

Real-Sample Analysis utilizing Supramolecular Chemical Sensor Chips and Devices

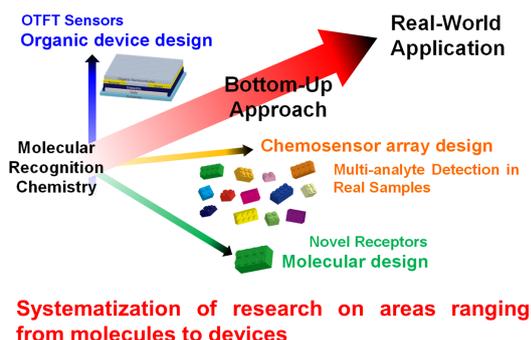
(Institute of Industrial Science, The University of Tokyo) ○Tsuyoshi Minami

Keywords: Supramolecular Device; Chemical Sensor; Molecular Recognition; Organic Transistor; Pattern Recognition

Supramolecular materials have the potential to be applied to analytical devices, while such materials have not fully satisfied the requirements for practical analysis to this date. To explore appropriate approaches for real-world applications, we have continued comprehensive and cross-hierarchical research on areas ranging from molecules to devices (Fig. 1). Indeed, the strategy was applied to realize supramolecular sensor devices and successfully performed real-sample analyses.^{1,2} As our recent achievements, easy-to-handle supramolecular sensor devices for anion detection in water, which is one of the hot topics in supramolecular chemistry, are introduced at this presentation.

Oxyanions such as phosphates, phosphonates, and carboxylates play important roles in metabolism. Among them, the quantification of herbicide glyphosate is in high demand because of its potential carcinogenic activity.³ Thus, we decided to develop two small types of chemical sensor devices for rapid on-site analysis of oxyanions including glyphosate.

A chemosensor array enables simultaneous discrimination of multiple chemical species utilizing powerful pattern recognition techniques.¹ To realize easy-to-prepare colorimetric chemosensors without synthetic burden, four off-the-shelf catechol dyes and a metal ion (*i.e.*, Zn^{2+}) were employed for practical analysis (Fig. 2(a)).⁴ The spontaneously formed coordination bond-based chemosensors exhibited colorimetric changes by adding target oxyanions in water, which stemmed from competitive



Systematization of research on areas ranging from molecules to devices

Fig. 1 Research concept.

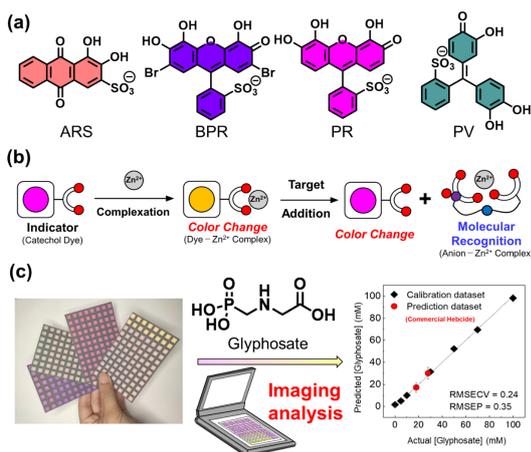


Fig. 2 (a) Chemical structures of catechol dyes. (b) Schematic illustration of a mechanism for oxyanion detection. (c) Scheme of imaging analysis-driven quantitative detection of glyphosate.

coordination binding (Fig. 2(b)). The coordination bond-based chemosensors, which showed various colorimetric responses depending on the structural differences of target oxyanions and those concentrations, were applied to imaging analysis-driven pattern recognition on paper toward on-site analysis.⁵ Notably, visible color changes on a paper-based chemosensor array were rapidly recorded using an office flatbed scanner, followed by automatic imaging analysis for accurate discrimination of oxyanions and quantification of commercial herbicides (Fig. 2(c)).⁵

A water-gated organic thin-film transistor (WG-OTFT), which can be referred to as a supramolecular device because of its transistor characteristics controlled by self-assembled structures of semiconductive polymer materials, was selected as a sensor device platform (Fig. 3(a)).² Very importantly, the WG-OTFT characteristics correspond to the accumulation and desorption of charged species at the interface, meaning that the transistor properties can be tuned by chemical stimuli. Moreover, appropriate functional side chains of π -conjugated polymers endow the semiconductive layer with two-dimensional molecular recognition sites. Therefore, a competitive assay using a carboxylate-attached polythiophene derivative (P3CPT) and a metal ion (*i.e.*, Cu^{2+})

was designed for the highly selective and sensitive detection of glyphosate (Fig. 3(b)).⁶ Indeed, the WG-OTFT-based chemical sensor displayed stepwise changes of transistor characteristics with an increase of glyphosate concentration.⁶ Furthermore, the real-time detection was also accomplished by the WG-OFET-based sensor integrated with a microfluidic system (Fig. 3(c)).⁷

In summary, we believe that proposed approaches can contribute to the real-world implementation of “supramolecular analytical devices” that further improve people’s quality of life.

1) T. Minami et al., *Coord. Chem. Rev.* **2021**, 429, 213607. 2) *Bull. Chem. Soc. Jpn.* **2021**, 94, 2613 (Cover). 3) *J. Am. Chem. Soc.* **2014**, 136, 11396, 4) *Anal. Chem.* **2019**, 91, 13627. 5) *ChemPlusChem* **2021**, 86, 798 (Cover and Highlighted by Wiley ChemistryViews). 6) *Chem. Eur. J.* **2020**, 26, 14525 (Cover and VIP). 7) *Langmuir* **2021**, 37, 7305 (Cover).

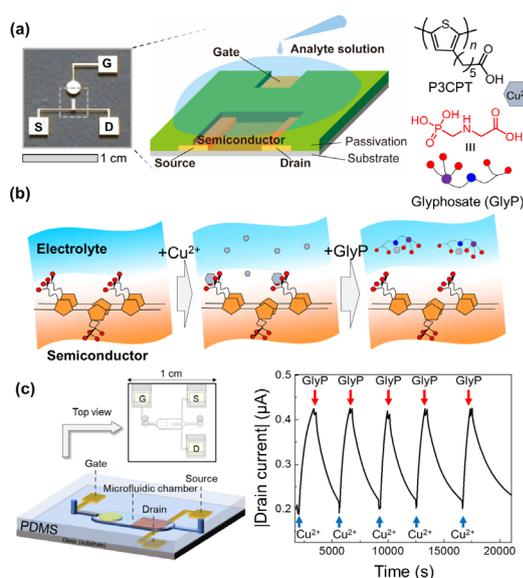


Fig. 3 (a) Photograph and schematic illustration of a WG-OTFT. (b) Schematic illustration of glyphosate sensing utilizing the competitive assay among P3CPT, the Cu^{2+} ion, and glyphosate in water. (c) Real-time monitoring of glyphosate using the microfluidic WG-OTFT device.