Electronic Supplementary Information (ESI)

Al^{3+}-induced far-red fluorescence enhancement of conjugated polymer nanoparticles and its applications in intracellular Al^{3+} ion sensing

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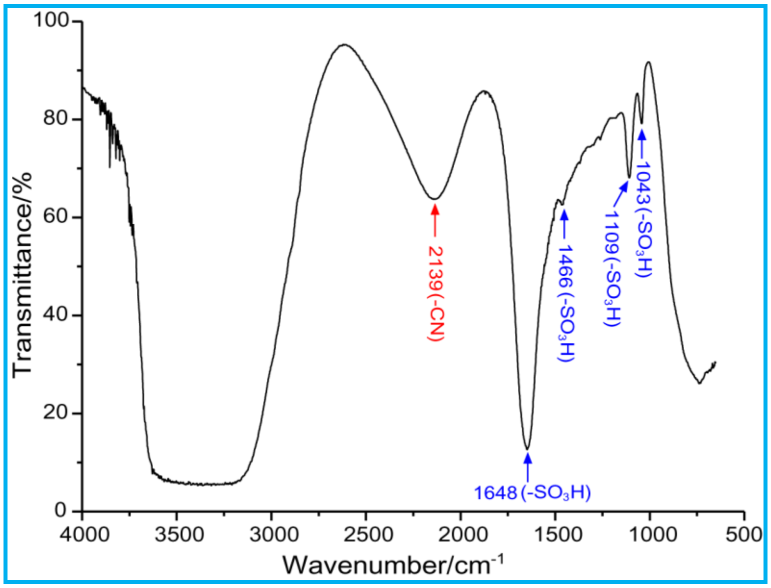

Figure S1: Typical Fourier transform infrared (FT-IR) spectrum of the as-prepared PCzDCN/PST-SO_3H NPs recorded using Bruker Vertex80 spectrometer.

This FT-IR spectrum was acquired from a thin layer of PCzDCN/PST-SO_3H NPs aqueous dispersion sample between two silicon wafers using Bruker Vertex80 spectrometer. The broad absorption band in the range of 3200-3600 cm^{-1} can be attributable to O-H bonds of H_2O. The characteristic absorption peak at 2139 cm^{-1}

belongs to the –CN component of the far-red fluorescent conjugated polymer PCzDCN and the peaks at 1648, 1466, 1109, and 1043 cm^{-1} arise from the $–SO_3H$ component of the amphiphilic polymer PST-SO_3H as discussed in the main text.

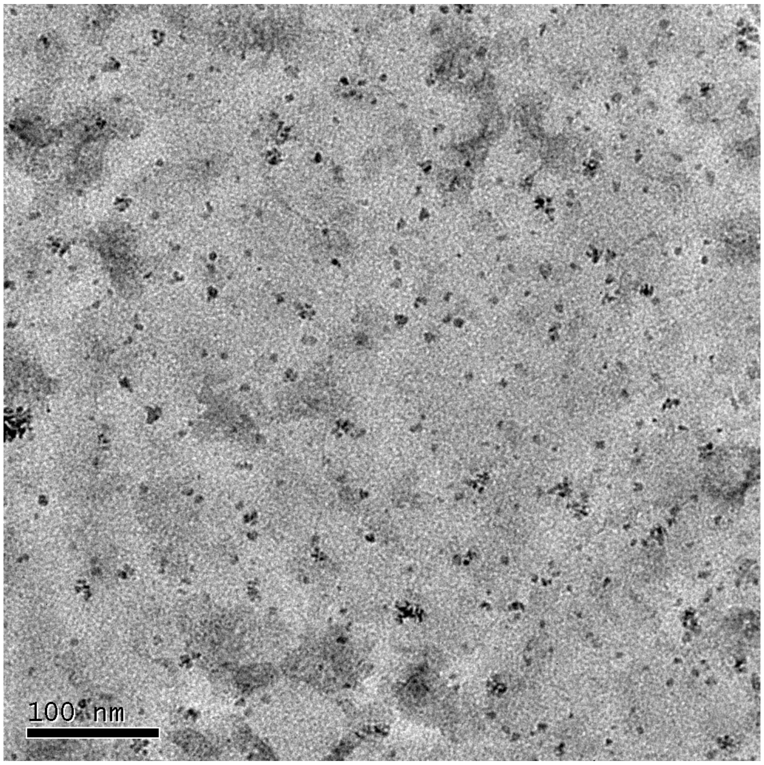

Figure S2: Typical transmission electron microscope (TEM) image of the as-prepared PCzDCN/PST-SO_3H NPs using Tecnai G^2 20 S-TWIN TEM.

The NPs sample for TEM characterization was prepared by placing a drop of the as-prepared PCzDCN/PST-SO_3H NPs aqueous dispersion on a carbon-coated Cu grid, followed by solvent evaporation at room temperature. TEM measurement results of the as-prepared NPs are roughly in accordance with the AFM characterization results as shown in the main text. However, TEM measurements presented a relatively smaller average diameter when compared to the hydrodynamic diameter obtained from DLS, probably attributable to the hydrodynamic swelling effect as the DLS measurement was carried out with the NPs suspended in an aqueous environment while the TEM measurement was made with dry NPs under high vacuum conditions.

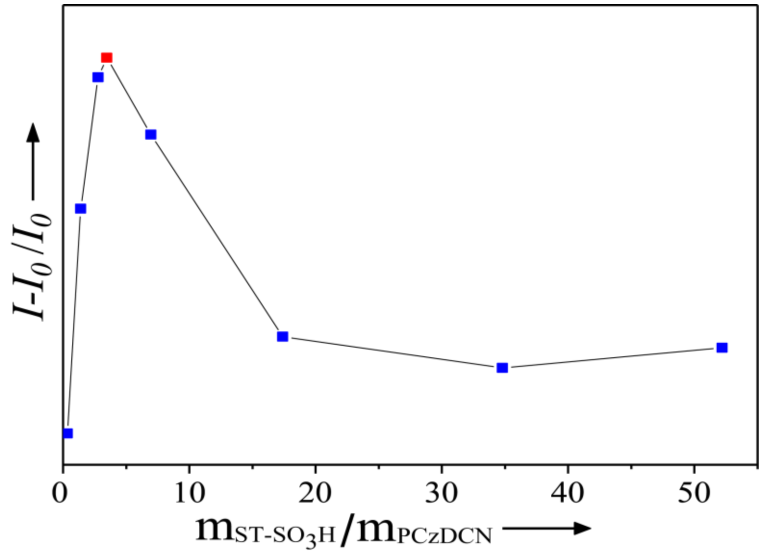

Figure S3: Al^{3+}-induced fluorescence enhancement of PCzDCN/PST-SO_3H NPs as a function of the ratio of sulfonated styrene units (ST-SO_3H) to the fluorescent polymer (PCzDCN) in the as-prepared NPs.

The ratio of sulfonated styrene units to the fluorescent polymer (ST-SO_3H/PCzDCN) in the complex PCzDCN/PST-SO_3H NPs was found to exert significant influence on the Al^{3+}-induced fluorescence enhancement. As discussed in main text, the fluorescence emission of the neat PCzDCN NPs (without PST-SO_3H component) was confirmed nearly independent of Al^{3+}. Upon adding the ST-SO_3H component into the NPs, Al^{3+}-dependent fluorescence emission was clearly observed. Additionally, by gradually increasing the content of PST-SO_3H component in the complex NPs, the extent of Al^{3+}-induced fluorescence enhancement was found augment accordingly, as shown in Figure S3. Specifically, the extent of fluorescence enhancement was found peak when the mass ratio of ST-SO_3H to PCzDCN in the as-prepared complex NPs reached 3.5:1 and further increase in the content of ST-SO_3H component resulted in obvious decrease in the extent of fluorescence enhancement. For the complex NPs in the present work, it is hypothesized that the hydrophilic ST-SO_3H units reside on the surfaces of the NPs and provides coordination sites for metal ions, which was demonstrated indispensable for Al^{3+} chelating and sensing as discussed in main text. Additionally, the hydrophobic alkyl main chains of PST-SO_3H entwine with PCzDCN's main chains due to hydrophobic interactions in aqueous media. As a result, PST-SO_3H could disrupt polymer-polymer interactions of PCzDCN component and therefore reduce aggregation-induced fluorescence quenching within the as-prepared NPs.

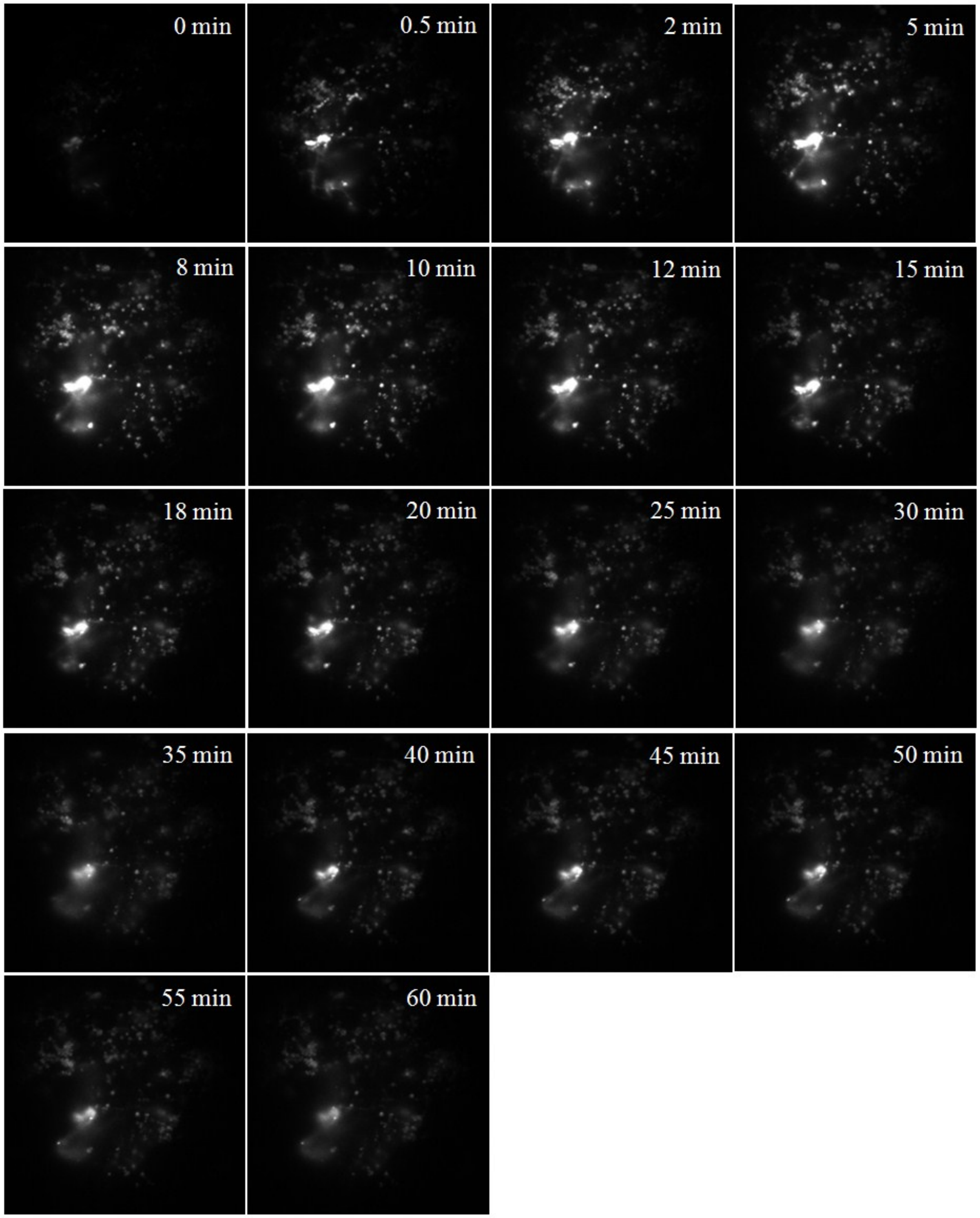

Figure S4: Time-lapsed intracellular fluorescence images of Vero cells with internalized PCzDCN/PST-SO_3H NPs in Dulbecco's Modified Eagle medium (DMEM) containing 170 μM Al^{3+}.

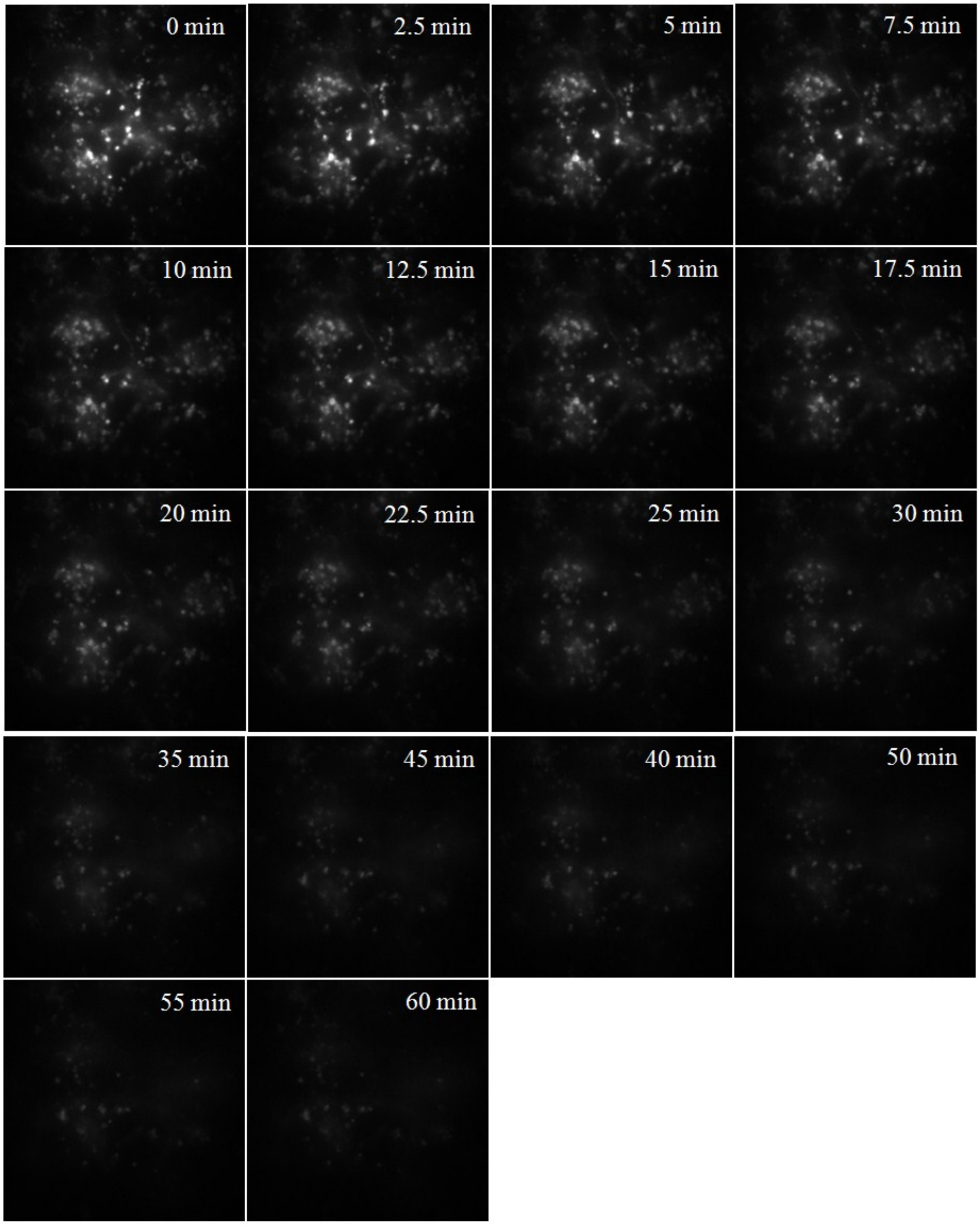

Figure S5: Time-lapsed intracellular fluorescence images of Vero cells with internalized PCzDCN/PST-SO_3H NPs in Al^{3+}-free Dulbecco's Modified Eagle medium (DMEM) buffer.