Electronic Supplementary Information

Change of Chemiresistive Properties Regulated by Nanoscale Curvature in Molecularly-Linked Nanoparticle Composite Assembly

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Additional Descriptions of Theoretical Considerations and Experimental Data:

Estimation of the density of the nanocomposite: The density of multi-walled carbon nanotubes (MWCNTs, diameter ~26 nm) (NanoLab) is about 1.3 g/cm^3.[52] Consider a length of 10 nm CNT, the volume is 5309 nm^3, the mass is 6.90 $\times 10^{-18}$ g, and the total surface area of one CNT is 817 nm^2. Consider gold nanoparticles of 2 nm core size capped with a full monolayer of decanethiolate (DT, molecular weight is 174.4 g/moL, length ~ 1.5 nm, diameter ~ 0.309 nm), the approximate projection area for one DT-Au$_{nm}$ would be 25 nm^2. There would be ~132 DTs on one Au particle and ~33 (DT-Au$_{nm}$) on each CNT. Consider the density of gold (19.3 g/cm^3), the total mass of DT-Au$_{nm}$ + CNT, and the the total volume, the average density of (DT-Au$_{nm}$)/CNT would be ~1. 5 g/cm^3.

Table S1. Average interparticle distances derived from analyses of the TEM data (Fig. 3).

Assembly	dimeter (nm)	Interparticle Distance (*d*) center-to-center d_{cc} (nm)	edge-to-edge d_{ee} (nm)
DT-Au$_{nm}$	1.8 ±0.2	3.6 (± 0.4)	1.8 (± 0.3)
NDT-Au$_{nm}$	2.1 ±0.4	3.6 (± 0.9)	1.5 (± 0.5)
NDT-Au$_{nm}$ /CNTs	2.1 ±0.3	5.0 (± 1.0)	2.9 (± 0.7)

Theoretical consideration of the electrical properties: The ratio of resistances before and after the change in radius of curvature can be expressed by the following equation (equation 1),[44]

$$\frac{R_t}{R_i} = \exp[-\beta(d_1 - d_2)]\exp\left[\frac{0.5e^2}{4\pi\varepsilon\varepsilon_0 RT}\left(\frac{1}{r+d_1} - \frac{1}{r+d_2}\right)\right] \quad (1a)$$

or in terms of relative resistance change,

$$\frac{R_t - R_i}{R_i} = \frac{\Delta R}{R_i} = \exp[-\beta(d_1 - d_2)]\exp\left[\frac{0.5e^2}{4\pi\varepsilon\varepsilon_0 RT}\left(\frac{1}{r+d_1} - \frac{1}{r+d_2}\right)\right] - 1 \quad (1b)$$

where the resistance changes from R_i to R_t with interparticle distances change from d_1 to d_2. β is the electron coupling term, r is the particle core radius, ε is dielectric constant of interparticle medium, and other parameters include $e = 1.6 \times 10^{-19}$ C, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m, $R = 1.38 \times 10^{-23}$ J/K, and $T =$ 300 K. The R_t to R_i ratio contains two exponential components. The first component is mainly determined by the interparticle distance change and the β value ("β–d term"), whereas the second component is largely dependent on the particle size, interparticle distance change, and ε value ("ε–r term").

Considering $\Delta L/L=(d_2-d_1)/(2r+d_1)= T_s/2R_b)$, where L represents the length of the device whereas ΔL represents the change of the length upon strain. The corresponding interparticle edge-to-edge distances are d_1 and d_2. For nanoparticle radius r = 1 nm, interparticle edge-to-edge spacing d_1 = 1.6 nm and β= 4.0 nm^{-1},[44] the above two terms can be derived as a function of R_b based on a PET substrate of thickness T_s = 125 μm[44] and a CNT wall thickness T_s = 2 nm (CNT: O.D. × wall thickness × L: (20-30 nm) × (1-2 nm) × (0.5-2 μm)). Consider now the case of tensile strain, the radius of curvature for CNT would be 13 nm. Substituting these values into logarithm of equation-1, the two components can be expressed as a function of R_b (μm in the equations):

$$"\beta - d"term: -\beta(d_1 - d_2) = \frac{900}{R_b}(for\ Ts = 125\ \mu m),\quad or\quad \frac{0.0144}{R_b}(for\ Ts = 2\ nm) \tag{2a}$$

$$"\varepsilon - r"term: \frac{0.5e^2}{4\pi\varepsilon\varepsilon_0 RT}\left(\frac{1}{r+d_1}-\frac{1}{r+d_2}\right) = \frac{27.8\ nm}{\varepsilon}\times\left(\frac{1}{2.6}-\frac{1}{2.6+\frac{225}{R_b}}\right) \tag{2b}$$

Calculation of interparticle interaction potentials based on a dimer model: For a symmetric dimer, the steric repulsive and van der Waals attractive interaction energies as a function of interparticle edge-to-edge distance (d_{ee}) are given below:[53,54]

$$E_{steric,sym} \approx \frac{100R_1\delta_{bruth}^3}{d_{ee}\pi\sigma_{thiol}^3}kT\exp\left(\frac{-\pi d_{ee}}{\delta_{bruth}}\right) \tag{3}$$

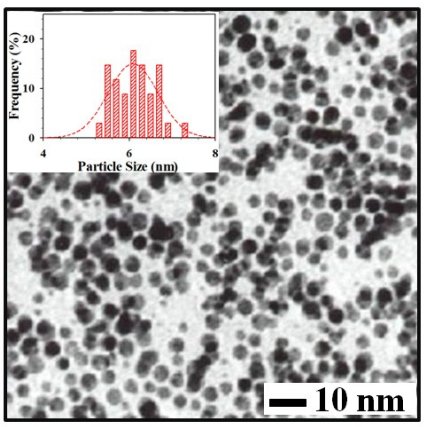
$$E_{vdW,sym} = -\frac{A}{12}\left[\frac{4R_1^2}{(d_{ee}+2R_1)^2-4R_1^2}+\frac{4R_1^2}{(d_{ee}+2R_1)^2}+2\ln\left(\frac{(d_{ee}+2R_1)^2-4R_1^2}{(d_{ee}+2R_1)^2}\right)\right] \tag{4}$$

where R_1 is particle radius; δ and σ stand for the length and the diameter of a capping molecule on the nanoparticle surface. A is Hamaker constant.

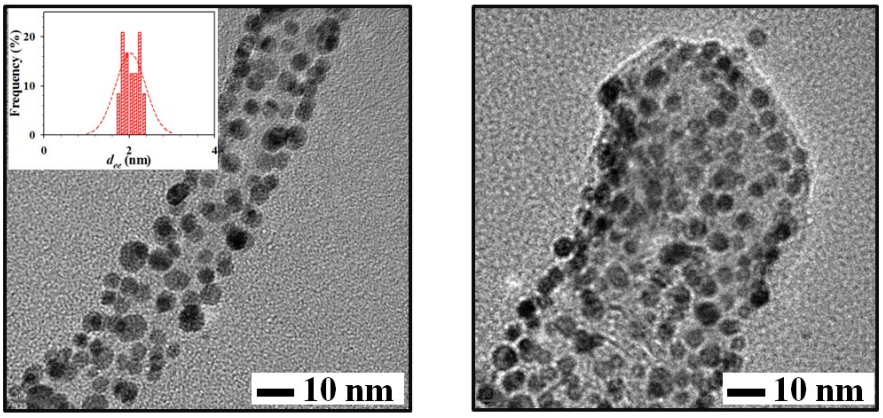
For an asymmetric dimer, the van der Waals attractive interaction energy as a function of interparticle edge-to-edge distance (d_{ee}) is given below:[53,54]

$$E_{vdW,asym} = -\frac{A}{6}\left[\frac{2R_1R_2}{(d_{ee}+R_1+R_2)^2-(R_1+R_2)^2}+\frac{2R_1R_2}{(d_{ee}+R_1+R_2)^2-(R_1-R_2)^2}+\ln\left(\frac{(d_{ee}+R_1+R_2)^2-(R_1+R_2)^2}{(d_{ee}+R_1+R_2)^2-(R_1-R_2)^2}\right)\right] \tag{5}$$

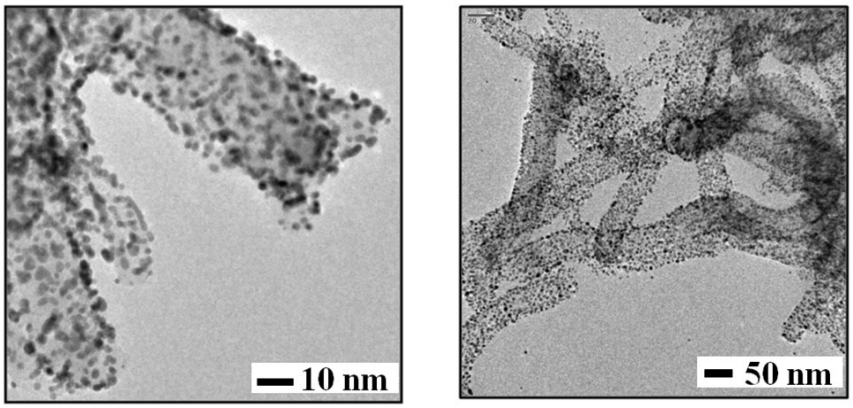
where R_1 and R_2 are particle radii; A is Hamaker constant.



(a)



(b)



(c)

Fig. S1. TEM micrographs: (a) NDT-linked Au NPs (6.1 ± 0.6 nm) assembly on C film. (b-c) TEM micrographs for NDT-Au_{nm} (6.0 ± 0.9 nm) on CNTs (d_{ee}), and the average interparticle edge-to-edge distance (d_{ee}) measured from image (b, left) ~ 2.0 ±0.5 nm.

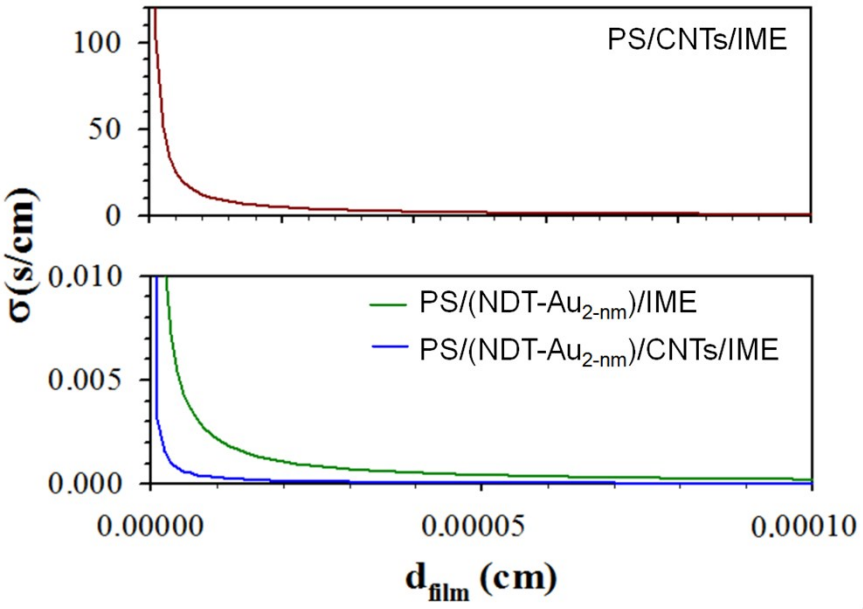


Fig. S2. Plots of the estimated electrical conductivity of the thin films on the IME device (σ = *(1/R)(w/dl)*)(*R*: resistance (Ω), *d*: film thickness (cm), *l*: microelectrode length (50 μm), and *w*: gap of the microelectrodes (5 μm)). Experimental resistances for thin films: 9.8 (±1.1) ×10^2 Ω (PS/CNTs/IME), 4.6 (±0.1) ×10^6 Ω (PS/(NDT-

Au_{nm})/IME), and 3.2 (±0.1) $\times 10^7$ Ω (PS/(NDT-Au_{nm})/CNTs/IME).

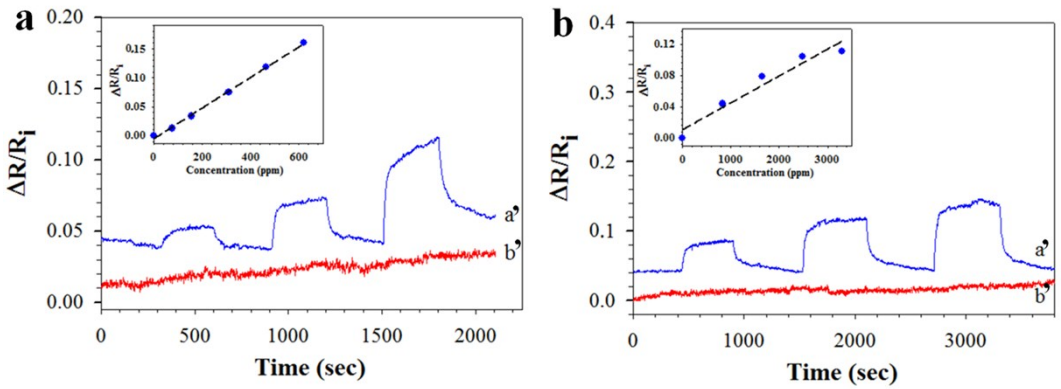


Fig. S3. (a) Response profiles of toluene (a) and hexane (b) vapors of increasing concentrations at: (NDT-Au_{nm})/CNTs/IME (a') and at CNTs/IME (b'). Insert: a plot of the response *vs*. toluene concentration (ppm (M)) with linear regression slope: 2.6×10^{-4} (a) and 3.4×10^{-5} (b). (Estimated average 3x noise level: 0.0048).

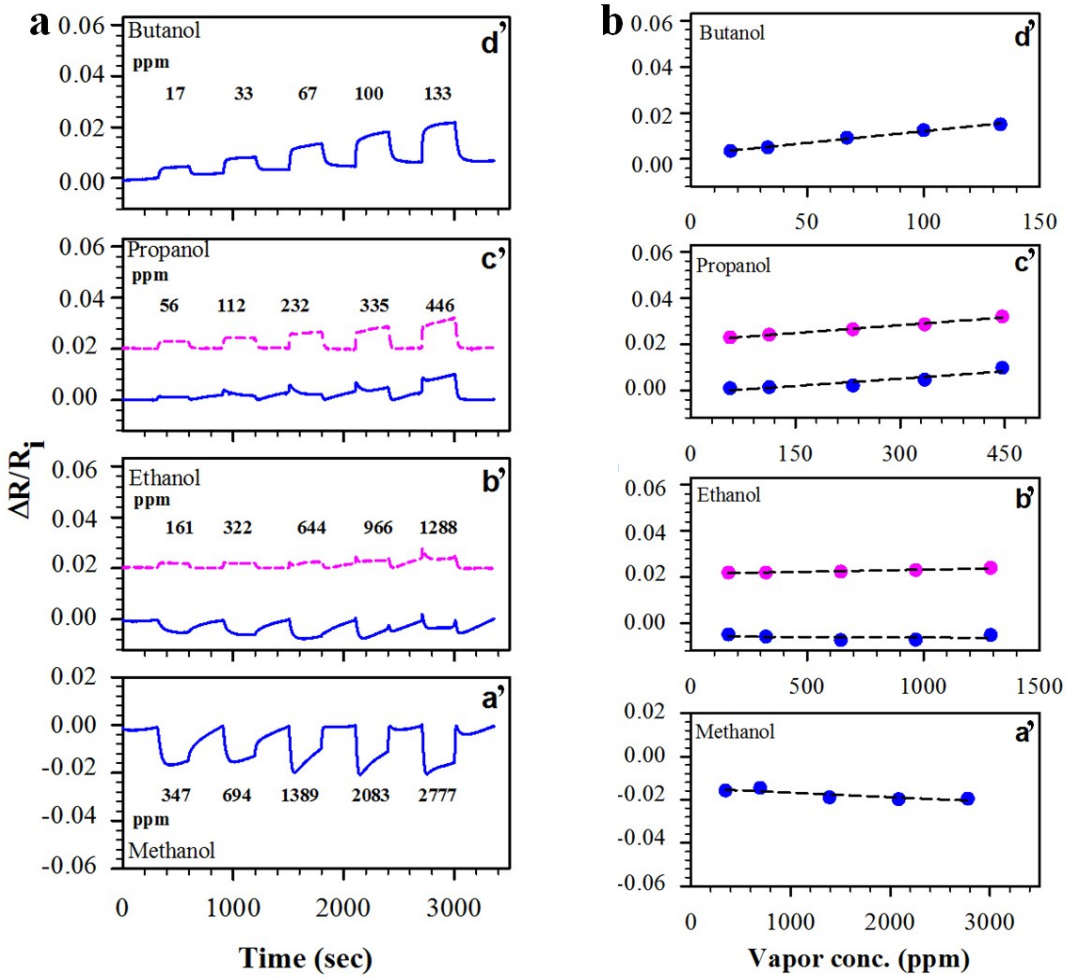


Fig. S4. (a) Response profiles of (NDT-Au_{nm})/IME in response to different R-OH vapors (MeOH (a', vapor concentrations: 347, 694, 1389, 2083, 2777 (in ppm (M)), EtOH (b', vapor concentrations: 161, 322, 644, 966, 1288 (in ppm (M)), PrOH (c', vapor concentrations: 56, 112, 232, 335, 446 (in ppm (M)) and BuOH (d', vapor concentrations: 17, 33, 67, 100, 133 (in ppm (M))). (b) Plots of the response *vs*. concentration of different R-OH

vapors (ppm in moles per liter) at (NDT-Au_{nm})/CNTs/IME (linear regression slopes: -2.1×10^{-6} (a'); -4.6×10^{-7} and 1.8×10^{-6} (b'); 2.1×10^{-5} and 2.3×10^{-5} (c'), and 1.0×10^{-4} (d')). (Estimated average 3x noise level: 0.0006).

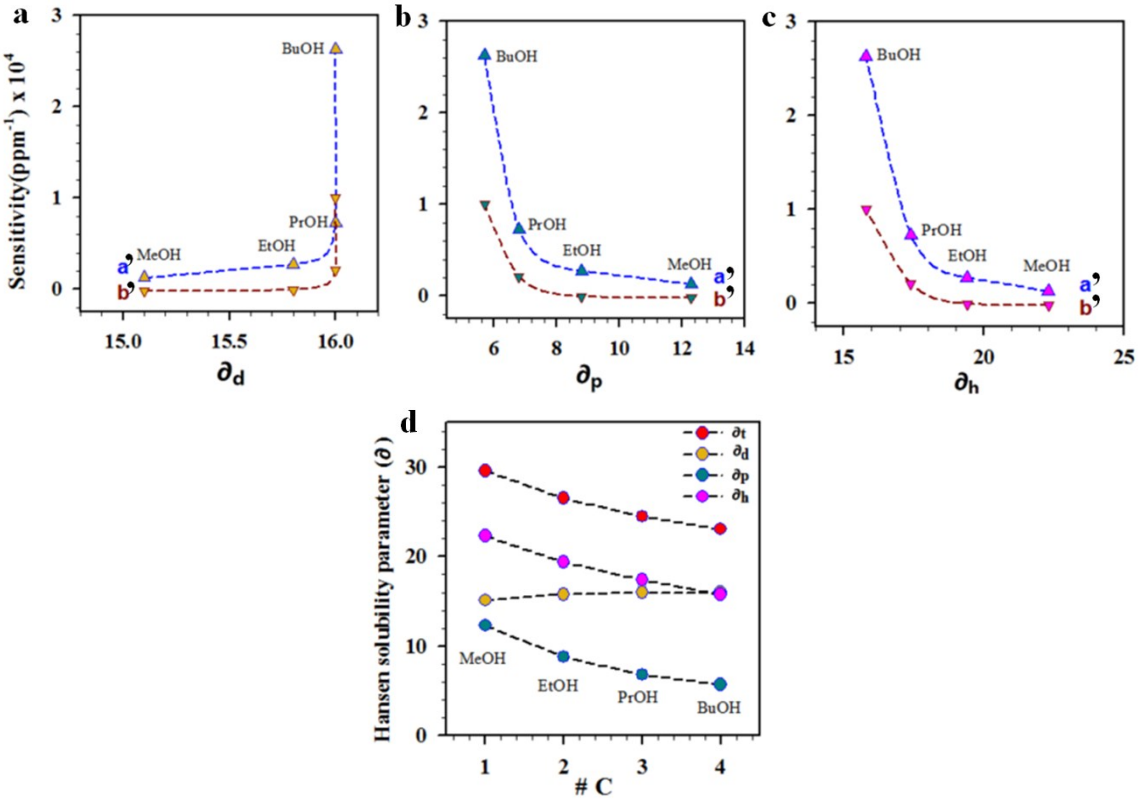


Fig. S5. (a-c) Plots of response sensitivities for a series of alcohol (R-OH) with (NDT-Au_{nm})/CNTs/IME (a', blue) and (NDT-Au_{nm})/IME (b', red) *vs*. the individual components in the solubility parameter ($\partial_t = \sqrt{\partial_d^{\,2} + \partial_p^{\,2} + \partial_h^{\,2}}$) for the VOCs. (d) Solubility parameters vs. #C in the alcohol molecules.

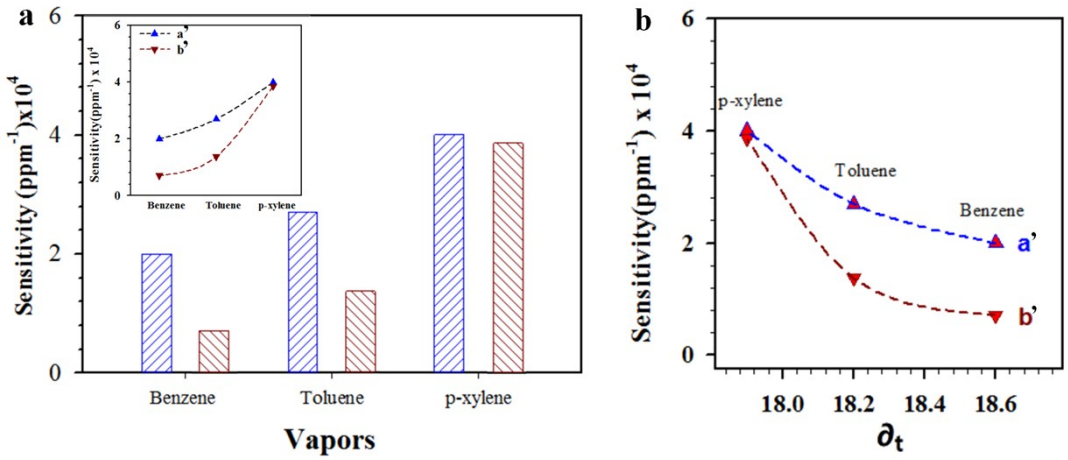


Fig. S6. (a) Comparison of response sensitivities for benzene, toluene, and p-xylene with (NDT-Au_{nm})/CNTs/IME (blue bars) and (NDT-Au_{nm})/IME (red bars). Insert: plots of the response sensitivity for the different vapor molecules ((a') (NDT-Au_{nm})/CNTs/IME); and (b') (NDT-Au_{nm})/IME). (b) Plots of the response sensitivity *vs*. total solubility parameter ((a') (NDT-Au_{nm})/CNTs/IME); and (b') (NDT-Au_{nm})/IME).

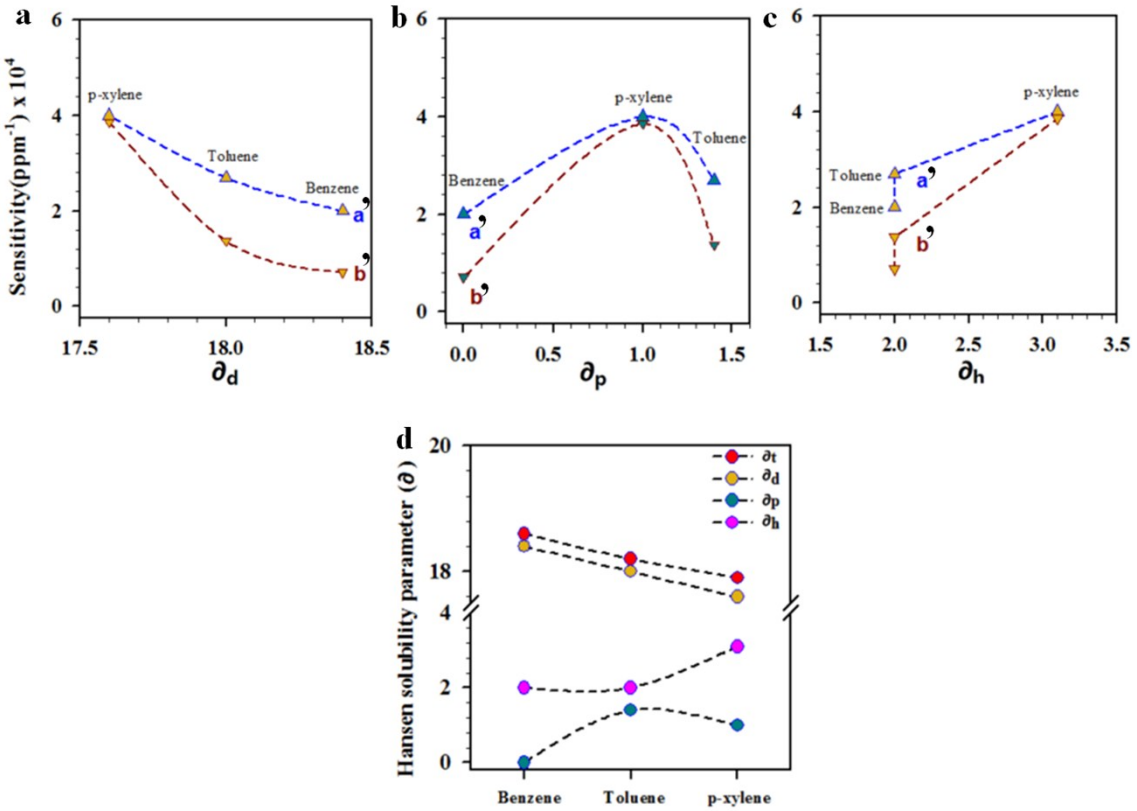


Fig. S7. (a-c) Plots of the response sensitivities for benzene, toluene and p-xylene vapors with (NDT-Au_{nm})/CNTs/IME (a', blue) and (NDT-Au_{nm})/IME (b', red) *vs*. the individual components in the solubility parameter ($\partial_t = \sqrt{\partial_d^{\,2} + \partial_p^{\,2} + \partial_h^{\,2}}$) for the VOCs. (d) Solubility parameters for the three different VOC molecules.