Environmental release of core-shell semiconductor nanocrystals from free-standing polymer nanocomposite films

SUPPORTING INFORMATION SECTION

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1. Additional descriptions of experimental methods

Characterization of QDs. *Optical characterization.* Optical characteristics of neat QD toluene solutions were determined using a Perkin-Elmer Lambda 35 spectrophotometer and a Perkin Elmer LS 55 fluorimeter. QD concentrations were $\approx$ 0.25 mg/mL for optical measurements in solution. Luminescence quantum yields (QYs) were determined using a standard as described by Fery-Forgues and Lavabre.[1] The standard used for **QD546** and **QD539** was Coumarin 153 (QY = 38 % in ethanol),[2] and the standard used for **QD617** and **QD609** was Cresyl Violet (56 % in ethanol).[3] For **QD546** and **QD539**, an excitation wavelength of 460 nm was used, and for **QD617** and **QD609**, the excitation wavelength was 550 nm. QYs determined in this manner are usually understood to have errors on the order of $\approx$10 %.

Compositional analysis. Compositional analysis of the as-received QDs was carried out using a 720-ES axial inductively-coupled plasma atomic emission spectroscopy (ICP-AES) system from Agilent Technologies. Acidified QD samples were introduced into the plasma using 2-stop, white-white tubing (ID = 1.02 mm) and a standard glass sample introduction system. Cs ionization buffer (2000 ppm (0.1 %)) and Y standard (5 ppm (0.0005 %)) were pumped into the sample introduction line using a Y-piece connector placed after the peristaltic pump but before introduction into the nebulizer. Typical instrument parameters utilized for these experiments were as follows. Plasma power: 1.2 kW; plasma flow rate: 15.0 L/min; auxiliary flow rate: 1.5 L/min; nebulizer flow rate: 0.75 L/min; replicate read time: 20 s; instrument stabilization delay: 20 s; sample uptake delay: 20 s; pump rate: 1.57 rad/s (15 RPM); rinse time: 35 s. All of these parameters were computer software controlled. Samples of QDs (3 mg to 5 mg, which included the QDs plus surfactants) were dissolved in a $\approx$ 10 mL mixture of 1:4 30 % hydrogen peroxide to concentrated nitric acid, and digested by microwave (Milestone Ethos-EZ, 180 ˚C, 20 min ramp time, 15 min hold time). The digestate was cooled, diluted to 50 mL in 18.2 MΩ·cm water, and introduced into the ICP-AES instrumentation. Compositional analysis of the QD/LDPE nanocomposites (see below) was performed using a similar sample preparation and analysis procedure, except the starting mass of QD/LDPE was $\approx$ 250 mg. For determination of concentrations of cadmium, selenium, zinc, and sulfur, respective spectral lines of 226.502 nm, 196.026 nm, 472.215 nm, and 181.972 nm were primarily used.

Particle size analysis. QD particle sizes were determined using one of two methods: scanning transmission electron microscopy (STEM) or analysis of the QD optical properties. For **QD617** and **QD546**, STEM was used. Details about the STEM imaging system and analysis procedures are reported below. QDs were suspended in chloroform (1.6 mg in 1.6 mL). 2 µL per sample were placed on copper 200 mesh grids with a carbon support film (# CFT200-Cu, EMS) and the grids were air-dried. The size distribution of $\approx$ 100 randomly measured particles from each sample was determined using publicly available ImageJ software. Using this method, the diameters of **QD617** and **QD546** were determined to be 8.5 ± 0.8 nm and 5.6 ± 0.8, respectively (the "±" uncertainty values represent one standard deviation). In the case of **QD609** particles, we were unable to acquire any images suitable for accurate size range determinations. In this case, the mean CdSe/ZnS diameter was determined in consultation with the manufacturer by using the CdSe core size from its first exciton peak ($\approx$ 573 nm) and assuming 3 monolayers of ZnS overcoating during shell fabrication. For **QD539**, we used both methods and arrived at similar mean diameters (4.21 nm and 4.3 nm), giving us confidence in the optical characterization method used for the QD types purchased from NanoOptical Materials (**QD609** and **QD539**). We note that the optical characterization method does not provide any information on the distribution of sizes about the mean, but the luminescence spectra of **QD609** and **QD539** have only minimal overlap (Figure S3), suggesting that their size distributions overlap only to a small degree.

Preparation of freestanding neat LDPE films. The micro-compounder was attached with extensional flow screws and heated to 150 °C. The cast film extrusion die was attached to the exit channel of the micro-compounder and heated to 150 °C. Once the heating blocks and die were equilibrated to 150 °C, the screw speed was set to speed control mode at 6.28 rad/s (60 RPM) with a maximum force tolerance value of 5000 N. 12 g of neat LDPE pellets was weighed out and added to the mixing chamber using the feed hopper. After mixing for 2 minutes, the screw speed control was set to force control mode with a force setting of 550 N, and a maximum speed setting of 12.57 rad/s (120 RPM). The cast LDPE film was spooled as described in the primary text for the QD/LDPE composite materials.

Characterization of QD/LDPE nanocomposites. *Thermal and thermomechanical characterization.* The thermal properties of LDPE and QD/LDPE PNCs were characterized by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DSC was used to measure melting points and % crystallinity, and was performed with a Mettler Toledo DSC823 instrument. Film samples (5 mg to 12 mg) were weighed and crimp sealed in 20 µL light aluminum pans. The temperature scan program used was heat-cool-reheat, from – 50 °C to 160 °C with a heating/cooling rate of 10 °C/min. Melting points and crystallinity of the samples were determined using the Mettler Toledo StarE software. DMA was used to reveal the thermo-mechanical and viscoelastic properties of the polymeric material. DMA of the LDPE and QD/LDPE films was performed using a TA Instruments Q800 model DMA, analyzed in tension mode. Films were cut to a fixed width of 13 mm using a film cutting blade accessory. To perform sub-ambient temperature testing, the instrument was attached to a gas cooling accessory (GCA) filled with liquid nitrogen. The DMA test involves the application of a sinusoidal stress on the test sample and recording the resulting strain. In the current study, the polymer film samples were tested at a frequency of 1 Hz, and in the temperature range of –140 °C to 85 °C at a heating rate of 3 °C/min. More details about the crystallinity calculations and DMA measurements are provided in the Supporting Information, section 2 (page S5).

Optical characterization. The optical characteristics of QD/LDPE materials were measured using the same equipment described above for the neat QDs. When dispersed in LDPE, significant light scattering precluded efficient measurement of electronic absorption spectra. To measure luminescence spectra, long sections of QD/LDPE films were wrapped several times around a square support to maximize the effective path length for excitation and affixed to a solid-phase accessory supplied with the instrument.

Imaging analysis. Ultrathin sections of 200 nm or 400 nm nominal thickness of the QD/LDPE nanocomposite films were obtained with a diamond knife (Diatome, Biel, Switzerland) using an ultramicrotome equipped with a cryo chamber (UC7/FC7, Leica, Vienna, Austria) at -140° C. The sections were placed on gold slot grids with a carbon-coated Formvar support film (# FCF2010-Au, Electron Microscopy Sciences, Hatfield, PA, USA) and observed unstained.

The prepared sections of QD/LDPE nanocomposite films, as well as neat QDs and evaporated liquid media after release experiments, were observed and analyzed with a dual EDS (Energy Dispersive X-ray Spectroscopy) system (Thermo Fisher Scientific, Madison, WI, USA) in a STEM (Scanning Transmission Electron Microscope) HD2300A (Hitachi, Tokyo, Japan) at 200 kV acceleration voltage, using a 75 µm objective aperture and 691 pA probe current. Areas were analyzed in "Point and shoot" mode with 120 s live time per area, and for elemental maps 50 to 100 frames were recorded with a dwell time of 400 µs per pixel per frame. EDS spectra were processed with a digital top hat filter and by using the Cliff-Lorimer matrix correction without absorption. All ED's data analyses were carried out with the NSS Noran System Seven 2.2 Software (Thermo Scientific).

Laser scanning confocal microscopy. A Zeiss model LSM510 META (LSM 510 META Carl Zeiss, Germany) reflection laser scanning confocal microscope (LSCM) was employed to map and quantify fluorescence images. The laser wavelength chosen as the excitation source was 405 nm (405 nm diode laser, 30 mW), and two emission configurations (META 488_550_650 and LP475) were selected to collect emission images/spectra. The META 488_550_650 configuration (referred as META mode) used a polychromatic detector (META) to collect the emission from 488 nm to 650 nm. In this configuration, a series of fluorescence spectra/image at each emission wavelength at each scan location can be recorded. While in the LP475 configuration, the regular PMT detector collected all emission lights for wavelength greater than 475 nm. The acquisition time in the LP475 configuration is much faster than the META mode; therefore most of images were taken using the LP475 configuration. All LSCM images presented here were taken using an objective of 150x (56 μm x 56 μm) magnification and a numerical aperture of 0.95 with optical slice (z-step) of 1 µm for META mode and 0.3 µm for LP475 configuration. LSCM images shown here were either (a) a single frame depth - profile image in xy plane (1024 pixel × 1024 pixel) at a designed z - depth, (b) two dimensional (2D) projection images in xy plane, and (c) three-dimensional (3D) images. The 2D projection was formed by summing the stacks of the image in the z direction, while 3D rendering was generated using the Zen software program provided by Carl Zeiss.

Trace metal analysis to determine released QDs or dissolved residuals*.* To quantitate QDs and residuals released into the external medium, 5 g of the residual liquid were gravimetrically diluted with 5 g of 4 % HNO_3 (v/v, double distilled) and 1 % HCl (v/v, double distilled) in deionized 18.2 MΩ cm water. Solution masses were recorded to the nearest 0.1 mg and then quantified by matrix-matched external calibration (Inorganic Ventures, Christiansburg VA USA) on a Thermo Finnigan Element 2 sector field inductively-coupled plasma mass spectrometer (ICP-MS) (Bremen, Germany). Calibration standards for water release samples were made in 2 % HNO_3/0.5 %HCl (v/v, double distilled) solution. Calibration standards for acetic acid samples also included 1.5 % glacial acetic acid (v/v, electronic grade). [111]Cd was measured in low (m/Δm > 300), [32]S and [66]Zn were measured in medium (m/Δm > 4000), and [78]Se was measured in 'high resolution' mode (m/Δm > 10,000). A 2 ng/g [103]Rh internal standard solution was made in 1 % HNO_3 and 0.5 % HCl (both v/v, double distilled) with 4 % isopropanol (v/v, electronic grade) and teed into the sample line immediately prior to nebulization. The NIST standard reference materials Trace Elements in Natural Water (lot #1640a) and Trace Elements in Water (lot #1643e) were gravimetrically diluted 1:10 in the same 2 % HNO_3 / 0.5 % HCl matrix for quality control and were measured every 10 samples along with a continuing calibration verification solution (CCV). Acceptable recoveries ranged from 90 % to 110 %. QDs are composed primarily of cadmium, zinc, selenium, and sulfur. Mean Cd, Zn, and Se recovery was 107 %, 98 %, and 100%, respectively, for the NIST SRMs. Solution detection limits (3 s) calculated from method blanks were (0.85, 0.20, 0.078 and 0.069) ng/g for S, Zn, Se, and Cd, respectively. The units of concentration (ng/g or pg/g) used throughout for reporting, referring to the ratio of mass solute to mass solvent.

Use of STEM to search for QDs released whole in the external medium*.* 6 mL of the liquid medium after the release experiments were completed was placed in a 15 mL poly(propolyene) (Falcon) tube in an aluminum rack and kept at 60 °C on a heating plate in a fume hood. When the volume was reduced to about 50 µL, 5 µL were placed on the Formvar side of Formvar carbon coated copper slot grid (FCF205-Cu, EMS, PA, USA) and air dried. The Formvar side of the support film was plasma-treated with Argon plasma for 20 seconds before the sample was applied (PC 2000, South Bay Technology Inc., San Clemente, CA, USA). This sample was then subjected to imaging analysis as described above.

2. Thermal and thermomechanical analysis of QD/LDPE nanocomposites

The DSC curves of the second heat for neat, free-standing LDPE and free-standing **QD546/LDPE** and **QD617/LDPE** nanocomposite films are shown in the Figure S1. The exothermic peak shown in Figure S1 that occurs at approximately 110 °C corresponds to the melting point of LDPE. LDPE is a semicrystalline polymer and melting is associated with the crystalline portion of the polymer. To derive the crystallinity value from the DSC curve, the methodology described in ASTM F2625-10 (Standard Test Method for Measurement of Enthalpy of Fusion, Percent Crystallinity, and Melting Point of Ultra-High-Molecular Weight Polyethylene by Means of Differential Scanning Calorimetry) was used. Briefly, a baseline was created by connecting the points between 50 and 150 °C, and the mass-normalized heat of fusion was calculated by integrating area under the heating endotherm divided by the sample mass. Percent crystallinity was calculated from the equation:

$$\% \text{ crystallinity} = \frac{\Delta H_m}{\Delta H_m^{\text{o}}} \times 100 \tag{1}$$

where ΔH_m is the heat of fusion of the sample, and ΔH_m is a reference value for a theoretically 100 % crystalline polymer. In this study a value of 293.6 J·g^{-1} was used for ΔH_m of poly(ethyelene).[4] The % crystallinity values are shown in Table S2, along with recorded melting points (peak maxima).

Dynamic mechanical analysis (DMA) of QD/LDPE films was used to determine the storage modulus and tanδ values for these materials. Plots of these values as a function of temperature for both **QD617/LDPE** and **QD546/LDPE** are shown in Figure S3. Storage modulus is indicative of the elastic response of the polymer to the applied sinusoidal stress. This is evident from the storage modulus curve (Figure S3B), which shows a decrease in the storage modulus with increasing temperature, due to softening of the polymer. Tan δ is the ratio of loss (viscous response) and storage moduli, indicating a loss or dissipative event. A peak in tanδ is often associated with a type of transition in molecular motion of the polymer. Typically, there are three types of observed transitions, namely α, β, and γ, where α is considered the higher temperature transition, also called glass transition or T_g. β and γ are generally attributed to localized side chain and functional group vibrations, which have onset at lower temperatures. However, LDPE and polyethylene in general do not conform to this norm. The broad α transition in LDPE at 53 °C (Figure S3A) is attributed to the motion within the crystalline phase rather than the T_g, which is associated with the onset of long chain motions of the amorphous (non-crystalline) component. The β transition, seen as a shoulder at -20 °C, is attributed to the motion of branches within the amorphous phase. The fact that the β transition originates from branches was established from the observation that it is completely absent in linear-LDPE (LLDPE) devoid of any branches.[5] The γ transition in LDPE, seen below -120 °C, has been interpreted to be the T_g.[6,7] Note that no significant changes were observed in the mechanical or thermal DMA response of the polymer films as a result of the dispersion of small quantities of QD in the polymer, suggesting that the nanocomposite material behaves mechanically and thermally like neat LDPE.

3. Estimation of water diffusivity in LDPE and determination of lag time

In 1984 McCall et al[8] published a semi-empirical relationship to estimate the diffusion constant (D) and solubility (S) of water in LDPE. These parameters were found to depend strongly on the extent of LDPE oxidation, expressed as a concentration of bound oxygen atoms. This relationship is given as

$$S = 7.5 \times 10^7 Fe^{-\frac{10500}{RT}} \tag{2}$$

$$D^{-1} = 0.35 Fe^{\frac{7500}{RT}} \tag{3}$$

$$F = 6.1 \times 10^{-8}[O]e^{\frac{7500}{RT}} + e^{\frac{1500}{RT}} \tag{4}$$

Here, the units of S and [O] are in ppm (0.0001 %), the unit of D is cm^2 s^{-1}, T is in K, and R is the gas constant, 1.987 cal K^{-1} mol^{-1}. [O] is the concentration of bound oxygen.

In a scenario in which a substance is diffusing through a sheet film of thickness L, where the initial concentration of the diffusing substance at all points in the film is initially zero, the permeation lag time λ is an extrapolation to the zero concentration based on the linear growth region in the concentration of the diffusing substance at the distal side of the film as a function of time. It may be taken as an idealized amount of time it takes for the diffusing substance to permeate through a film and begin accumulating at the other side. Based on a diffusion coefficient, D, the permeation lag time for a film of thickness L in seconds is given by equation 5[9]:

$$\lambda = \frac{L^2}{6D} \tag{5}$$

4. Supporting Figures
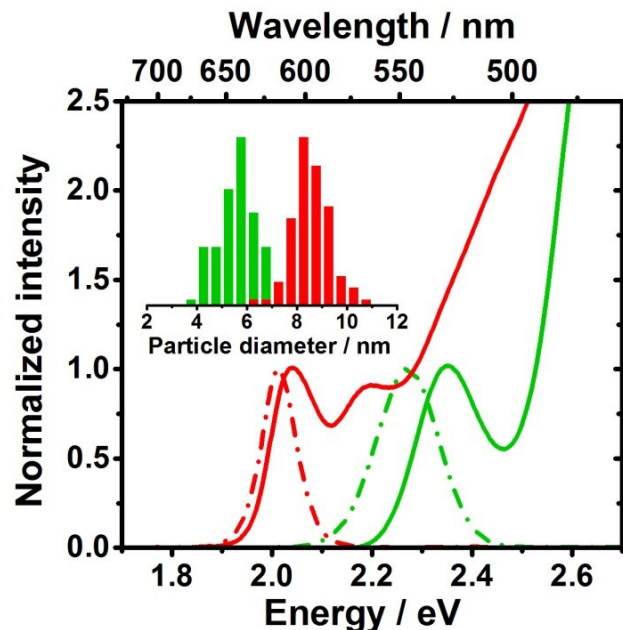
Figure S1. Normalized UV-Vis absorption (solid lines) and luminescence spectra (dashed lines) of **QD617** (red) and **QD546** (green), respectively, in dilute toluene. The inset shows size histograms of 100 randomly measured particles of **QD617** (red bars) and **QD546** (green bars), as determined by TEM.
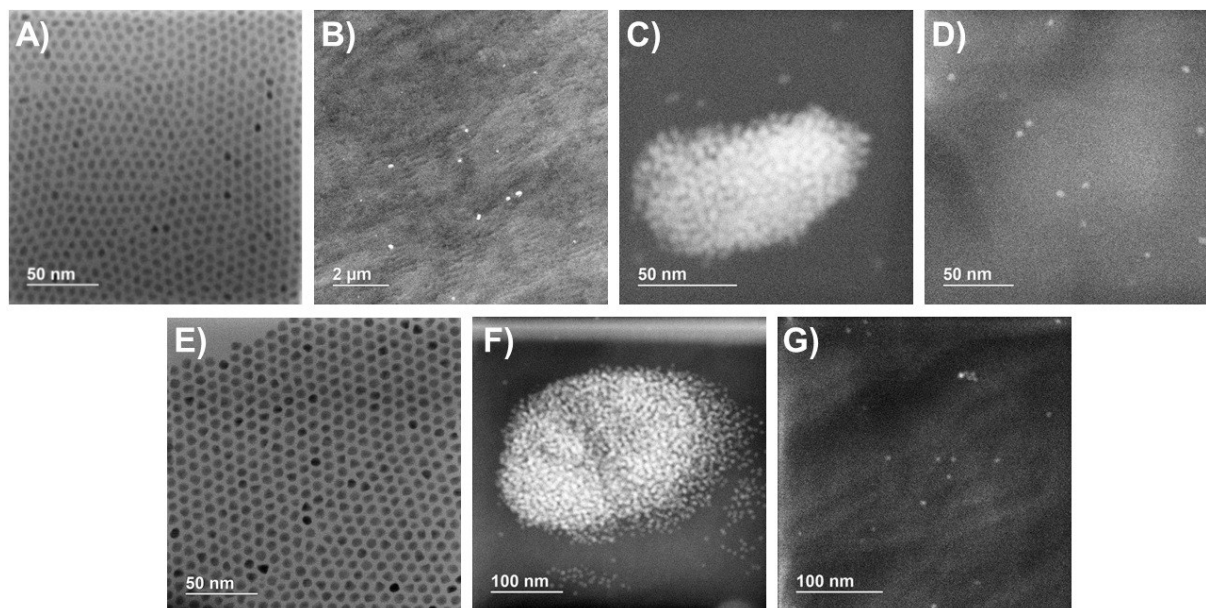

Figure S2. Z-contrast contrast (B, C, D, F, G), and TE-mode (A, E) STEM images of pristine and LDPE-dispersed **QD546** (A-D) and **QD617** (E-G). Panels (A) and (E) show images of the respective pristine QDs. In LDPE polymer, a portion of the QDs are found in clusters/aggregates, although individual QDs can still be resolved, as seen in the zoomed out image of the **QD546/LDPE** sample (panel B). Panels (C) and (F) show close up images of clusters from each sample. Panels (D) and (G) show close up images of film regions between clusters, indicating the presence of individually-dispersed QDs. The inorganic mass fraction in **QD617/LDPE** and **QD546/LDPE** was 1.30 mg/mL and 1.08 mg/mL, respectively.
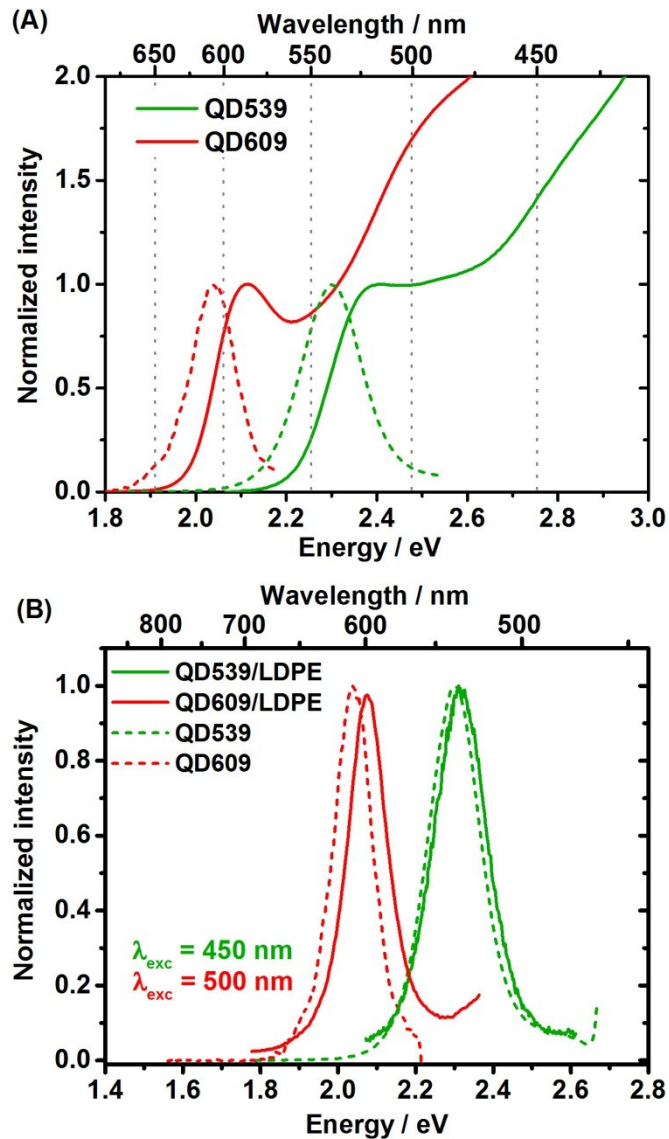
Figure S3. (A) UV/Vis (solid lines) and photoluminescence spectra (dashed lines) of **QD539** (green) and **QD609** (red), respectively, recorded in dilute toluene. (B) Photoluminescence spectra of **QD539/LDPE** and **QD609/LDPE** (solid lines), as well as the corresponding QDs in solution (dashed lines). The excitation wavelengths are listed in the Figure.
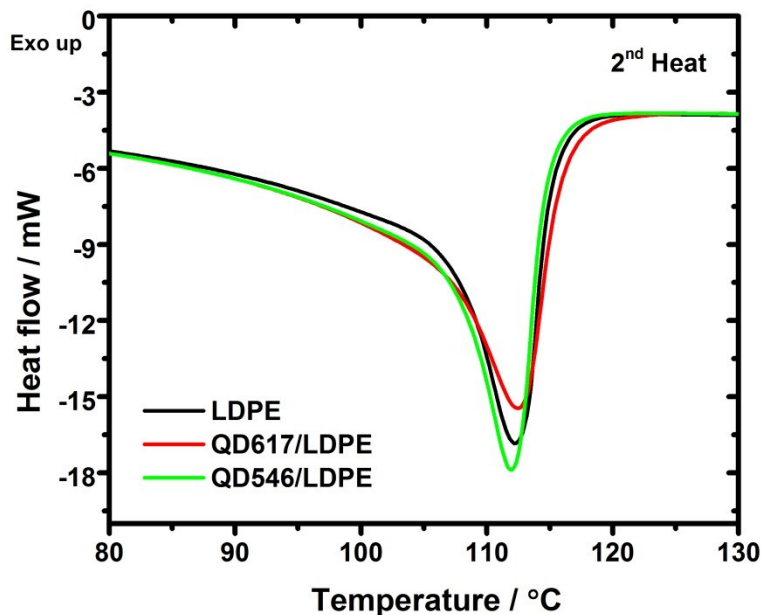
Figure S4. DSC thermograms showing the melting endotherm in second heat of neat-LDPE, **QD546/LDPE** and **QD616/LDPE** nanocomposite films. The inorganic weight fraction in **QD617/LDPE** and **QD546/LDPE** was 1.30 mg/mL and 1.08 mg/mL, respectively.
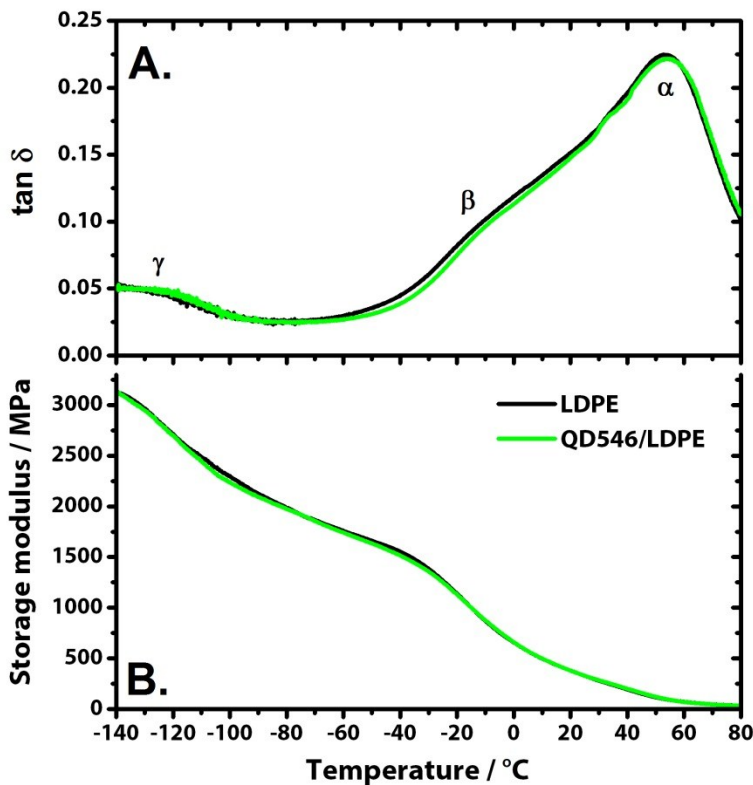
Figure S5. (A) Tan δ curve showing the three different transitions (α, β, and γ) of **LDPE** and **QD546/LDPE** from a tensile DMA test. (B) Storage modulus curve of **LDPE** and **QD546/LDPE** from a tensile DMA test. The inorganic mass fraction in **QD546/LDPE** was 1.08 mg/mL.
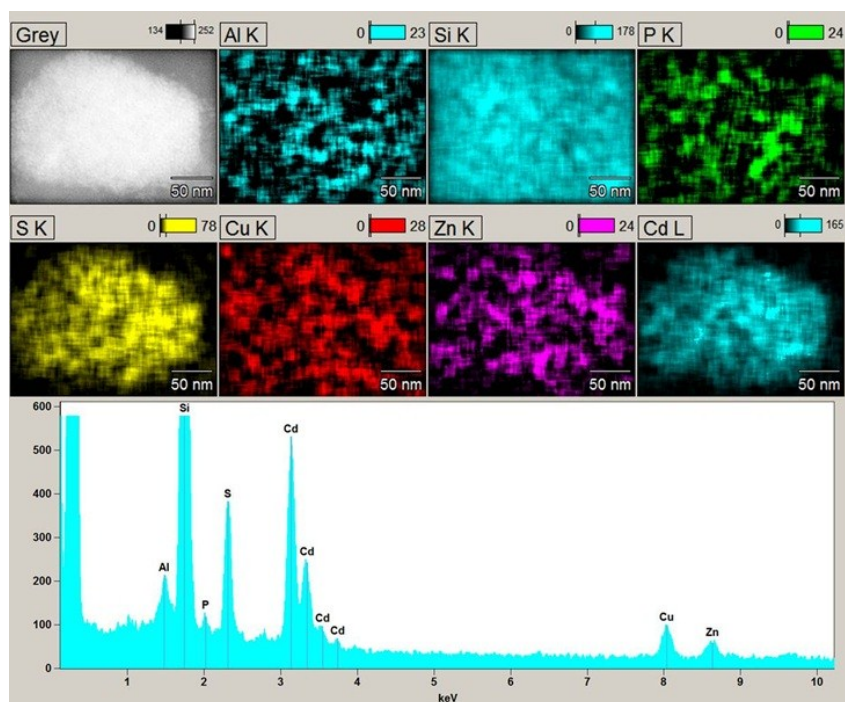
Figure S6. TEM/EDS compositional map analysis of a cluster of embedded **QD546** nanoparticles in LDPE. The EDS spectrum shows that the cluster contains significant traces of cadmium, zinc, and sulfur, three of the primary elements in the QDs. The fourth element, selenium, typically manifests peaks at ≈1.38 keV and ≈ 11.21 keV, the former of which is likely buried under the aluminum peak and the latter of which is not within the range of the depicted experiment. The Cd-, Zn-, and S-based compositional maps (images on top) nicely reproduce the shape of the QD-cluster, verifying that the cluster is composed of CdSe/ZnS QDs and not some other incidentally present nanostructure.
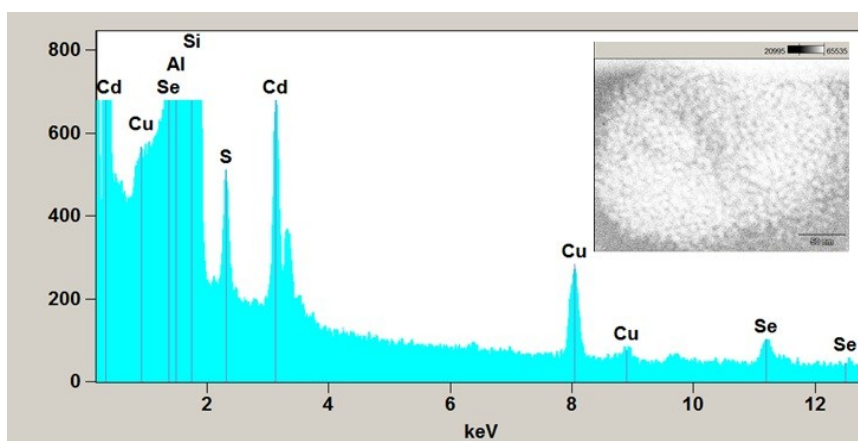
Figure S7. TEM/EDS spectrum of a cluster of embedded **QD617** nanoparticles in LDPE. As in Figure S4, the EDS spectrum shows that the cluster contains constituent elements in CdSe-ZnS QDs. The Zn peak at ≈ 8.63 keV is not evident in this spectrum likely due to the comparatively low concentration of Zn in the QD620 particles (see text). In this spectrum, the selenium peak is clearly observed due to the larger scanning range used in this experiment.
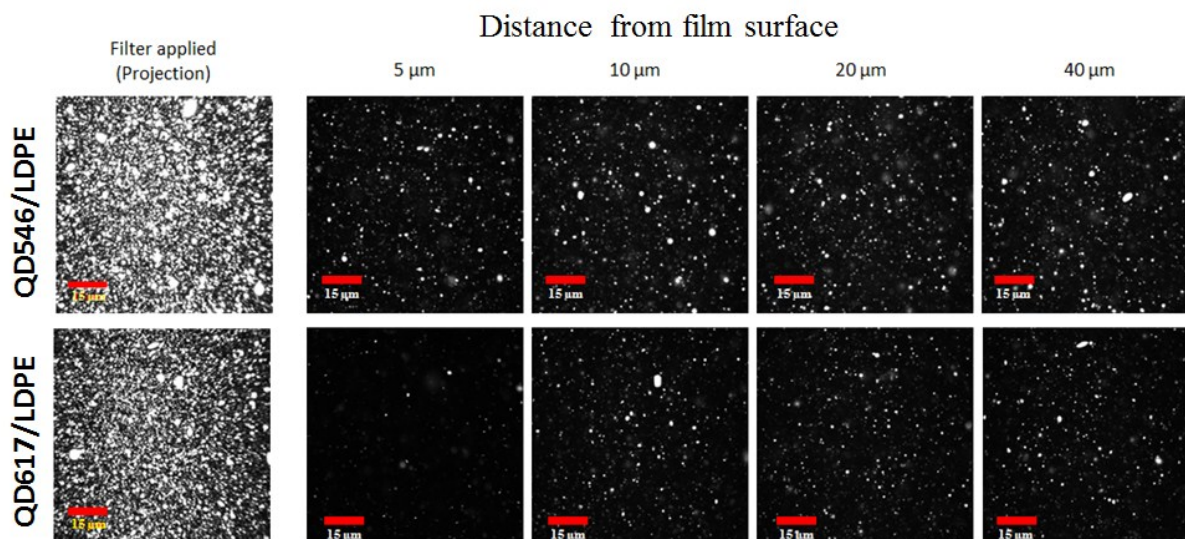
Figure S8. LSCM images of QD/LDPE film sections prior to immersion tests, showing uniform dispersion of QDs and QD clusters in both lateral and vertical dimensions as well as retention of photoluminescence during film manufacture. The top and bottom rows show images of films dispersed with **QD546** and **QD617**, respectively. The leftmost images are the composite images and the remaining images correspond to cross-sectional confocal planes at specified depths below the film surface. The thickness of each focal plane is approximately 3 μm. Samples were excited with 405 nm laser light and focused on the sample using a 100x oil immersion objective. Red scale bars correspond to 15 μm. The inorganic weight fraction in **QD617/LDPE** and **QD546/LDPE** was 1.30 mg/mL and 1.08 mg/mL, respectively.
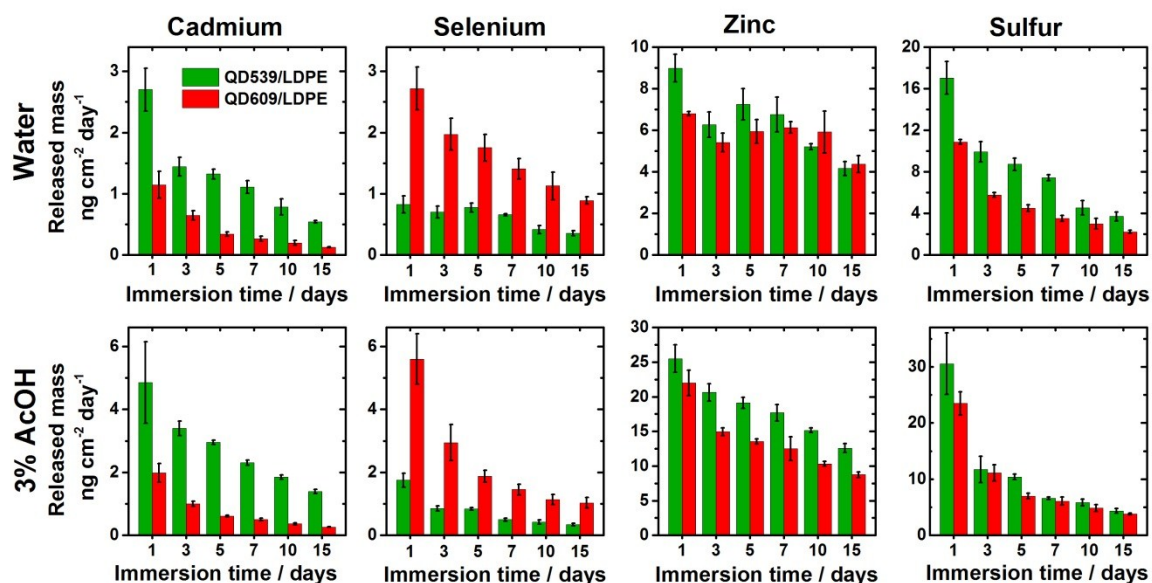
Figure S9. Daily-averaged release of cadmium, selenium, zinc, and sulfur from QD/LDPE nanocomposite films into water held at 75 °C as a function of immersion time, expressed as the total amount of released mass of each element into 25 mL of the immersion volume per unit surface area of exposed film. Green and red bars refer to release experiments using **QD539** and **QD609**, respectively. Each reported value is the average of measurements from four independent samples. Error bars are standard deviations. The inorganic mass fraction in both films was 2.08 mg/mL.
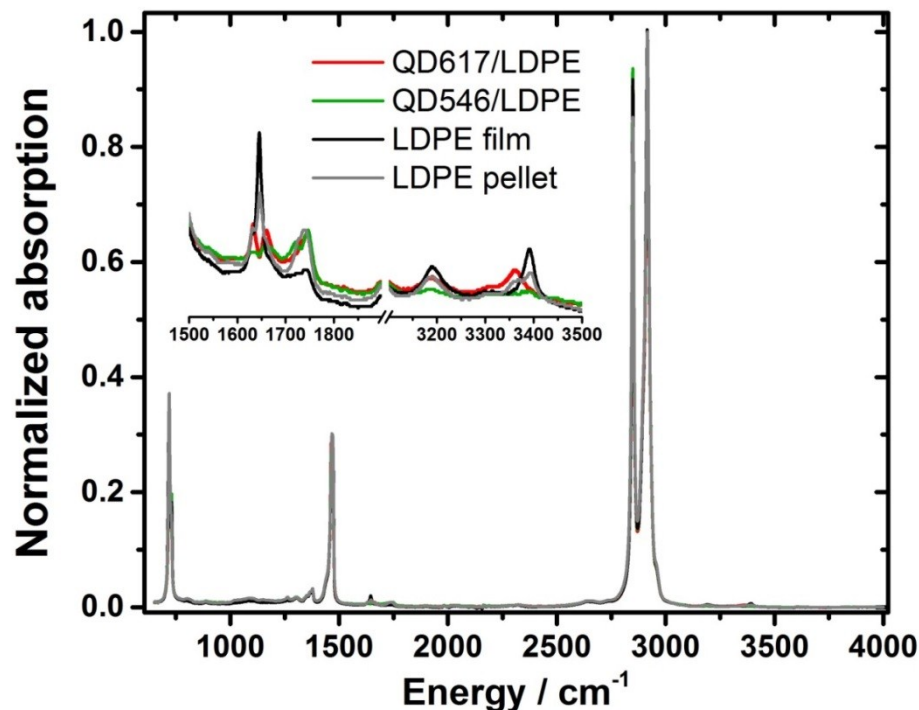
Figure S10a. FTIR-ATR spectra of QD/LDPE films as well as neat LDPE films and LDPE pellets before processing (as received from the manufacturer). The insets show expanded views of the 1500 cm^{-1} to 1900 cm^{-1} and 3100 cm^{-1} to 3500 cm^{-1} regions, where carbonyl and other functional group resonances resulting from polymer oxidation would typically appear. In the neat LDPE samples (black and gray for post- and pre-processing as thin films, respectfully), resonances at 1646 cm^{-1}, 3192 cm^{-1}, and 3389 cm^{-1} correspond to bending and stretching modes of amine-based UV-stabilizers incorporated into the commercial resin.[10] The peak appearing at $\approx$ 1741 cm^{-1} likely corresponds to a carbonyl resonance, signifying a small degree of polymer oxidation, although this may be strictly a surface phenomenon because the ATR method does not probe deep within the material. In any case, it does not appear that film processing results in any significant additional oxidation of these materials based on the spectra shown here. Note that the QD/LDPE films exhibit slightly more complex amine absorption bands, likely due to the presence of octadecyl amine surfactants used to stabilize the QD suspensions prior to incorporation within the LDPE matrices
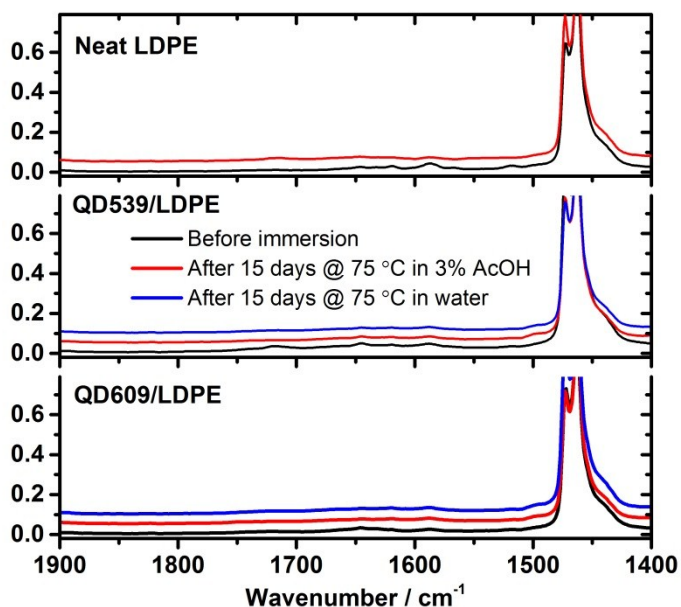
Figure S10b. FTIR-ATR spectra in the carbonyl-stretching region of neat LDPE, **QD539/LDPE** and **QD609/LDPE** both before immersion (black lines) and after 15 day immersion tests performed at 75 °C in either 3% aqueous acetic acid (red lines) or water (blue lines). Spectra are offset for clarity. Note the lack of any new peaks in the carbonyl stretching region after the immersion tests, signifying no significant oxidative degradation of the polymer that could account for the release of embedded particles.
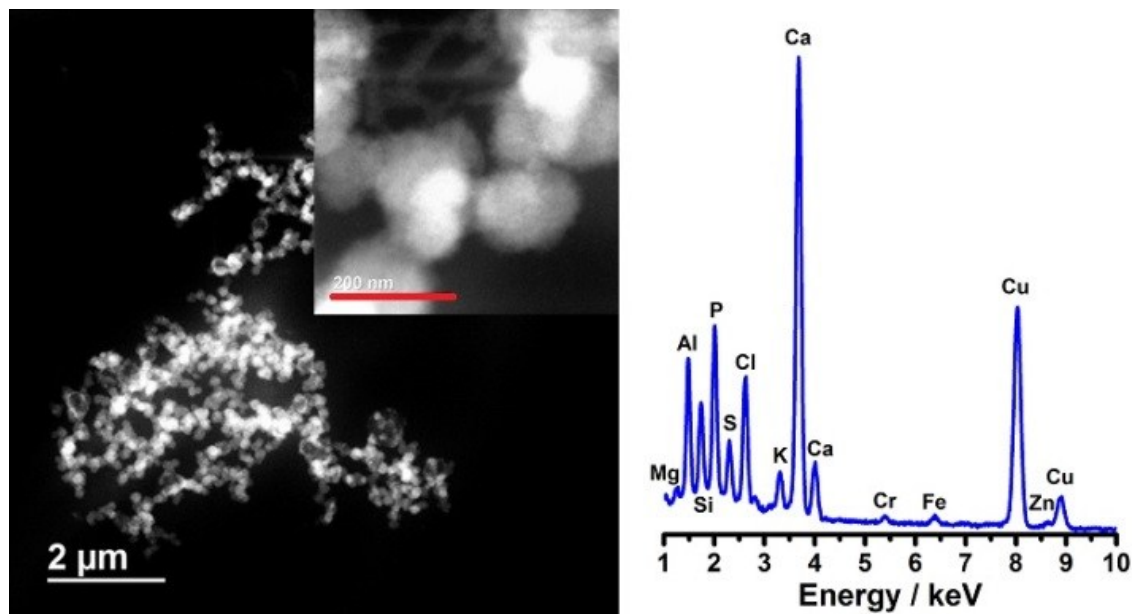
Figure S11. STEM image and EDS analysis of air-dried droplet of 3 % acetic acid after exposure to a section of **QD617/LDPE** film at 75 °C for 15 days. The inset shows a zoomed in view (red size bar = 200 nm). The EDS spectrum (see supporting information, Figure S9, for EDS mapping) shows that particles are primarily composed of aluminum, potassium, phosphorous, sulfur, and iron.
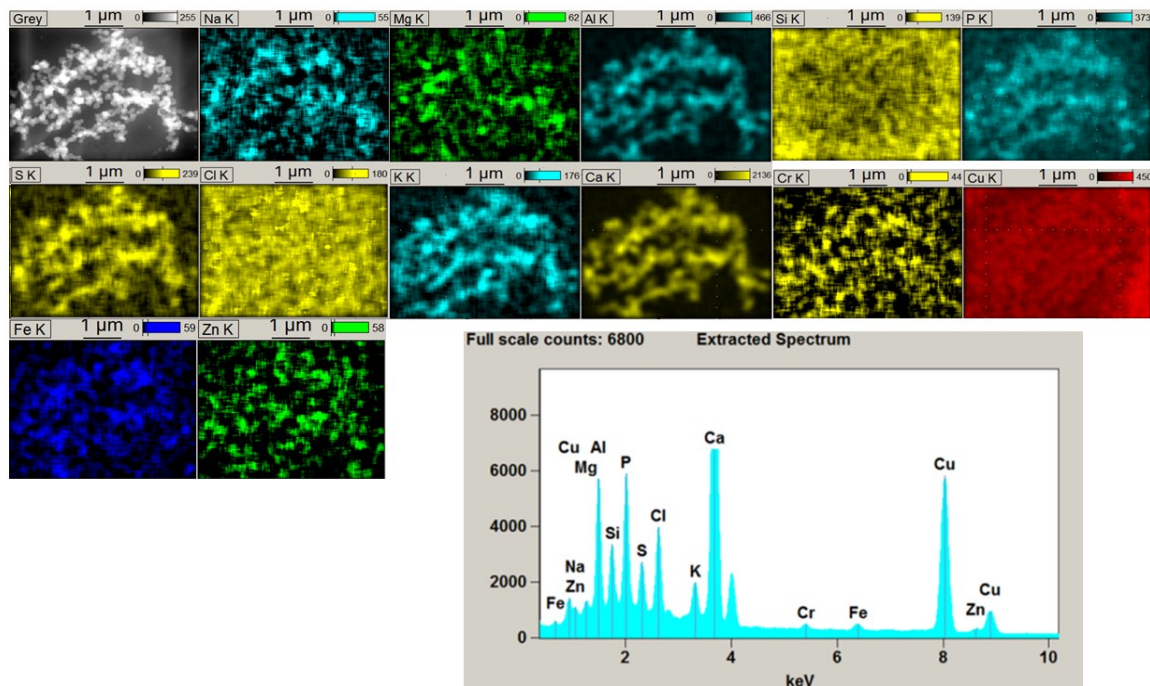
Figure S12. STEM-EDS compositional map of an air-dried droplet of 3% acetic acid after exposure to a section of **QD617/LDPE** film at 75 °C for 15 days. The map indicates presence of Al, P, S, K, Ca, Cr, Fe, and Zinc in the concentrated samples. Si is present in the carbon film. Cu is present in the sample holder material (also Al). The support grid was made of Cu.
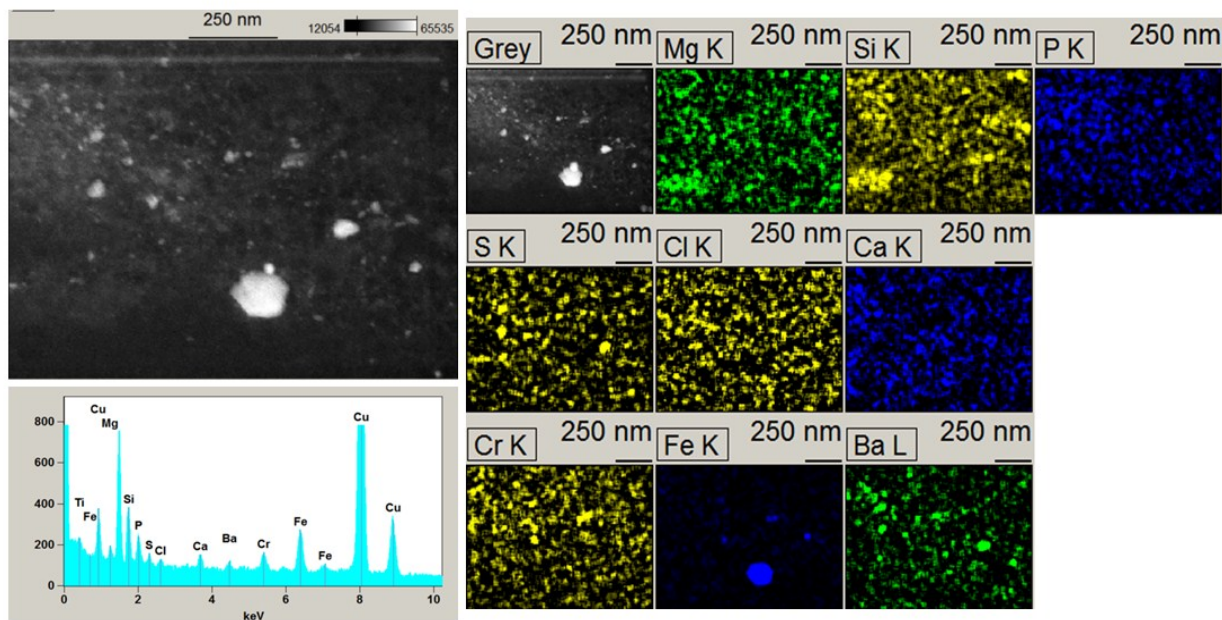
Figure S13. STEM-EDS compositional map of an air-dried droplet of 3% acetic acid after exposure to a section of **QD546/LDPE** film at 75 °C for 15 days. The EDS map indicates accumulation of Fe, P, S, Ca, Ba, Cr, and Fe in the particles. Al and Cu are present in the sample holder material. Si is also present in the carbon film. The support grid was made of Cu.
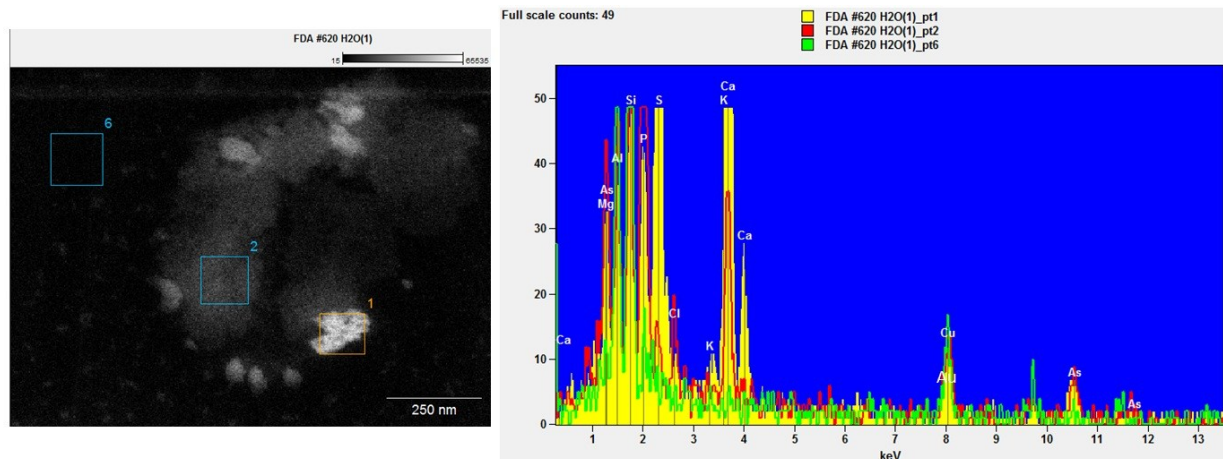
Figure S14. STEM-EDS compositional map of an air-dried droplet of water after exposure to a section of **QD617/LDPE** film at 75 °C for 15 days. The EDS map indicates accumulation of Na, Mg, P, S, Cl, K, Ca, and As in the analyzed areas 1 and 2. Al and Cu are present in the sample holder material. Si is present in the carbon film. The support grid was made of Cu.
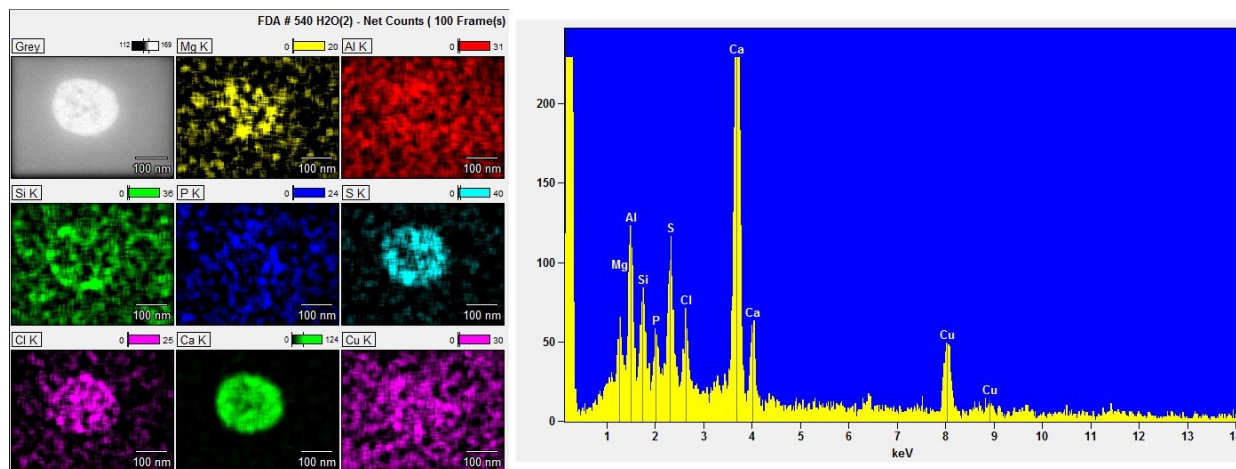
Figure S15. STEM-EDS compositional map of an air-dried droplet of water after exposure to a section of **QD546/LDPE** film at 75 °C for 15 days. The EDS map indicates accumulation of Mg, P, S, Cl, and Ca in the analyzed area. Al and Cu are present in the sample holder material. Si is present in the carbon film. The support grid was made of Cu.
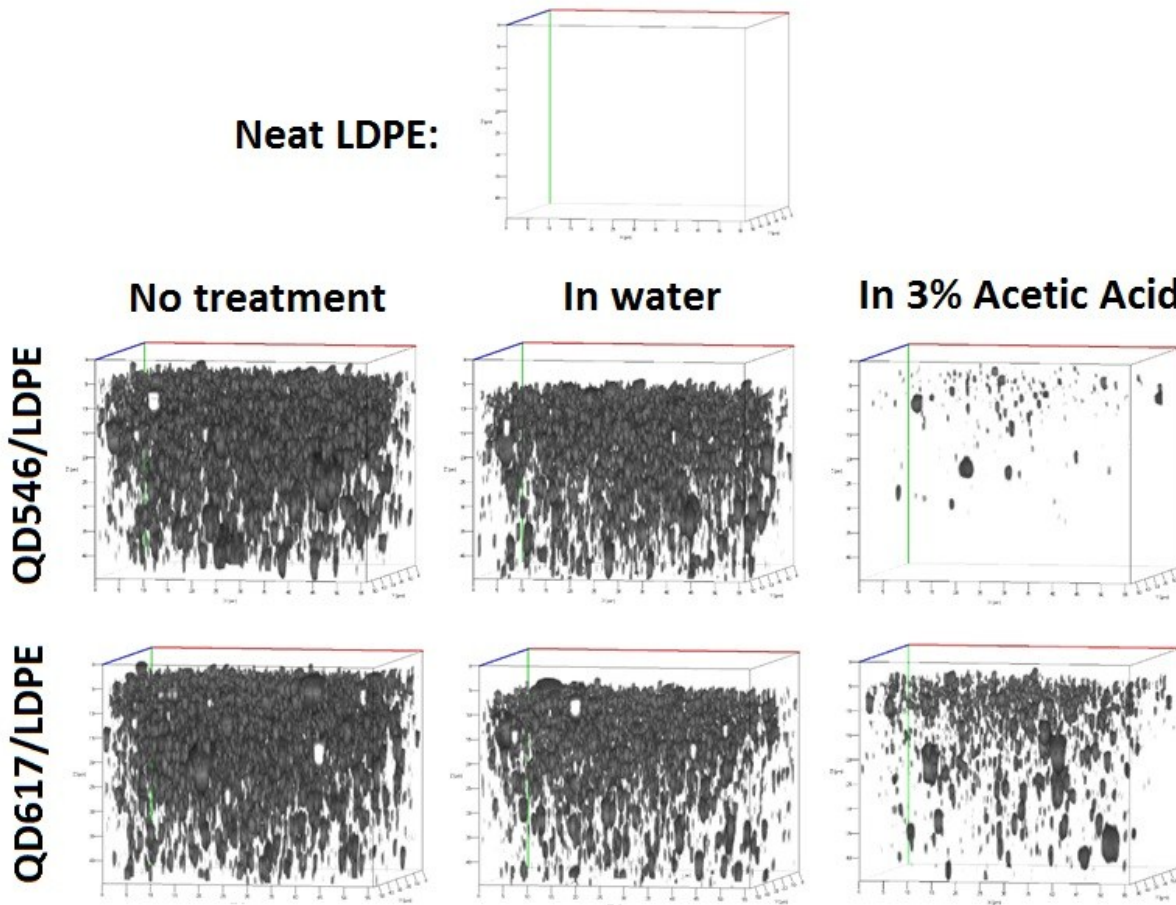
Figure S16. Comparative 3D LSCM images of neat LDPE and **QD546/LDPE** and **QD617/LDPE** after no immersion treatment (left column) and after immersion in water (middle column) or 3 % aqueous acetic acid (right column) at 75 °C for 15 days. Each image represents a lateral area of approximately 84 μm x 84 μm and a depth of approximately 45 μm. The top of each image corresponds to the film surface. The inorganic weight fraction in **QD617/LDPE** and **QD546/LDPE** was 1.30 mg/mL and 1.08 mg/mL, respectively. The neat LDPE shows no luminescent intensity either before or after immersion treatments.
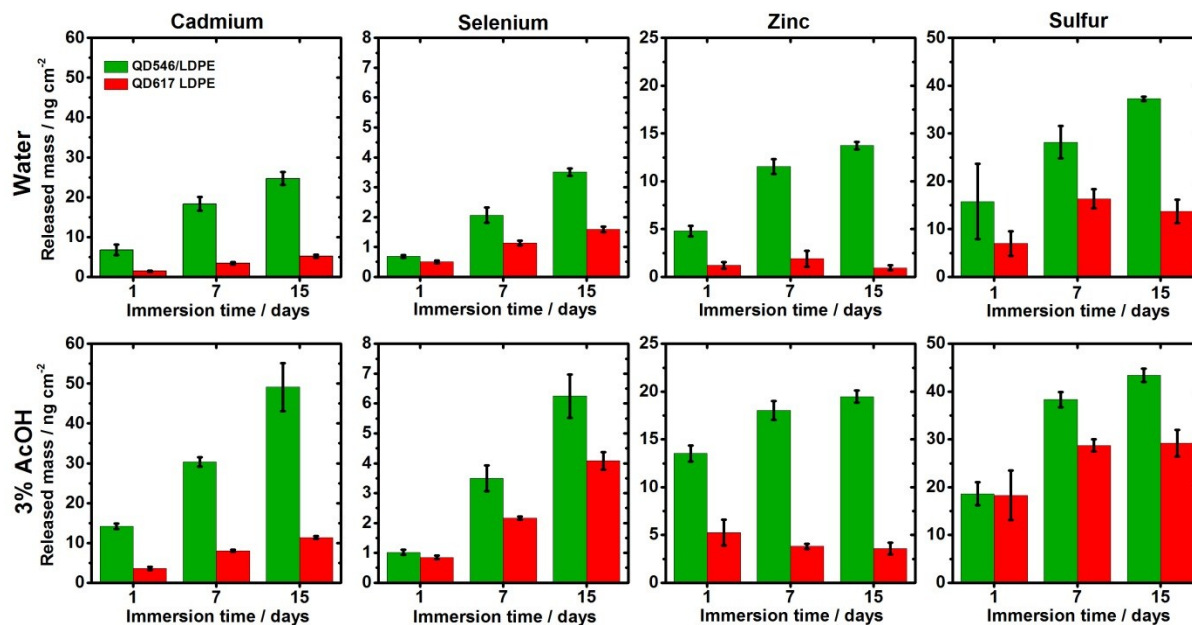
Figure S17 Release of cadmium, selenium, zinc, and sulfur from **QD546/LDPE** (green bars) and **QD617/LDPE** (red bars) nanocomposite films into water (top row) and 3 % aqueous acetic acid (bottom row) held at 75 °C as a function of immersion time, expressed as total released mass of the analyte in the volume of analyzed solution per unit surface area of exposed film. The inorganic weight fraction for **QD546/LDPE** and **QD617/LDPE** films was 1.30 and 1.08 mg/mL, respectively. Each reported value is the average of measurements from four independent samples. Error bars represent standard deviations.
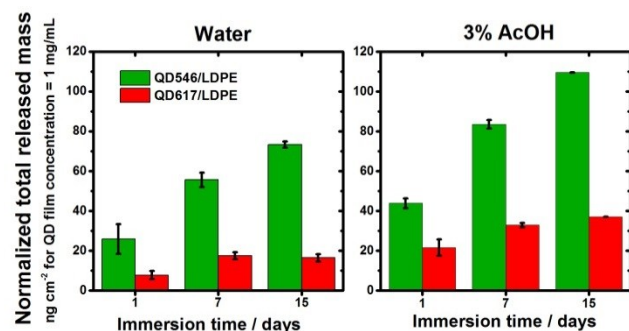
Figure S18. Normalized total release of cadmium, selenium, zinc, and sulfur from **QD546/LDPE** (green bars) and **QD617/LDPE** (red bars) nanocomposite films into 25 mL of water (left panel) and 3 % aqueous acetic acid (right panel) held at 75 °C as a function of immersion time, expressed on a per-film-surface area basis. The total release values have been normalized to account for the different starting concentrations of inorganic mass in each film; this was accomplished by dividing the total release value, as measured with ICP-MS, by the initial inorganic mass concentration in **QD546/LDPE** and **QD617/LDPE** (1.08 and 1.30 mg/mL, respectively). Each reported value is the average of measurements from four independent samples. Error bars represent standard deviations.

5. **Supporting Tables**

Table S1. Compositional analysis of QD/LDPE PNC films and QD starting materials using ICP-AES

Film or QD type[a]	Elemental mass fraction[b]							
	Cd		Se		Zn		S	
	Mean	Std	Mean	Std	Mean	Std	Mean	Std
QD546	0.734	0.011	0.040	0.001	0.053	0.001	0.174	0.011
QD546/LDPE	0.682	0.002	0.042	0.001	0.056	0.000	0.220	0.002
QD617	0.751	0.003	0.117	0.002	0.002	0.001	0.130	0.004
QD617/LDPE	0.694	0.008	0.114	0.003	0.006	0.001	0.187	0.005
QD539	0.211	0.003	0.029	0.000	0.455	0.006	0.305	0.009
QD539/LDPE	0.214	0.002	0.034	0.000	0.441	0.004	0.311	0.005
QD609	0.201	0.000	0.106	0.001	0.439	0.001	0.255	0.002
QD609/LDPE	0.201	0.001	0.115	0.001	0.429	0.003	0.255	0.004

[a]The numerical part of the QD designation reflects the emission maximum recorded in dilute toluene solution. Note that neat films (without QDs) were also subjected to compositional analysis, but due to the fact that the analyte concentrations were below the method detection limit, mass fractions for these materials could not be determined. [b]This value reflects the mass of each element divided by the summed mass of all four analyzed elements in an analyzed quantity of material, as determined by ICP-AES analysis of QDs after microwave digestion. The data is based on three independent replicates. The STD is one standard deviation.

Table S2. Thermal properties of neat LDPE and **QD/LDPE** PNC films, as determined by discrete scanning calorimetry.

Material type	Crystallinity [%]	Melting Point [°C]
Neat LDPE	38	111
QD546/LDPE	36	110
QD616/LDPE	38	111

Table S3. Masses[a] of Cd, Se, Zn, and S released from **QD539/LDPE** and **QD609/LDPE** films released into water at 75 ℃, on a per-film-surface-area basis, and respective elemental mass ratios.

PNC	Time [days]	Released mass [ng per cm² film area]								Ratio of Zn to Cd		Ratio of Cd to Se		Ratio of Zn to S		Ratio of S to Se	
		Zn		Se		Cd		S									
		Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
QD539 2.08 mg/mL in LDPE	1	8.98	0.66	0.82	0.14	2.70	0.35	17.02	1.56	3.34	0.24	3.35	0.74	0.53	0.05	20.86	1.71
	3	18.76	1.84	2.09	0.29	4.32	0.45	29.74	2.91	4.37	0.54	2.08	0.15	0.63	0.06	14.34	1.46
	5	36.21	3.81	3.87	0.37	6.60	0.41	43.56	2.92	5.47	0.26	1.71	0.11	0.84	0.14	11.33	1.23
	7	47.31	5.85	4.58	0.14	7.77	0.72	51.94	2.05	5.90	0.86	1.70	0.18	0.92	0.15	11.33	0.20
	10	51.95	1.48	4.13	0.67	7.84	1.31	45.26	6.85	6.77	1.16	1.90	0.05	1.17	0.16	10.97	0.55
	15	62.30	5.09	5.29	0.62	8.12	0.30	55.45	6.36	7.69	0.73	1.55	0.18	1.14	0.20	10.49	0.14
QD609 2.08 mg/mL in LDPE	1	6.79	0.10	2.72	0.35	1.15	0.22	10.86	0.23	6.09	1.11	0.43	0.14	0.63	0.02	4.04	0.46
	3	16.19	1.34	5.91	0.78	1.94	0.23	17.29	0.70	8.43	1.18	0.33	0.07	0.94	0.05	2.97	0.44
	5	29.65	2.85	8.76	1.08	1.71	0.17	22.32	1.62	17.46	1.93	0.20	0.01	1.34	0.23	2.58	0.40
	7	42.86[b]	1.96	9.86	1.17	1.83	0.27	24.51	1.95	23.63	4.98	0.19	0.04	1.75	0.10	3.25	1.38
	10	59.07[b]	10.08	11.26	2.24	1.94	0.38	29.82	5.05	27.33	1.29	0.18	0.08	2.19	0.33	3.03	0.46
	15	65.44	6.18	13.34	0.90	1.86	0.12	33.05	2.02	35.50	5.48	0.14	0.00	1.99	0.29	2.48	0.12

[a]Each reported value is the average of four independent replicates and reflects the mass of the analyte in 25 mL solution per unit surface area of test film. Reported errors for mass values are standard deviations. The reported errors for the mass ratios reflect a propagation of the associated errors for each individual mass measurement. [b]These data points contained replicates that exhibited zinc values that were >50% larger than the average of the remaining replicates. In these cases, the anomalous datum was discarded as an outlier and the reported value reflects the mean value and standard deviation of the remaining replicates.

Table S4. Masses[a] of Cd, Se, Zn, and S released from **QD539/LDPE** and **QD609/LDPE** films released into 3% aqueous acetic acid at 75 ℃, on a per-film-surface-area basis, and respective elemental mass ratios.

PNC	Time [days]	Released mass [ng per cm² film area]								Ratio of Zn to Cd		Ratio of Cd to Se		Ratio of Zn to S		Ratio of S to Se	
		Zn		Se		Cd		S									
		Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
QD539 2.08 mg/mL in LDPE	1	25.51	2.01	1.75	0.22	4.85	1.29	30.56	5.49	5.49	1.14	2.74	0.40	0.85	0.16	17.42	1.25
	3	61.86	3.81	2.55	0.25	10.19	0.67	35.12	7.00	6.08	0.47	3.64	0.79	1.82	0.39	12.18	1.19
	5	95.67	3.92	4.19	0.22	14.76	0.31	51.95	2.33	6.48	0.16	3.53	0.20	1.84	0.10	12.42	0.22
	7	123.81	8.50	3.49	0.35	16.16	0.55	46.09	1.46	7.66	0.36	4.66	0.40	2.69	0.20	13.30	1.28
	10	151.57	3.49	4.19	0.65	18.45	0.65	58.35	6.01	8.23	0.46	4.49	0.82	2.62	0.25	14.12	2.12
	15	188.67	9.53	5.09	0.65	20.86	1.08	65.20	6.12	9.05	0.27	4.14	0.47	2.91	0.18	12.87	0.68
QD609 2.08 mg/mL in LDPE	1	21.99	1.83	5.60	0.80	1.98	0.30	23.49	2.08	11.24	1.47	0.36	0.10	0.94	0.10	4.22	0.23
	3	44.91[b]	1.67	8.84	1.71	2.99	0.24	33.33	4.35	15.05	0.76	0.35	0.09	1.36	0.20	3.80	0.22
	5	67.60	1.85	9.39	0.94	3.06	0.14	35.01	2.63	22.13	0.94	0.33	0.03	1.94	0.14	3.77	0.60
	7	87.55	12.16	10.17	1.15	3.50	0.30	42.58	4.94	24.92	1.85	0.35	0.03	2.06	0.27	4.19	0.11
	10	103.32	3.16	11.39	1.63	3.63	0.37	48.26	6.11	28.66	2.55	0.32	0.04	2.17	0.29	4.35	1.19
	15	131.12	6.29	15.47	2.54	3.95	0.12	57.36	2.24	33.21	1.66	0.26	0.04	2.29	0.15	3.76	0.43

[a]Each reported value is the average of four independent replicates and reflects the mass of the analyte in 25 mL solution per unit surface area of test film. Reported errors for mass values are standard deviations. The reported errors for the mass ratios reflect a propagation of the associated errors for each individual mass measurement. [b]These data points contained replicates that exhibited zinc values that were >50% larger than the average of the remaining replicates. In these cases, the anomalous datum was discarded as an outlier and the reported value reflects the mean value and standard deviation of the remaining replicates.

Table S5. Masses[a] of cadmium, zinc, and selenium released from **QD539/LDPE** and **QD609/LDPE** films into water and 3% aqueous acetic acid at 75 ℃, expressed on a per-film-mass basis

PNC	Liquid	Time [days]	Released mass [ng per g film mass]							
			Zn		Se		Cd		S	
			Mean	Std	Mean	Std	Mean	Std	Mean	Std
QD539 2.08 mg/mL in LDPE	Water	1	5.23	0.39	0.48	0.06	1.57	0.15	9.90	0.69
		3	11.09	2.14	1.22	0.05	2.53	0.17	17.41	1.69
		5	18.86	2.36	2.01	0.20	3.44	0.26	22.63	1.10
		7	21.40	2.49	2.10	0.13	3.56	0.32	23.83	1.58
		10	31.18	7.10	2.41	0.17	4.57	0.33	26.52	2.96
		15	34.87	7.55	2.90	0.18	4.50	0.66	30.39	1.73
	3 % (v/v) aq. acetic acid	1	16.44	4.03	1.11	0.18	3.00	0.44	19.16	2.63
		3	40.90	11.49	1.82	0.14	6.67	1.63	22.17	2.31
		5	43.54	4.63	1.90	0.19	6.71	0.57	23.61	2.02
		7	75.10	7.03	2.12	0.25	9.79	0.53	27.91	0.92
		10	84.24	6.74	2.32	0.27	10.25	0.72	32.51	5.04
		15	96.94	21.19	2.57	0.30	10.72	2.41	33.16	5.20
QD609 2.08 mg/mL in LDPE	Water	1	5.27	0.28	2.10	0.16	0.89	0.21	8.44	0.56
		3	13.02	1.09	4.75	0.68	1.56	0.16	13.90	0.40
		5	21.08	1.79	6.21	0.56	1.21	0.11	15.91	1.64
		7	31.52[b]	2.39	7.20	0.80	1.35	0.30	17.97	0.34
		10	48.23[b]	9.07	7.16	0.71	1.30	0.48	21.49	1.79
		15	44.12	8.12	8.90	0.27	1.24	0.07	22.09	1.66
	3 % (v/v) aq. acetic acid	1	13.30	2.91	3.31	0.25	0.89	0.43	14.02	1.68
		3	25.07[b]	5.26	4.81	0.19	1.68	0.44	18.27	1.19
		5	39.62	3.13	5.53	0.97	1.80	0.21	20.43	0.32
		7	47.17	9.76	5.53	0.34	1.92	0.24	23.13	1.36
		10	57.72	1.69	6.34	0.63	2.02	0.17	27.04	4.19
		15	63.98	5.39	7.51	0.94	1.92	0.09	27.93	0.83

[a]Each reported concentration value is the average of three independent replicates and reflects the concentration of the analyte in solution per unit mass of test film. Reported errors are standard deviations. The reported errors for the mass ratios reflect a propagation of the associated errors for each individual mass measurement. [b]These data points contained replicates that exhibited zinc values that were >50 larger than the average of the remaining replicates. In these cases, the anomalous datum was discarded as an outlier and the reported value reflects the mean value and standard deviation of the remaining replicates.

Table S6. Masses of zinc, sulfur, cadmium and selenium released from **QD546/LDPE** and **QD617/LDPE** into water and 3% aqueous acetic acid at 75 ℃, expressed on a per-film-surface-area basis.[a]

| Material | Liquid | Time days | Released mass [ng per cm² film area][a] | | | | | | | | Ratio of Zn to Cd | | Ratio of Cd to Se | | Ratio of Zn to S | | Ratio of S to Se | |
| | | | Zn | | Se | | Cd | | S | | | | | | | | | |
			Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std	Mean	Std
QD546 1.08 mg/mL in LDPE	Water	1	4.80	0.55	0.68	0.04	6.77	1.29	15.77	7.88	0.72	0.13	10.02	2.45	0.37	0.19	23.26	11.49
		7	11.54	0.77	2.07	0.26	18.33	1.73	28.15	3.38	0.63	0.05	9.03	1.87	0.41	0.06	13.64	0.70
		15	13.72	0.39	3.51	0.12	24.70	1.58	37.25	0.44	0.56	0.04	7.05	0.50	0.37	0.01	10.63	0.40
	3 % (v/v) aq. acetic acid	1	13.52	0.85	1.02	0.09	14.18	0.65	18.63	2.43	0.95	0.03	13.98	1.49	0.73	0.06	18.27	2.04
		7	18.05[b]	0.98[b]	3.49	0.43	30.36	1.16	38.31	1.62	0.60	0.02	8.76	0.88	0.47	0.02	11.06	1.09
		15	19.47	0.63	6.25	0.73	49.13	6.01	43.39	1.40	0.40	0.05	7.87	0.62	0.45	0.03	7.00	0.67
QD617 1.30 mg/mL in LDPE	Water	1	1.19	0.33	0.50	0.04	1.40	0.14	6.98	2.58	0.85	0.19	2.80	0.12	0.18	0.03	13.84	4.59
		7	1.89	0.82	1.13	0.08	3.40	0.33	16.32	1.20	0.54	0.20	3.02	0.30	0.11	0.04	14.42	1.29
		15	0.95[b]	0.26[b]	1.59	0.10	5.13	0.39	13.68[b]	2.44[b]	0.18	0.05	3.22	0.10	0.07	0.01	8.43	1.76
	3 % (v/v) aq. acetic acid	1	5.25	1.33	0.85	0.06	3.62	0.41	18.28	5.18	4.30	0.74	1.48	0.46	0.30	0.08	21.73	6.55
		7	3.81	0.25	2.16	0.05	8.04	0.23	28.75	1.27	3.72	0.12	0.47	0.02	0.14	0.01	13.29	0.41
		15	3.58[b]	0.60[b]	4.08[b]	0.30[b]	11.36	0.33	29.19	2.79	2.76	0.16	0.31	0.06	0.12	0.03	6.84	0.57

[a]Each reported value is the average of four independent replicates and reflects the mass of the analyte in the volume of test solution per unit surface area of test film. Reported errors for mass values are standard deviations. The reported errors for the mass ratios reflect a propagation of the associated errors for each individual mass measurement. [b]These data points contained one replicate that exhibited either zinc, sulfur, or selenium values that were >50% larger than the average of the values for the remaining replicates. In these cases, the anomalous datum was discarded as an outlier and the reported value reflects the mean value and standard deviation of the remaining replicates.

Table S7. Masses of zinc, sulfur, cadmium and selenium released from neat (QD-free) low-density polyethylene films and from sample tubes without films into water and 3% aqueous acetic acid at 75 ℃, expressed on a per-film-surface-area basis.[a]

| Material | Liquid | Time [days] | Released mass [ng per cm² film area][a] | | | | | | | |
| | | | Zn | | Se | | Cd | | S | |
			Mean	Std	Mean	Std	Mean	Std	Mean	Std
Control LDPE film (No QDs)	Water	1	1.08	0.14	ND	ND	0.07	<0.01	4.91	1.02
		15	0.90	0.05	ND	ND	0.09	<0.01	11.81	0.94
	3 % (v/v) aq. acetic acid	1	1.41	0.28	0.04	0.01	0.07	0.01	ND	ND
		15	3.37	1.34	0.06	0.02	0.10	0.01	16.70	1.87
Control / No film, sample tube only	Water	1	0.05	0.02	ND	ND	ND	ND	1.91	0.34
		15	ND	ND	ND	ND	ND	ND	13.64	4.39
	3 % (v/v) aq. acetic acid	1	0.14	0.10	ND	ND	0.01	<0.01	ND	ND
		15	0.47	0.26	0.02	0.01	0.01	<0.01	14.68	3.70

[a]Release experiments were conducted identically to those described for QD/LDPE PNCs, except that either neat LDPE films or no films were used. The release masses for the analytes have been scaled by the total surface area of test films to facilitate direct comparisons with the release data from QD/LDPE PNCs, even though not all of the control samples have films. "ND" means that the concentration of the analyte was below the detection limit (see section 1 of this supporting information file for a list of the detection limits for each analyte).

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