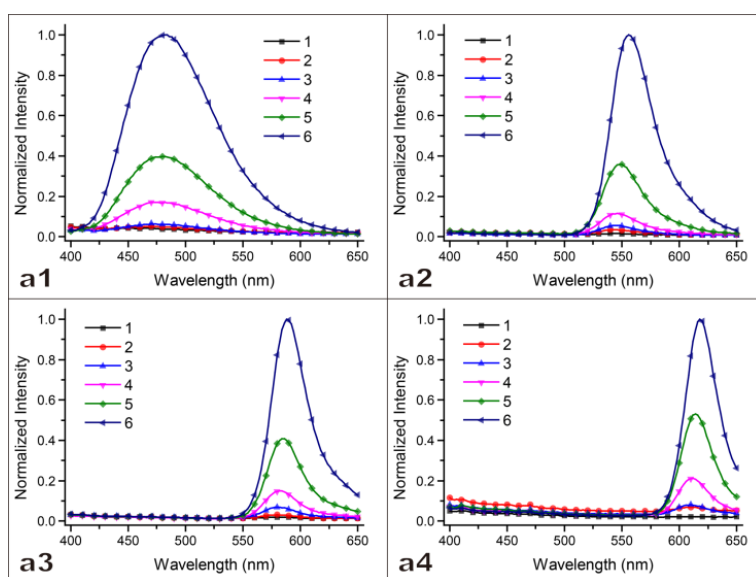
Figure S7. Emission spectra of the dye doped microspheres samples with different doping concentrations. From a1 to a4: emission spectra of ANS, Rh 110, Rh B and SRh 101 dye doped microsphere samples with doping concentrations(from 1 to 6): 35nmol·g^{-1}, 105nmol·g^{-1}, 320nmol·g^{-1}, 960nmol·g^{-1}, 2.9μmol·g^{-1} and 8.7μmol·g^{-1}, with excitation 380nm.

Calculation of the average inter-distance of the doped dyes

Assume the doped dyes are evenly distributed in the microsphere, their average inter-distance (d, m) could be expressed as follows:

$$d = \frac{1 \times 10^{-2}}{\sqrt[3]{\rho_m \times C \times N_A}}$$

Where C is the doping concentration, in unit of mol·g-1, ρ_m is the relative density (take water as 1.0, at 25°C) of the microsphere, N_A is Avogadro's constant. As MF microspheres have relative density of 1.6, a d versus C curve could be calculated as follows:
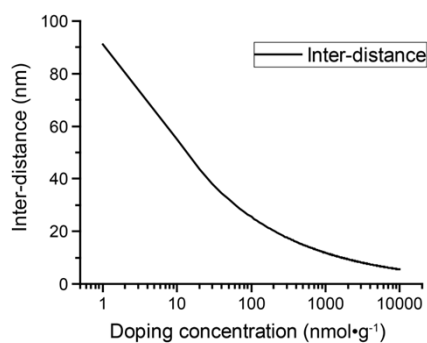

Figure S8. Calculated dye inter-distance versus doping concentration curve

When doping concentrations are 35, 105, 320, 960, 2900 and 8700 nmol·g^{-1}, the calculated inter-distances of the doped dye molecules are: 31, 21, 14, 10, 7 and 4 nm.
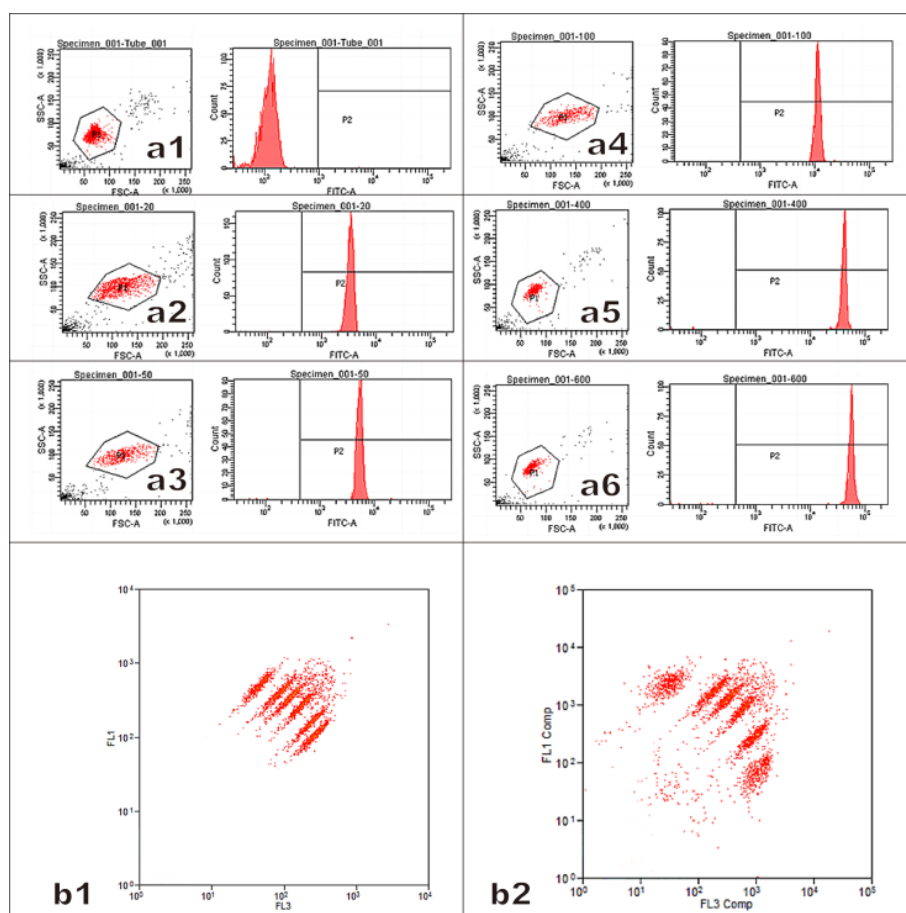
Figure S9. Flow cytometry analysis of dye doped MF microspheres. (a1-6) Fluorescent intensity distribution of microsphere samples doped with different amounts of Flu dyes. The doping concentrations are (from a1 to a6): 0, 35, 105, 320, 960 and 2900 nmol·g^{-1}. (b1) Fluorescence profiles results of a mixed sample of 6 sets of Rh 110 and SRh 101 dual doped microspheres in a flow cytometer. Axes scales are light intensity through a filter "FL1, Green" for wavelengths 515–545nm and a filter "FL3, Red" for wavelengths 650-670nm. (b2) Fluorescence profiles results of the same mixture sample, with adjusted composition sets in both FL1 and FL3 channels.
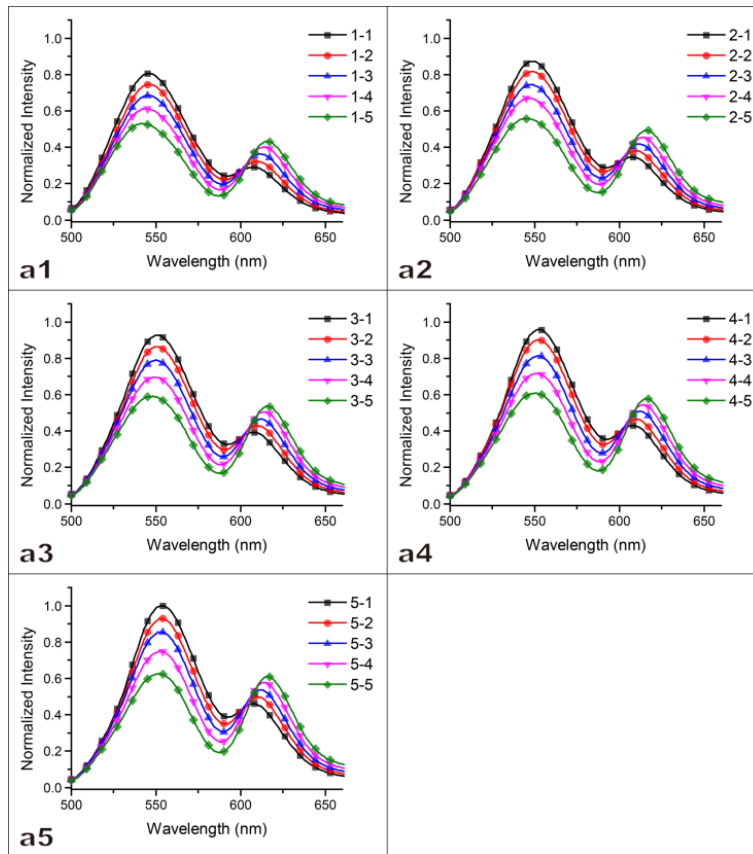
Figure S10. (a1-5) Emission spectra of all 5 groups (25 sets) of the dual encoded (Rh 110 and SRh 101) MF microsphere samples.
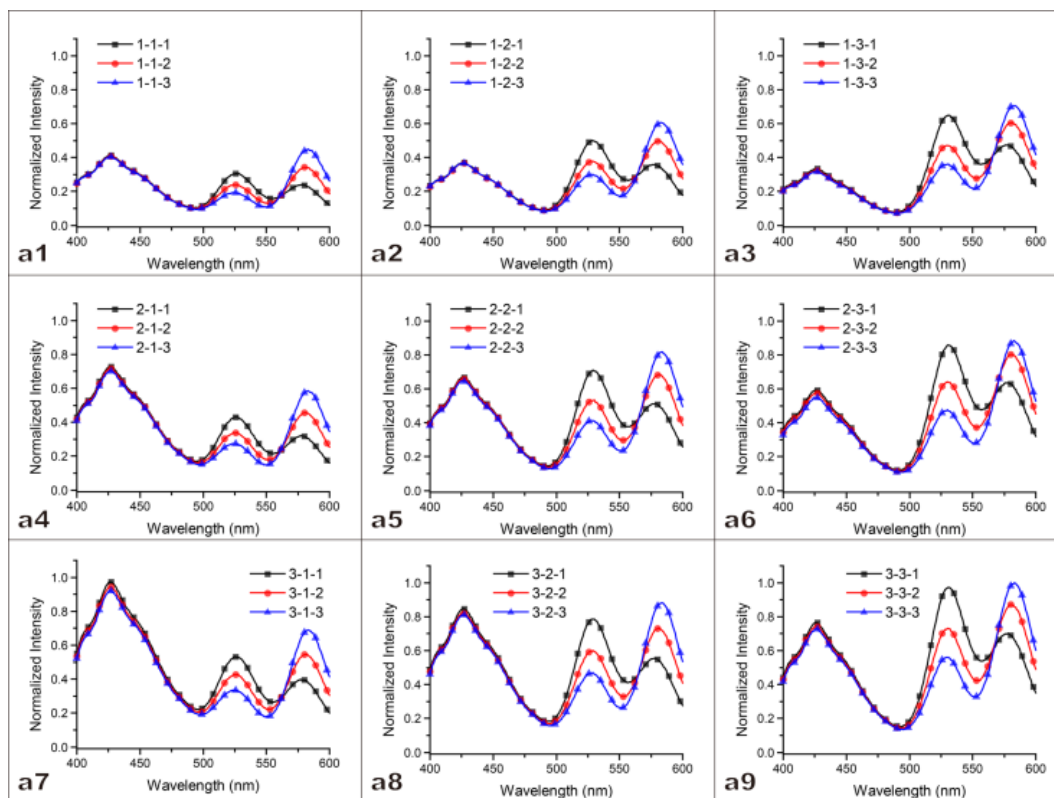
Figure S11. (a1-9) Emission spectra of all 9 groups (27 sets) of the triple encoded (Acr, Flu and Rh B) MF microsphere samples.
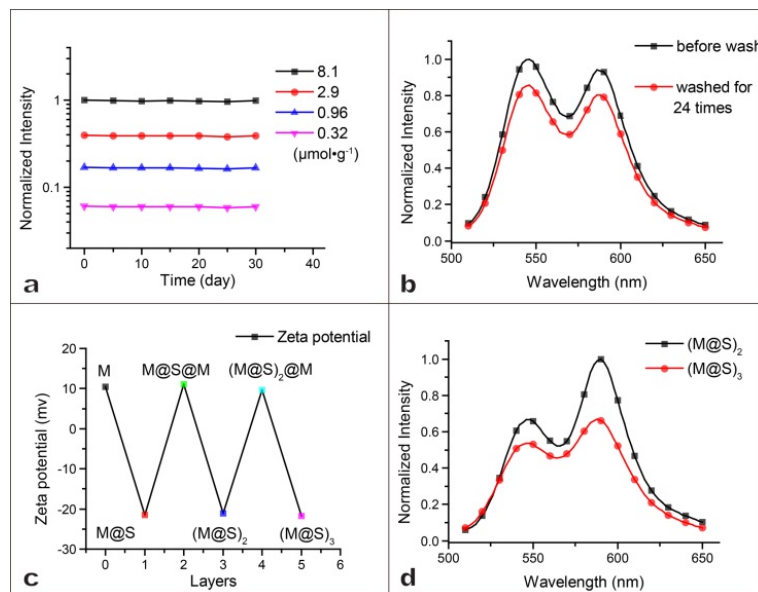
Figure S12. (a) Emission intensity versus time curve of ANS doped MF microspheres during storage. (b) Emission spectra of dual doped (Rh 110 and Rh B) MF microspheres samples before and after 24 washes. (c) Zeta potential changes during the preparation of the multi-shell structured $(M@S)_3$ composite microspheres. (d) Emission spectra of dual doped (Rh 110 and Rh B) $(M@S)_2$ and $(M@S)_3$ microspheres