Fabrication of Photoluminescent Quantum Dot Thiol-yne Nanocomposites Via Thermal Curing or Photopolymerization

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Figure S1. Figure showing the reverse mold (left) used to form the ‘NRL’ polymer (right) that was composed of both native thiol-yne polymer and red QD thiol-yne nanocomposite.

The freestanding ‘NRL’ polymer in Figure S1 was fabricated by pouring red QD thiol-yne nanocomposite prepolymer into the ‘letter wells’ of the NRL reverse mold. The material in the wells was then photopolymerized by UV irradiation. Native thiol-yne prepolymer (devoid of QDs) was then poured into the reverse mold on top of the wells containing red QD thiol-yne nanocomposite material and photopolymerized via UV irradiation. Finally, the polymerized material was removed from the reverse mold to yield a free-standing, photoluminescent material containing both native and red QD thiol-yne.

Figure S2. Representative TEM image of red QDs (1.5 uM) within a thiol–yne nanocomposite. Scale bar represents 200 nm.
Figure S3. Raw measured photoluminescence (PL) data for red and green QDs before and after incorporation into thiol-yne polymer matrices. PL for thiol-yne polymer also indicated in the plot as ‘polymer.’

Figure S3 shows the PL of green and red QDs prior to ligand cap-exchange and prior to incorporation into the thiol-yne polymer matrix in comparison with the PL of the final QD thiol-yne nanocomposite material. The final nanocomposite materials show a blue-shift in wavelength expression, but the shift is very slight for both green and red QDs, meaning that the expression of color is essentially unaltered by the process of ligand cap-exchange and polymer incorporation. When comparing the QD PL to that of the nanocomposites, we do note that there is a decrease in PL intensity, with that decrease being less pronounced for green than red. However, the PL intensity of the QD thiol-yne nanocomposites remains substantial.

Table S1. Refractive index (n), glass transition (T_g) and degradation temperature data with extended decimal place values for native thiol-yne polymer and QD thiol-yne nanocomposites.

| Sample          | n (@ 635.4 nm) | T_g (°C) | Degradation Temperature (°C) |
|-----------------|----------------|----------|-----------------------------|
| Native Thiol-yne| 1.56492        | 46.6     | 326.8                       |
| Green QD Thiol-yne | 1.55386     | 45.8     | 312.5                       |
| Red QD Thiol-yne | 1.56079       | 46.3     | 317.9                       |
Figure S4. Thermal gravimetric analysis plots indicating the temperature at which 90 wt% of the polymer remains.

Figure S4 shows data obtained from thermogravimetric analysis of native and QD thiol-yne materials. The addition of 1.5 µM QDs decreases the degradation temperature slightly. However, when 90 wt% of each material remains, the range in degradation temperature between the native material and QD incorporated material is less than 15 °C. A complete data set is provided in Table S1.