4-(2-Pyridylazo)-resorcinol Functionalized Thermo-Sensitive Ionic Microgels for Optical Detection of Heavy Metal Ions at Nanomolar Level

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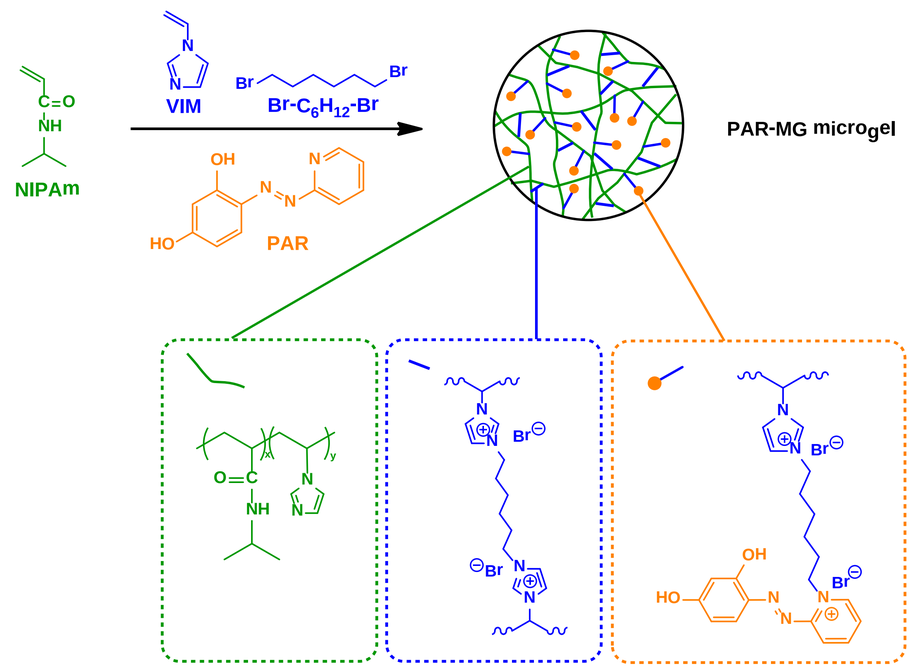
BACKGROUND

- Excessive levels of heavy metal ions can cause great damage to human health and environment.
- Microgels are polymeric colloidal particles with three-dimensional cross-linked networks that are swollen in good solvents.
- In this work, novel functional microgels were designed and synthesized for fast colorimetric detection of various heavy metal ions, namely Cu^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, and Ni^{2+}, in aqueous solution at nanomolar level.

METHOD

- Functional thermo-sensitive ionic microgels were synthesized via a one-pot quaternization reaction during the surfactant free emulsion copolymerization (SFEP) of *N*-isopropylacrylamide (NIPAm) and 1-vinylimidazole (VIM) with the presence of 1, 6-dibromohexane and hydrophobic indictor, i.e. 4-(2-pyridylazo)-resorcinol (PAR).



3. Selectivity of PAR-MG for Detecting Cu^{2+}

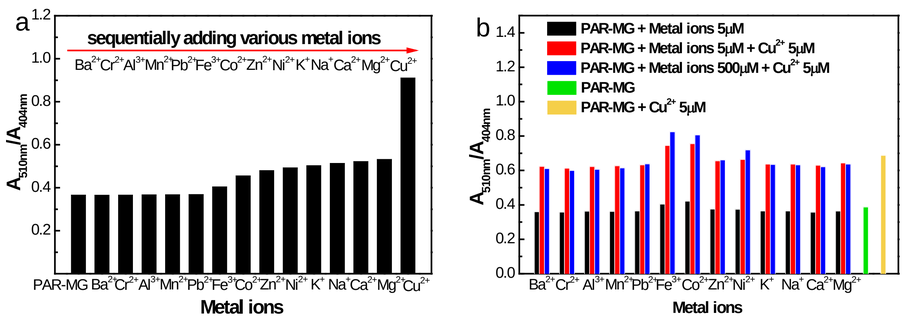


Figure 3. (a) A_{510nm}/A_{404nm} ratios of PAR-MG microgels at pH 3 after sequential addition of various metal ions. The adding sequence of metal ions was Ba^{2+}, Cr^{2+}, Al^{3+}, Mn^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Zn^{2+}, Ni^{2+}, K^{+}, Na^{+}, Ca^{2+}, Mg^{2+}, and Cu^{2+}. The concentrations of PAR-MG microgels and each metal ion were 0.125 mg/mL and 5 μM, respectively. (b) Interference studies of different metal ions on detection ability of PAR-MG microgels for Cu^{2+} at pH 3. The concentration of Cu^{2+} was 5 μM.

4. Detection Limits

$$D_L = \frac{kS_b}{m}$$

Detection Limits		U. S. EPA	
Cu^{2+} (pH = 3)	38 nM	Cu^{2+}	20 μM
Cu^{2+} (pH = 7)	12 nM		
Mn^{2+} (pH = 11)	14 nM	Mn^{2+}	909 nM (50 μg/L)
Zn^{2+} (pH = 11)	20 nM	Zn^{2+}	76 μM (5 mg/L)
Ni^{2+} (pH = 11)	21 nM	Ni^{2+}	680 nM (40 μg/L)
Pb^{2+} (pH = 11)	79 nM	Pb^{2+}	72 nM (15 μg/L)

RESULTS AND DISCUSSION

1. Morphology and Thermo-sensitive Behavior of Microgels

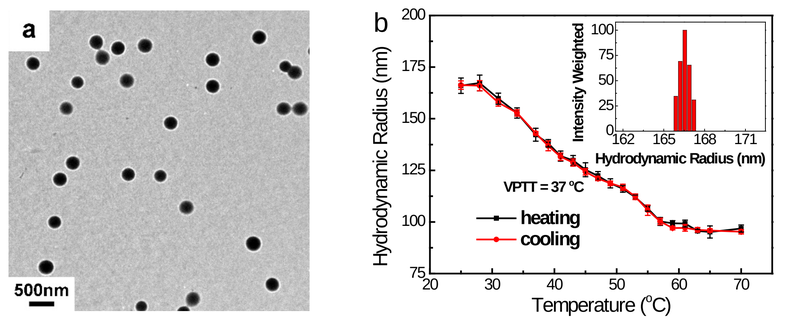
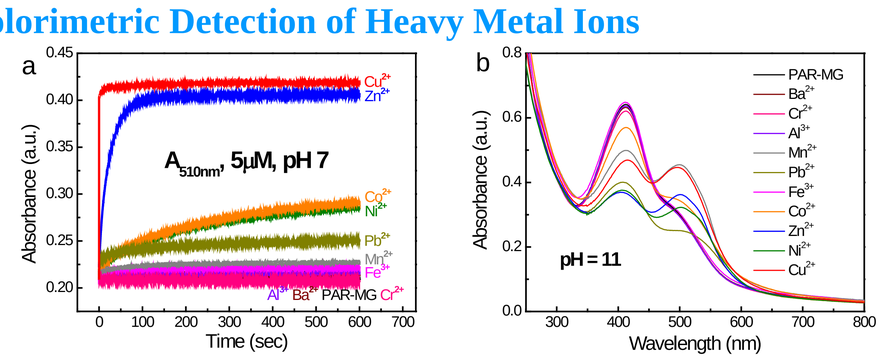


Figure 1. (a) The representative TEM image of PAR-MG microgels and (b) the hydrodynamic radius of PAR-MG microgels measured by DLS as a function of measuring temperature. The inset showed the size distribution of PAR-MG microgels at 25 °C.

2. Colorimetric Detection of Heavy Metal Ions



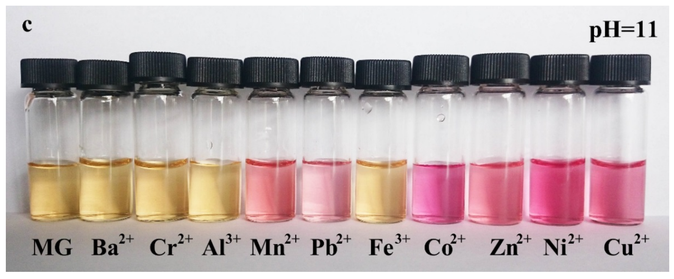


Figure 2. (a) The intensity evolution of UV absorption peak at 510 nm for PAR-MG microgel suspensions at pH =7 with the presence of various heavy metal ions (5 μM) as a function of time. (b) The UV-vis adsorption spectra of PAR-MG microgel suspensions with the presence of different heavy metal ions (5 μM) at pH = 11. (c) The digital photos of PAR-MG microgel suspensions with the presence of 5 μM various heavy metal ions at pH = 11. The concentration of PAR-MG microgels was 0.125 mg/mL.

CONCLUSIONS

- The PAR-MG could optically detect trace heavy metal ions in aqueous solutions, especially exhibit high sensitivity and excellent selectivity toward Cu^{2+} over other metal ions under strongly acidic.
- The limits of colorimetric detection for Cu^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+}, and Ni^{2} were lower than (or close to) the U. S. EPA standard for the safety limits of these heavy metal ions in drinking water.
- The PAR-MG also exhibited characteristic color with the presence of various trace heavy metal ions, which could be visually distinguished by naked eyes.

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