



# Poly(ionic liquid) as an efficient carrier of hydrophobic small-molecule probes for ion detections in pure aqueous environments



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## ABSTRACT

Expanding the availability of hydrophobic small-molecule probes in pure aqueous environments is an important issue likely to significantly impact their application prospects in sensing detections. The present work demonstrates for the first time that poly(ionic liquid) (PIL) can serve as a superior carrier, which not only enables hydrophobic small-molecule probes to readily disperse in pure water and but helps maximize their sensing performances. As a proof-of-concept, a hydrophobic rhodamine derivative carried by PIL, P(RhBHSA-co-META), was designed and applied for the colorimetric determination of Cu<sup>2+</sup> and further for CN<sup>-</sup> in fully aqueous solutions. Due to the positively charged nature of polymeric backbone, the P(RhBHSA-co-META) was highly water-soluble and could avoid non-specific bonding. Moreover, the strong inter- and intra-chain electrostatic repulsions made the P(RhBHSA-co-META) possible to be fully free and highly stretched in water, facilitating the accessibility of receptor binding sites. Excellent sensing performance of P(RhBHSA-co-META) toward Cu<sup>2+</sup> was achieved in terms of high sensitivity, ultrafast color/absorption response, and excellent anti-disturbance ability. Furthermore, the pre-formed P(RhBHSA-co-META)-Cu<sup>2+</sup> complex was also verified to be highly efficient for colorimetric determination of CN<sup>-</sup>, exhibiting high sensitivity and selectivity. This study provides a simple, effective, and extendable approach for designing water-soluble chemosensors for ion detections and other sensing applications.

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## 1. Introduction

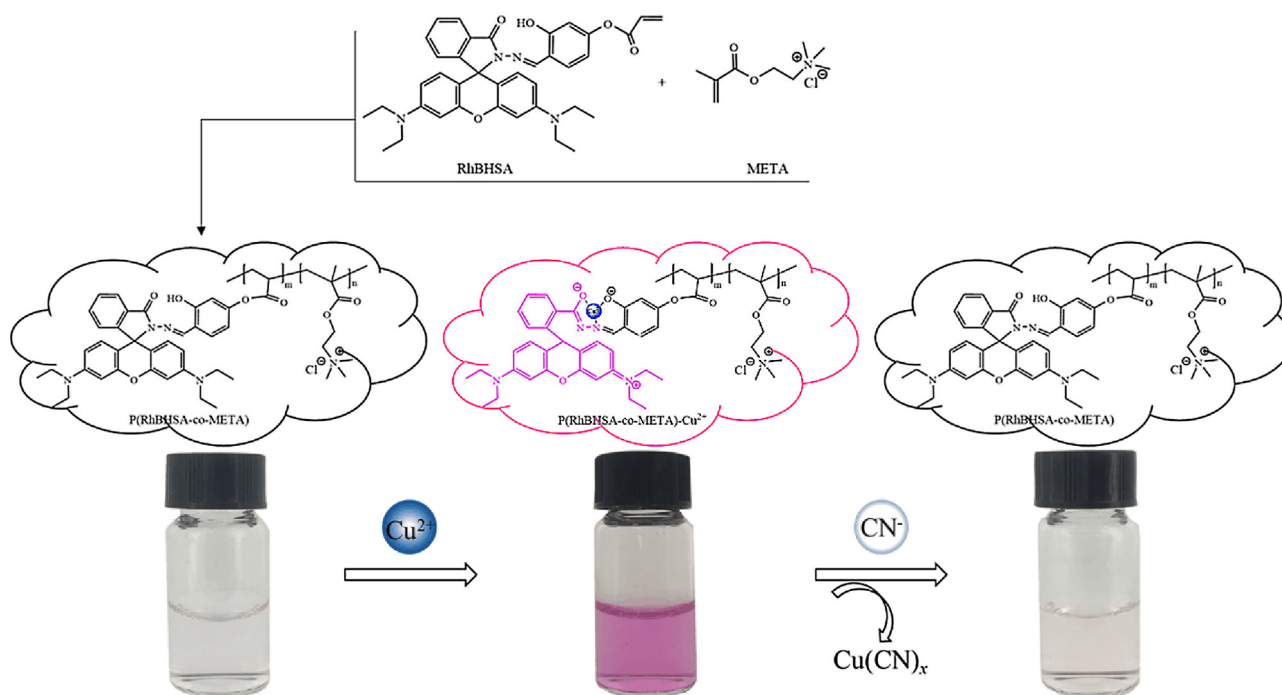
Using small-molecule probes, including acridine, BODIPY, coumarin, fluorescein, and rhodamine derivatives etc., to detect metal ions or anions has become a focal interest in recent years [1–4]. However, most of these sensing probes are strongly hydrophobic and only function in a medium of pure organic solvent or an aqueous solution containing a significant amount of organic co-solvent, which greatly limits their potential applications in ion detections, especially for analyses of biological samples [5,6].

To make these hydrophobic probes applicable in pure aqueous environments, an efficient strategy is to incorporate them into the hydrophilic polymer carriers [7], such as poly(ethylene glycol) (PEG) [8], polyvinylalcohol (PVA) [5], poly(4-vinylpyrrolidone)

(PVP) [6,9,10], poly(N-isopropylacrylamide) (PNIPAM) [11,12], poly(2-hydroxyethyl acrylate) (PHEA) [13], poly(acrylic acid) (PAA) [14], and poly(acrylamide) (PAM) [15]. In the majority of cases, such incorporation is implemented through the copolymerization reaction of polymerizable small-molecule probe with hydrophilic monomer. Indeed, many hydrophobic small-molecule probes, by virtue of their bonding to hydrophilic polymer carriers, become available to work in pure aqueous solutions. Moreover, these water-soluble chemosensors are fairly stable and do not suffer from leaching of probe units [11,13]. Nevertheless, due to the difficulty in counterbalancing the hydrophobicity of small-molecule probes, a considerably high feeding ratio of hydrophilic monomer to polymerizable hydrophobic probe molecule (at least 39:1, mol/mol) is experimentally proven to be necessary in order to produce a completely water-soluble chemosensor (Table S1, Supporting Information) [6,9–11,13,14]. This is less economically efficient and somewhat hinders the wide application of these chemosensors. Moreover, in some cases (e.g., the use of PAA or PAM as carrier) [14,15], the non-receptor bonding sites existing in polymer

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**Fig. 1.** The synthetic strategy of P(RhBHSA-co-META) and its applications for ions detections in pure aqueous solutions.

carrier might competitively capture target metal ions, which is disadvantageous for metal ion determination in term of sensitivity. Additionally, the inter- and intra-chain interactions (e.g., hydrogen bonding and hydrophobic interaction) usually induce polymer molecules to curl and entangle in aqueous solution [12], probably causing relatively slow and even inadequate binding of the target ions to the probe units. Therefore, new alternative polymer carriers are highly desired to offer stronger hydrophilicity, be devoid of non-specific bonding sites, and allow the carried probe units to be highly exposed on the polymeric backbone.

Poly(ionic liquid)s (PILs) refer to a new special subclass of polymers that feature an ionic liquid cations (e.g., alkylammonium, imidazolium, or pyridinium) in each monomer repeating unit, connected through a polymeric backbone to form a macromolecular architecture [16,17]. To date, PILs have been widely used in polymer electrolytes for batteries, CO<sub>2</sub> separation membranes, catalysis, adsorption, and some bio-related fields [18]. Very recently, PILs have been used as additives or auxiliary agents of some sensors to improve the sensing performances [19]. For example, in some nanomaterial-based sensors, PILs are added to serve as dispersants or capping agents of active nanoparticles (e.g., SWNTs [20], fluorescent nanoparticles [21], Ag-RGO [22], PPy/GO [23], and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [24]), which can efficiently prevent particle aggregation or restacking during sensing process. Also, it has been demonstrated that the PILs can act as complexation agents of stimuli-responsive polymers (e.g. PAA) to construct polymer membrane-based sensors with rapid solvent diffusion [25,26]. Up till now, however, little work has been done on exploring the carrier function of PILs to fabricate new water-soluble chemosensors. In fact, owing to the positively charged nature of polymeric backbone, many PILs (especially the short alkyl-chain PILs with halide ions as counter-anions) are extremely soluble in water and possess a natural advantage in avoiding cationic species to be adsorbed by the polymeric backbones [16,27]. Thus, we speculate that PILs can be used as promising carriers of hydrophobic small-molecule probes to construct new efficient chemosensors that are not only highly water-soluble but sensitive in response to target ions. Moreover, unlike traditional hydrophilic polymer carriers, the PIL carrier can be fully free and

highly stretched in water due to the strong inter- and intra-chain electrostatic repulsions [28], which is also expected to be beneficial for rapid access of target ions to receptor binding sites.

Herein, we reported the first attempt of employing short alkyl-chain PIL as the carrier of hydrophobic small-molecule probes and further investigating the possible application of the resulting water-soluble chemosensor for ion detections in pure aqueous environments. As a proof-of-concept, a hydrophobic rhodamine derivative moieties-incorporated PIL with methacrylic alkylammonium backbone, P(RhBHSA-co-META), was designed and applied for the colorimetric determination of Cu<sup>2+</sup> and further for CN<sup>-</sup> in fully aqueous solution (Fig. 1). The convenient synthesis of P(RhBHSA-co-META) was achieved via a copolymerization of the polymerizable RhBHSA (recognition unit [11]) and the ionic liquid monomer methacryloyloxyethyl trimethyl ammonium chloride (META) [29,30]. In significant contrast from previously reported hydrophilic copolymer chemosensors, only a low molar ratio of META to RhBHSA (i.e., 1:1) was used in our synthesis. The resulting P(RhBHSA-co-META) was found to be favorably and instantaneously dissolved in pure water. Moreover, upon the addition of Cu<sup>2+</sup>, even at a trace level (<1 × 10<sup>-6</sup> M), the color of the P(RhBHSA-co-META) solution would significantly change from colorless to pink within 3 s, indicating high sensing sensitivity and ultrafast response rate. Excellent selectivity was also verified in the presence of other competitive metal ions. Furthermore, on the basis of strong coordination interaction between Cu<sup>2+</sup> and CN<sup>-</sup>, the pre-formed P(RhBHSA-co-META)-Cu<sup>2+</sup> complex was demonstrated to be capable of serving as an efficient probe for CN<sup>-</sup> determination, which exhibited highly sensitive and selective recognition through the fading of pink color.

## 2. Experimental

### 2.1. Chemicals and reagents

The initiator azo-bis-isobutyronitrile (AIBN) was purchased from Shanghai No. 4 Reagent & H.V. Chemical Reagent Co., Ltd. (Shanghai, China), which was recrystallized from ethanol before

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