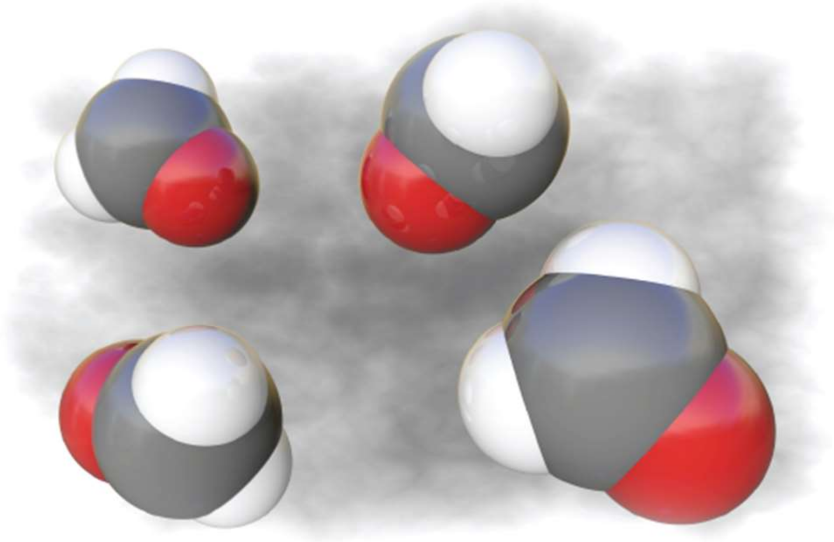
Chemistry Research and Applications

A Comprehensive Guide to Formaldehyde



Natasja A. Bach
Editor

NOVA

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Chapter 2

FORMALDEHYDE: POLYMER SURFACE CHEMISTRY AND DETECTION

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ABSTRACT

The global market trend predicts that the growth trajectory of the chemical "formaldehyde" will substantially increase production marking an unprecedented global economic expansion. The chemical profile of formaldehyde particularly in view of its reactive and volatile nature raises much concern about the potential chemical effects on disease progression due to inhalation at multi-levels in both natural and biological environments at bulk and nanoscale dimensions. As the global

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dependency on the use formaldehyde surges with no signs of slowing, much effort has been directed to investigate health-related issues and how nanotechnological advancement might play a greater role in in reducing the harmful impact of the chemical. The issues addressed in this chapter will converge upon a discussion and review of environmental and biological implications of the industrial growth of formaldehyde and a comprehensive evaluation of measures addressing the potentialities through the development of sensitive detection technologies.

Keywords: formaldehyde, nanomaterials, sensing technologies

INTRODUCTION

Formaldehyde formally known as methanal is the simplest hydrocarbon of the aldehyde group of chemicals and is considered to be ubiquitous in physical and chemical environments. It likely functions as a chemical precursor for many compounds produced in in living species from simple to more complex forms of life. Hence, its reputation as a primary source of carbon emphasizes its importance as a building block precursor in metabolic processes of life [1] and pathway regulation [2] with a possible evolutionary role [3, 4] and in synthetic intermediate to many important functional structures particularly at the nanoscale. Synthetically, the industrial relevance of formaldehyde has skyrocketed globally trending with economic growth on a global scale. This originates from its primary role as a fixative enabling biological materials to retain their 'life-like' state in the form of formalin or chemically hydrated formaldehyde. The global rise of formaldehyde correlates well with key adhesive characteristics in terms of binding strength, accessibility and durability and also its affordability as a polymeric material. Figure 1 demonstrates the applicability of bio-based formaldehyde complex resins in the bonding of wood for example where the adhesive performance is judged by mechanical strength, toughness and tensile strength aligned to greener properties. More importantly its role as a general preservative in diverse industries has been important from an economic point of view.

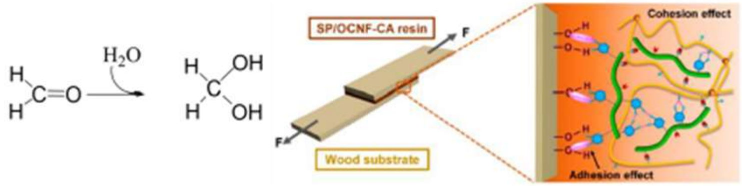

Figure 1. The application of hydrated formaldehyde (bio-resin) based materials for adhesion of wood. Adapted with permission from [5].

Formaldehyde as mentioned is notably be used for its adhesives properties for binding wood based materials and plastics and therefore is extensively utilized across diverse material surfaces to form chemically adhered layers in many industrial products. Some wood based furnishing for example comprise of hard polymer resins for manufacturing assembly parts for larger house-hold structures. The useful binding characteristics have also been used for textiles, domestic hygiene and medical products such as anti-bacterial materials, stationary items and more broadly as preservatives for many types of constituents. More so, formaldehyde remains a prevalent gas both indoor and out-door as it forms an important constituent of many house-hold items in wooden floors and furniture composed of different wood-types, interior and exterior wall coatings, thermal insulation materials, everyday textiles, in cleaning agents and chemicals as illustrated in Figure 2. Consumer products in the form of oral medicines have also been found to contain aldehyde derivatives. The nature of the pollutant and its wide spread use imply that it is not just restricted to the home but also the work place since the material is built into the fabric of numerous products.

High levels found in 'outside' environments are associated with car exhaust emissions and fuel sources with high formaldehyde content or through secondary events such as combustion of parent hydrocarbons and smoking. Its use in the agricultural and food industry has been particularly beneficial in food preservation.

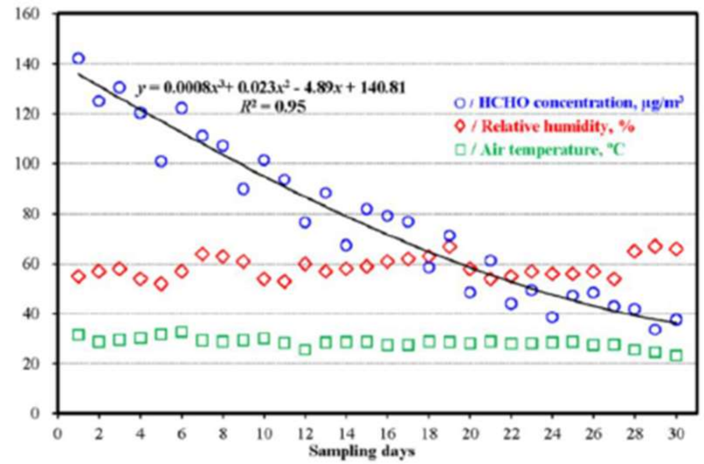

Figure 3. Data profiling of formaldehyde humidity and temperature variations in air cabins. Reproduced with from [10].

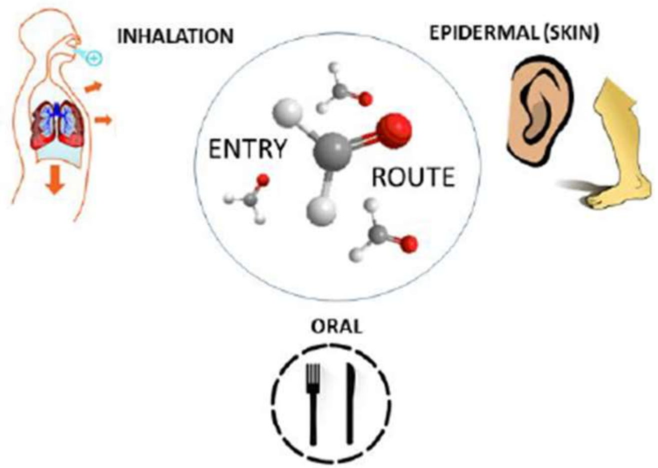

Figure 4. Different routes to the exposure of formaldehyde leading to the harmful effects inside the body.

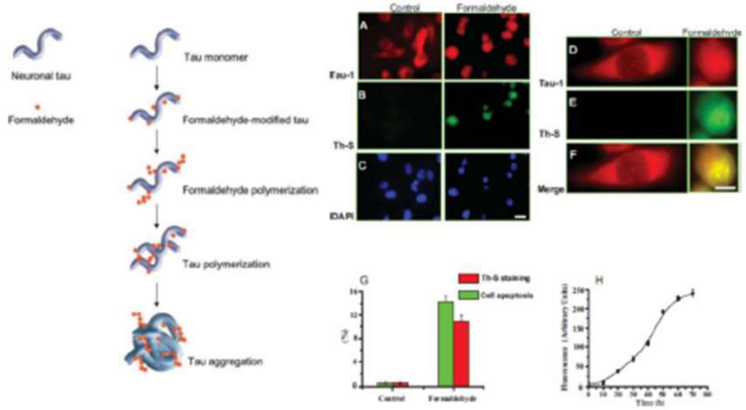

Figure 5. (Top panel left) The process of Tau protein aggregated assembly in the presence of formaldehyde. (Top panel right) Tau aggregation in the presence of formaldehyde in cells visualized by red fluorescence with Tau- antibody via ThS (amyloid-like aggregates). Blue fluorescence imaging are associated with nuclei of diminished size apoptotic arrest. (Bottom panel) Correlation between cell activity and antibody targeting signified by increased signals during apoptotic events relative to the control sample as a function of time Reproduced from [56].

Extensive investigations on the effects of formaldehyde have made clear that both domestic and occupational environments effect human health and defense barriers in the skin, respiratory tract and organs and tissues of the stomach are inadequate against the potent and reactant nature of the gas. It is freely absorbed into the respiratory tract and more limitedly by the skin but can enter through skin pores in the hydrated state. Food intake is another common way of entry into the blood which can be readily distributed among the organs, cells and tissues. Hence the severity of effects may be manifested by the period of exposure across short, intermediate and longer term durations. A more accurate correlation of the systematic effects on disease progression and mortality due to formaldehyde exposure could be ascertained by measuring and detecting formaldehyde levels in the surrounding atmosphere.

implications in reducing environmental pollution and slow poisoning by inhalation.

ADSORPTION OF FORMALDEHYDE

Control of formaldehyde pollutants through adsorption from the surrounding air by adsorbent materials particularly indoors from trapped air has been considered as a possible effective route remove the harmful effects on the human body. This is becoming an important directive as many house-hold items emit the gas from electronic equipment, furniture, wall paints, floor polish and cleansing chemicals routinely used in confined environments. If ventilation is poor in rooms with little no measures in place to remove toxicity build of volatiles in the air we breathe, the day-to-day accumulative effects of gas inhalation can easily escalate from levels of low toxicity to chronic elevated concentrations. This often leads to the state of ‘sick building syndrome’ that manifests symptoms of fatigue, dullness and low libido [62].

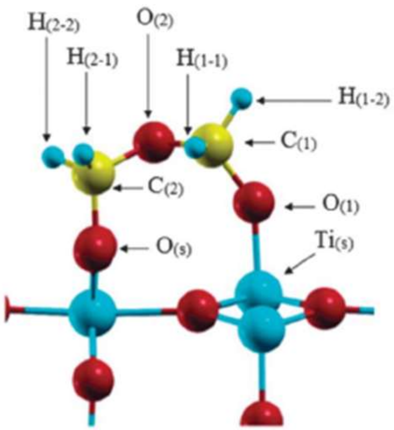

Figure 6. Computational model of the favourable binding of formaldehyde to TiO_2 surface in the gaseous adsorbed phase [61].

The application of adsorbent materials have recently been reported. Microporosity intrinsic to the nature of indoor materials has been suggested and investigated as a viable solution to limit the release of toxic gaseous vapors in the home or office environment. Such innovative materials have been evaluated by sorptive building materials test (SBMT) and researchers have found celite as a very effective adsorbent reducing HCHO allowing reduced concentrations of the volatiles to 0.2 ppm under a loading factor of 0.4 m^2/m^3 [63]. Figure 7 shows the application and evaluation of HCHO adsorption and its retainment by selected materials in this study. Similarly, advanced functional materials have been designed in the form of metallorganic frameworks to perform under ambient conditions. One such example is UiO-66-NH2 which exhibited an adsorption capacity of formaldehyde of 69.7 mg g^{-1} and was mainly attributed to regions between framework linkers and the affinity of hydrocarbon chains at the vicinity of metal sites and their association with carbonyl groups [64].

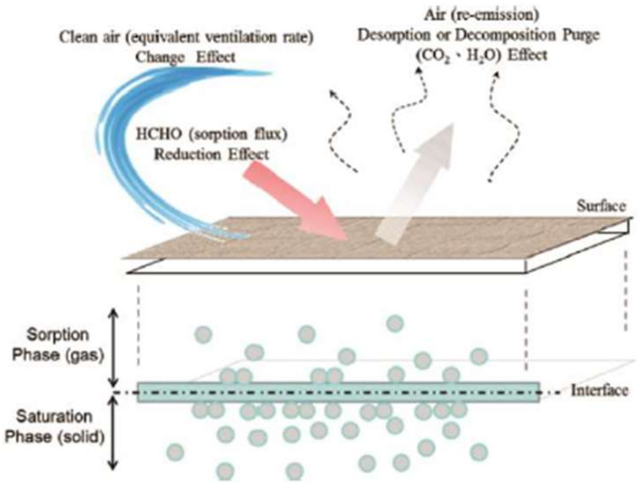

Figure 7. Material evaluation for the effective adsorption and retainment of the contaminant formaldehyde released into the local environment from household objects. Reproduced from [63].

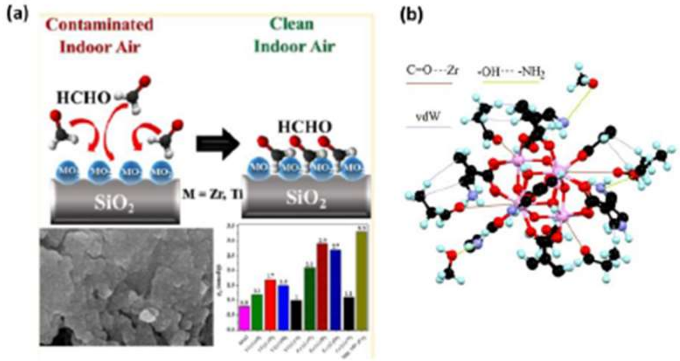

Figure 8. (a) An example of removal of HCHO vapors using ZrO_2/SiO_2 and TiO_2/SiO_2 metal-organic frameworks (MOFs) (b) Molecularly adsorbed contaminates of Zr clusters permitting their active removal. Reproduced with permission from [69] and [64].

Further investigations in this direction have provided support a range of materials including mesoporous silica organic frameworks (Si-(OH)-Al), zeolites and magnesium and aluminum complexes for formaldehyde capture. A copper complexed material designated HKUST-1 provide a promising example of porous materials to accommodate and retain HCHO molecules. The observation however, that humidity is a major player in reducing gas adsorption capacity suggests that the dimensional pores in these porous materials are very small scale to be effective in the entrapment of formaldehyde [65].

Porosity as an essential feature of all applicable materials include porous carbon and silica materials [66], activated carbon [67], diatomite, bentonite and zeolite [68], mixed metal oxides ZrO_2/SiO_2 [69] and TiO_2/SiO_2, covalent-organic polymers [70] and amine-functionalized mesoporous silica materials [71] among others. Further, the removal of formaldehyde by photocatalytic oxidation was observed to occur proportionally to the semiconductor content and shown to be dependent on surface contact [72]. Correlations between functional group chemistry at the nanoscale and nanopore size in relation to the physical, chemical and functional nature of formaldehyde is proving to be an important both in technicality and usability. Gasparini et al. [83] addressed the greener aspects of the use of chromotropic acid by using magnesium for the complexation generating a spectroscopically detectable intermediate Mg^{2+}/cycl-o-tetra-chromotropylene with HCHO molecules in the range of 3 to 11 mg L^{-1}. This enabled a more ecologically acceptable spectroscopic reagent contributing to a greener environment (Fluoral-P) as a colorless agent which readily reacts with formaldehyde in brain tissues of rats to generate a spectrophotometric measurement of 3,5-diacetyl-1,4-dihydrolutidine (DDL) with limits of detection of 0.5 μM and 2.5 μM [84]. Spectroscopic methods have found utility in standardizing the development of non-spectroscopic approaches to the quantification of HCHO (Figure 10) capable of detection. For example, Lamarca et al. [85] used an instrument for the applicability of spectroscopic procedure for biological tissue analysis has advanced the technique for utility potentially for clinical samples. For example, the availability of 4-amino-3-penten-2-one detection of HCHO in cosmetics was based on gas-diffusion microextraction integrated with a smartphone reader. Validation of the new method by spectroscopic analysis as the reference method is shown in Figure 11. The smart phone method was able to generate signals with the same degree of sensitivity to the reference method in range that was quantifiably agreeable (range limit ~ 0.200 mg kg^{-1} and 0.500 mg kg^{-1}).

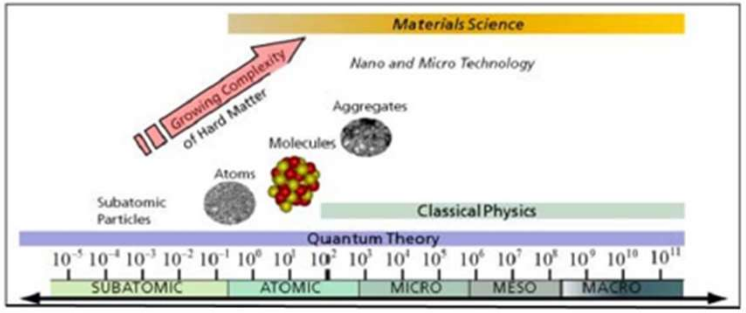

Figure 9. (a) Hierarchical scale of particles in materials engineering. Reproduced from [78].

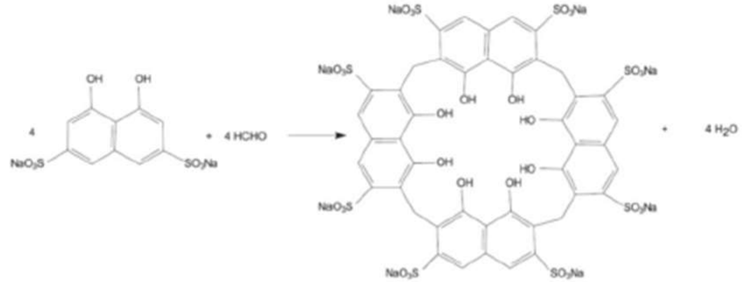

Figure 10. Modification of chromotropic acid to Mg^{2+}/cyclo-tetra-chromotropylene. Reproduced from [83].

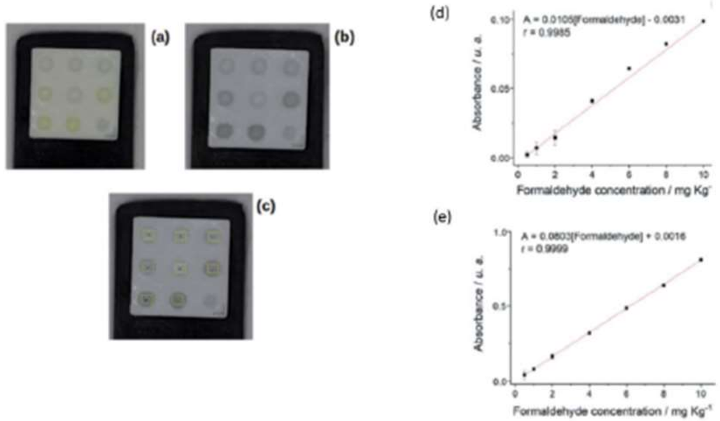

Figure 11. (a-c) A direct route for the quantification of formaldehyde in cosmetic products by a smart phone approach and validation of detection (d-e) spectroscopic determination. Reproduced with permission from [85].

opportunities to screen and profile new recognition features and atomic efficiencies for catalysis for example. Such intrinsic properties are often emergent from the transition from bulk to nano- or sub-nano scales. Scale reduction bring new inherent reactivities that are intrinsic to physical and chemical processes used in the assembly process. Interatomic spaces that arise from geometric constructions at the smallest scales and the accompaniment of charge distributions can play a pivotal role in the capture of diffusible small molecules with capabilities to entrap them. The structures can exist at very complex interfaces complicating our understanding of structure functional relationships. In materials of low dimension, parameters such as material shape, size, morphology, composition and newly emergent properties that do not exist in the bulk phase become important facets to developing innovative technologies in gas sensing. Figure 12 depicts the free energy changes that accompany nucleation processing directing the self-assembly of morphologies and interchanges. Such morphological properties are a useful addition to gas sensing applications and manifest in different physical and chemical functionalities at the nano and quantum scales. We aim to provide some insight in the remarkable and special utility in their interaction with formaldehyde.

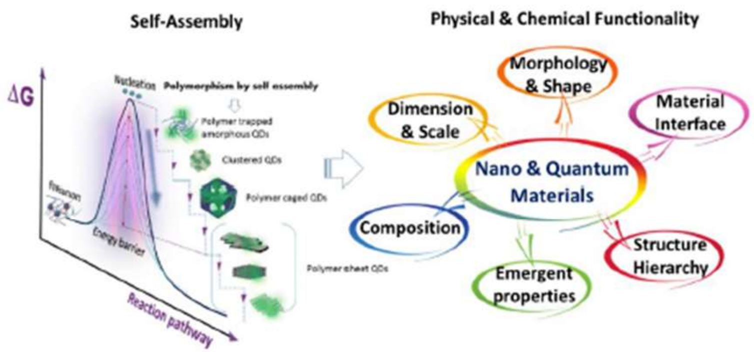

Figure 12. Pathways to evolving self-assembled structures and defining physical and chemical functionality of materials. Reproduced from Khare and Sonkaria [86].

One example demonstrates how nanoscale nano-gold particles divergent in shape and morphology behave intrinsically differently as sensors for HCHO the properties enabled by the setup shown in Figure 13. This was signified by the difference in the plasmonic properties for spherical particles and nanorods shaped morphologies. In this case, spherical particles were associated with an increase in sensing activity against formaldehyde from 25 to 35 nm indicating a strong size dependency for spherical shaped particles [87]. Shape induced changes in surface properties due to alteration in morphology revealed that nano-rods generated two absorption peaks at 578 and 650 nm mapped by transverse and longitudinal surface plasmon resonance (SPR). This response was distinctive to the spherical particles resulting in a decrease in the peak signals in the presence of decreasing concentrations of formaldehyde suggesting that new functionalities could be liberated from plasmonic properties by a change in surface morphology. This leaves the potential to further configure novel sensing strategies for portable sensing technologies.

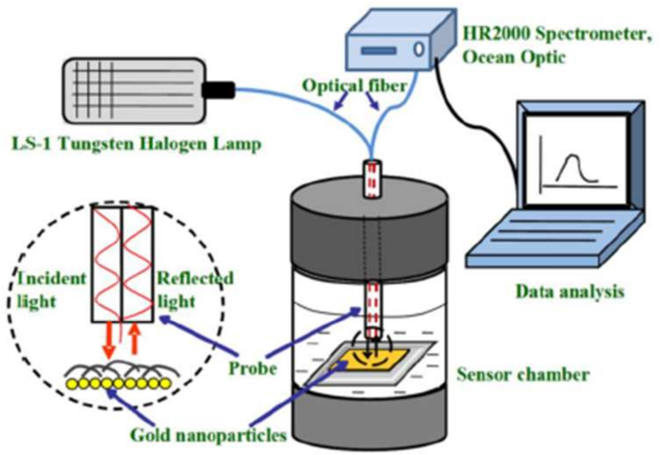

Figure 13. Setup used for formaldehyde using morphologically different gold nanoparticles. Reproduced from [87].

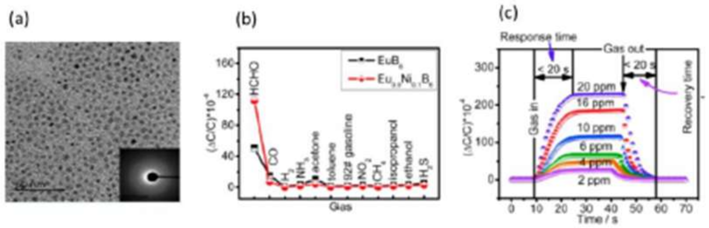

Figure 14. (a) HRTEM image of $Eu_{0.9}Ni_{0.1}B_6$ nanoparticles and the (b) gas selectivity of $Eu_{0.9}Ni_{0.1}B_6$ towards HCHO in comparison to EuB_6 particles (c) Detection of formaldehyde as a function of time versus the ratio between capacitance change and capacitance in the absence of the gas. Reproduced with permission from [90].

At the nanoscale, understanding the interactive chemistry of formaldehyde has become an integral part of developing new multi-complex molecular systems that exploit functionalities and dynamics of coordinate chemistry. More than a decade on, functionalised polymer films on pH paper have shown great utility in low sensitive detection of formaldehyde [91]. Despite the simplicity, remarkable sensitivity (20 – 250 ppm) and speed of detection with visible color change as a portable device, new chemistries have been explored. A particularly useful feature in advancing new strategies of greater sensitivity of vapor detection has been fluorophore excitation chemistry. For example, the synthetic labeling of pyrene molecules with a fluorophore (PPB) and its subsequent aqueous phase reaction with a sugar monosaccharide provided a platform for formaldehyde detection [92]. The equation in Figure 15 shows that the formation of an excimer proceeds from an excited pyrene monomer which combines with a ground state pyrene. Also, the fluorescence intensity profile in Figure 15 shows a lower energy (red-shift) peak-shift with increasing absorbance change at 490 nm which correlates well with an increase in HCHO accompanied by a decrease in pyrene emission. The dynamics is controlled by the re-arrangment of HCHO molecules on the PPB scaffold allowing pyrene molecules to be positioned closer to each other and thus altering the fluorescent properties of the complex.

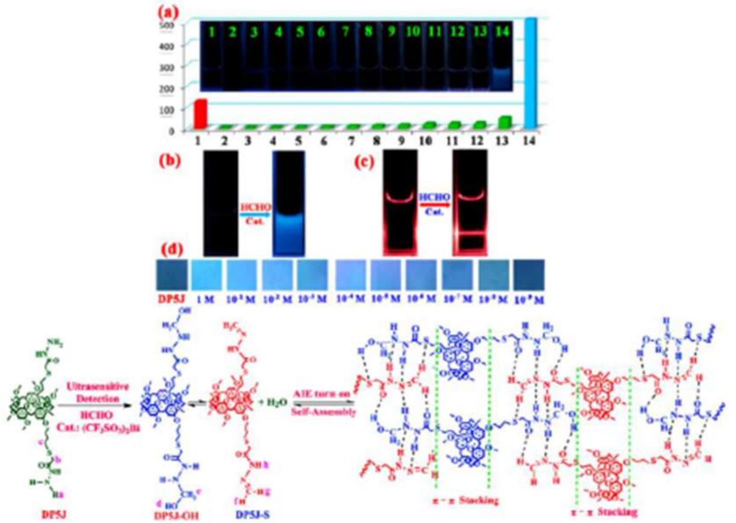

Figure 16. (a) Emitted fluorescence measured against a range of aldehydes (b) Fluorescence imaging in the presence of formaldehyde in DMF (c) Imaging of the Tyndall effect supported by stronger blue light emission under excitation (d) The effect of increasing formaldehyde concentration on fluorescence imaging. A structural representation of the molecular anchoring of HCHO molecules to the fluorescent scaffold. Reproduced with permission from [94].

Table 2. Sensing parameters based on the conductance resistance of NiO nanoparticles measured at 230°C. Reproduced from [96]

Concentration (ppb)	R_g(kΩ)	R_a(kΩ)	$S = R_g/R_a$	T_{re} (s)	T_{re}(s)
50	109.6	62.7	1.75	47.2	8.2
100	181.9	67.3	2.70	46.4	8.4
200	204.6	64.3	3.17	45.3	11.6
500	205.6	63.8	3.22	58.5	11.3
800	210.5	62.5	3.37	55.2	12.1
1000	211.9	61.8	3.43	53.7	13.3