Supplementary Material (ESI) for Analyst

Electronic Supplementary Information for *Analyst*

"TURN-ON" FLUORESCENT POLYMERIC MICROPARTICLE SENSORS FOR THE DETERMINATION OF AMMONIA AND AMINES IN THE VAPOR STATE

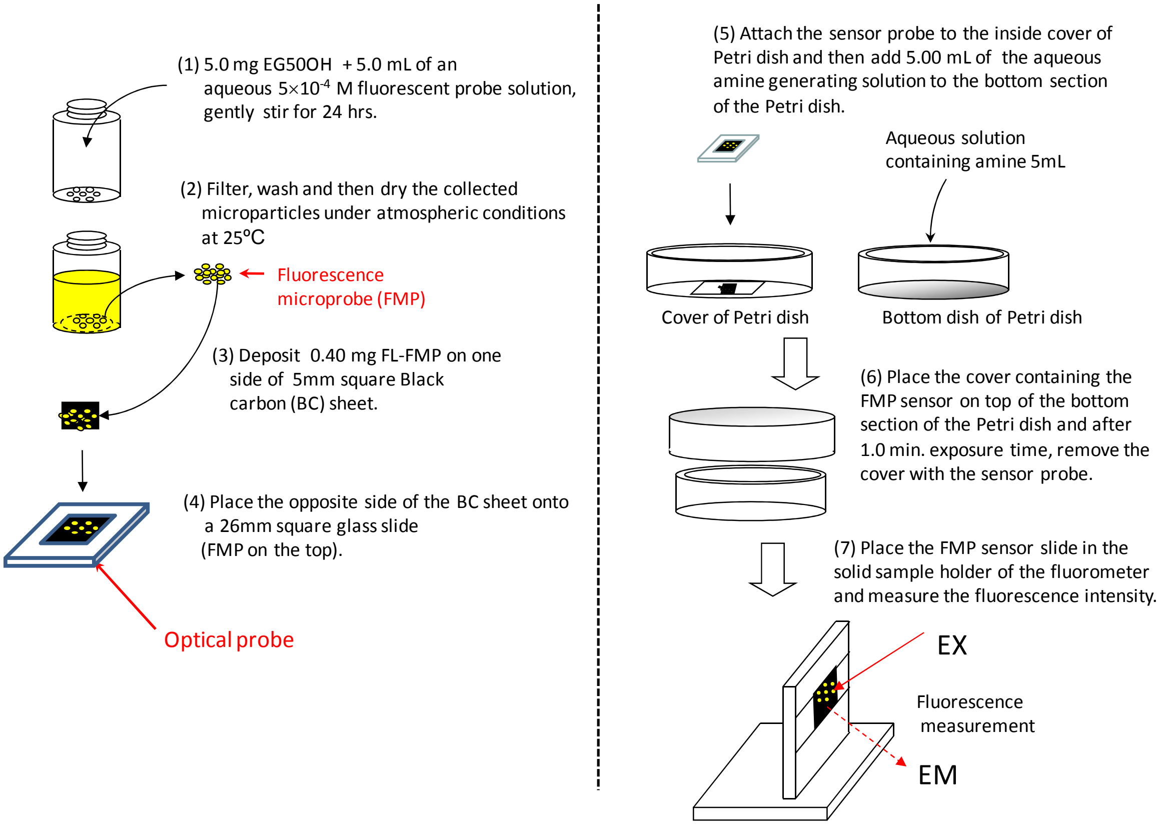
Yoshitaka Takagai,[*a,b] *Yuki Nojiri,*[a] *Tsugiko Takase,*[a] *Willie L. Hinze,*[b] *Michio Butsugan* [c]
and Shukuro Igarashi [d]

[a]*Cluster of Science and Technology, Faculty of Symbiotic Systems Science, Fukushima University, Kanayagawa 1, Fukushima 960-1296 JAPAN*

[b]*Department of Chemistry, Wake Forest University, P. O. Box 7486, Winston-Salem, North Carolina 27109 U.S.A*

[c] *Hitachi Chemical Techno Service Co. Ltd., 4-13-1 Higashi-cho, Hitachi, Ibaraki 317-8555 JAPAN*

[d]*Department of Biomolecular Functional Engineering, Faculty of Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511 JAPAN*



<u>Fig. S1.</u> Schematic representation of the steps involved in the preparation of the fluorescent microparticles (steps 1 and 2), sensor fabrication (steps 3 and 4), and amine vapor measurement sequence protocol (steps 5 through 7). Fluorescein was the fluorescent sensor probe molecule used in this illustration.

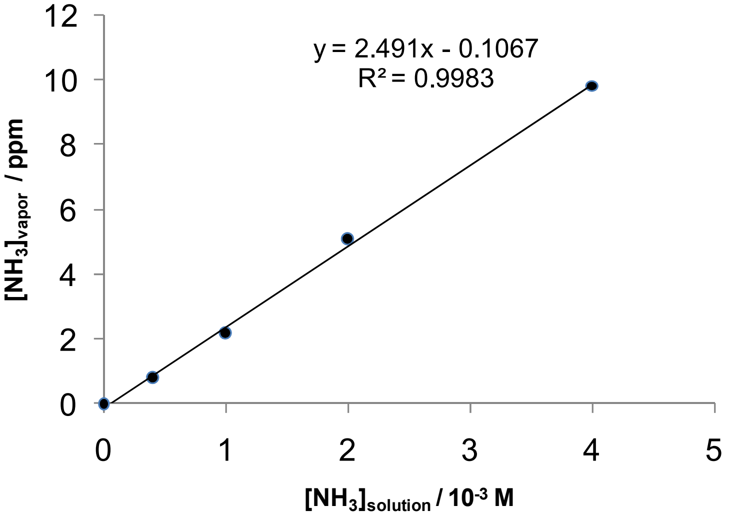


Fig. S2. Calibration plot showing the relationship between the ammonia concentration in the vapor phase generated from an aqueous ammonia containing solution after 1.0 min. under atmospheric conditions.

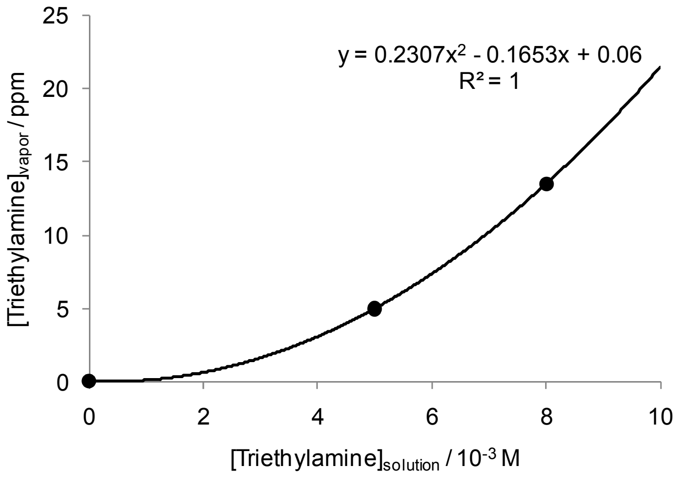


Fig. S3. Plot showing the correspondence between the triethylamine concentration in the vapor phase generated from an aqueous triethylamine-containing solution after 1.0 min. under atmospheric conditions.

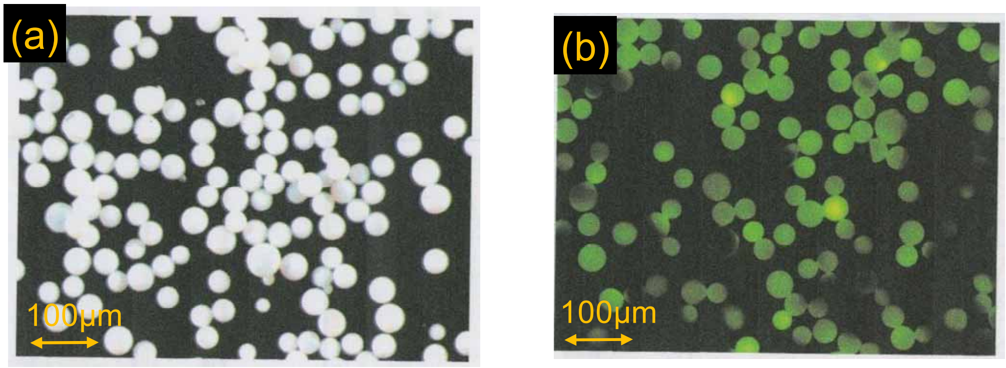


Fig. S4 Microscopic images of the FL – FMP particles: (a) stereomicroscopic and (b) fluorescence microscopic images (×100 magnification in both instances). The fluorescence was observed through GFP filter (λ_{ex} = 470 nm; λ_{em} = 520) with a mercury lamp serving as the light source.

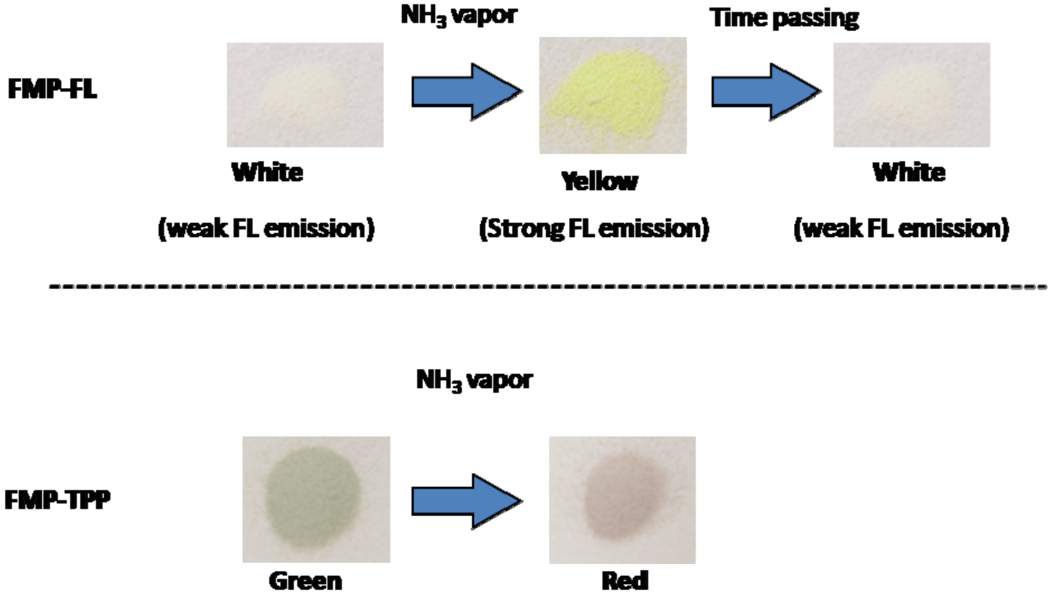


Fig. S5. Color changes observed for fluorescent microparticles upon their exposure to ammonia vapor: (top panel) the color of the FL – FMP sensor changes from white to yellow (and then back to white within ca. 20 min after being removed from the NH$_3$ vapors) and (bottom panel) shows the green to red color change observed upon exposure of the *meso*-tetraphenylphorphine impregnated microparticle sensor (TPP – FMP) to ammonia. The response of these sensors could be conveniently observed with the naked eye as a detection device although visual quantification is problematic. (Ammonia vapor was generated from 5 mL of an aqueous 10^{-3} molar solution; result (pictures) obtained after 1 min exposure to the microparticle.)

Thermal Analysis of EG50OH Microparticles. The moisture content (i.e. weight) of the microparticles was determined by thermal analysis. Namely, TG-DTA runs were conducted using aluminum oxide as the reference material. A FL – FMP which had been “naturally” dried by just sitting at room temperature (25 ˚C) for 3-days (under atmospheric conditions) was prepared. The TG-DTA temperature ramp increased from 0 up to 400 ˚C and the sample consisted of 5.5 mg of FL – FMP. Analysis of the TG-DTA data (refer to Figure S6 below) indicated the presence of 6.1% (w/w) water (61 mg water per gram of the fluorescent microparticle).

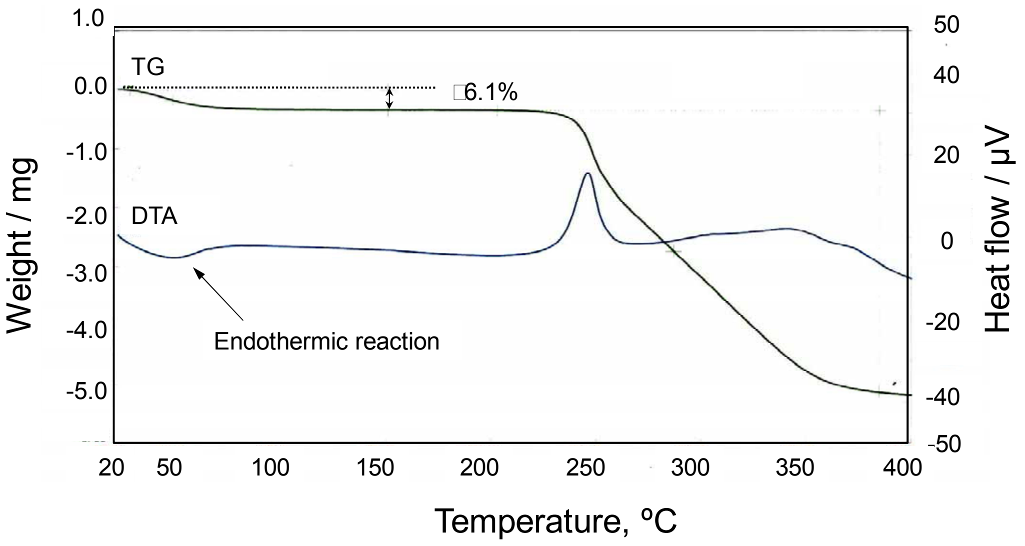


Fig. S6. TG-DTA data for FMP. The TG curve indicates the presence of 6.1% moisture included within the FMP matrix (i.e., 6.1 mg H_2O/g microparticles). The endothermic reaction which is indicative for water begins at approximately 60 to 80 ^{o}C; the large surface area of the microparticle presumably facilitates the evaporation of the water present. At ca. 250 ^{o}C, the microparticles melt and decompose with continued heating.

Table S1. Summary of Spectral Parameters and Acidity Constants for the Sensor Fluorescent Probe Molecules*

	Fluorescein	Rhodamine B	Acridine orange	Eosin Yellow	TPP
λ_{ex} / nm	450	500	450	490	420
ε / M^{-1} cm^{-1}	7.69×10^4 [a]	1.1×10^5 [b]	3.7×10^4 [c]	9.42×10^4 [d]	4.78×10^5 [e]
λ_{em} / nm	528	570	530	540	650
Φ^{**}	0.93 [46,47]	0.5 [f]	0.11 [g]	0.2 [h]	0.10 [i],
pKa	2.22,4.34, 6.68[54]	3.2 [b]	9.8 [j]	3.25, 3.80 [k] 2.85, 4.37[m]	4.38, 3.85 [l]

*Except for the excitation and emission wavelengths, the values for the other parameters reported were taken from the literature.

** The given quantum yields are for the deprotonated form(s).

[a] At 440 nm; value taken from literature.[45]

[b] At 556 nm; K. Ueno, T. Imamura, K. L. Cheng, *Handbook of Organic Analytical Reagents*, 2nd Ed., CRC Press, 1992, pp.525-526.

[c] At 459 nm; D. A. Makarov, N. A. Kuznetsova, O. L. Kaliya, *Russian J. Phys. Chem. A*, 2006, **80**, 268-274.

[d] At 525 nm; W. J. Jones, A. Grofcsik, M. Kubinyi, D. Thomas, *J. Mol. Struct.*, 2006, **792–793**, 121–129.

[e] At 419 nm; A. Stone, E. B. Fleischer, *J. Am. Chem. Soc.*, 1968, **90**, 2735-2748.

[f] In methanol as solvent; T. Karstens, K. Kobs, *J. Phys. Chem.*, 1980, **84**, 1871-1872.

[g] In distilled water as solvent (pH = 6.9); A. K. Shaw, S. K. Pal, *J. Phys. Chem. B,* 2007, **111***,* 4189-4199.

[h] In distilled water as solvent; R. Livingston, *J. Phys. Chem.*, 1940, **44**, 865–873.

[i] G. D. Luca, A. Romeo, L. M. Scolaro, G. Ricciardi, A. Rosa, *Inorg. Chem.*, 2007, **46**, 5979-5988.

[j] G. Uber, G. Achtert, *Biopolymers*, 1969, **8**, 595.

[k] P. Levillain, D. Fompeydie, *Anal. Chem.*, 1985, **57**, 2561-2563.

[l] S. Aronoff, *J. Phys. Chem.*, 1958, **62**, 428-431.

[m] F. Amat-Guerri, M. M. C. Lopez-Gonzalez, R. Sastre, R. Martinez-Utrilla, *Dyes Pigments*, 1990, **13**, 219-232.

Nature of the Fluorescein Emitting Species.

As shown in Figure 3, the wavelength of the emission observed from the FL – FMP sensor exhibits a slight shift towards longer wavelength with increases in the ammonia vapor concentration. This presumably reflects the progressive conversion of the monoanionic form of fluorescein to its dianionic form with increasing ammonia (or amine) concentration. In water as solvent, more recent literature reports indicate that both the monoanion (-1) and dianion (-2) forms of fluorescein exhibit their fluorescence emission maximum around 515 nm with that of the dianion being more intense; but that of the monoanion occurring at slightly smaller wavelength and having a shoulder at ca. 540 nm.[n,o] Literature reports also indicate that these emission wavelengths exhibit a bathochromic shift as the polarity (water content) of the medium is decreased.[p,q] For instance, the emission wavelength for the fluorescein dianion was found to shift to 543 – 549 nm if the solvent was switched from water to anhydrous dimethylsulfoxide.[q,r] Likewise, the emission maximum for the monoanion shifted to slightly longer wavelengths with both the maximum and its shoulder broadening.[q] Thus, the emission band monitored at 528 nm is thought to be due to the fluorescein dianion in the more hydrophobic microenvironment of the EG50OH microparticle sensor material.

[n] J. M. Alvarez-Pez, L. Ballesteros, E. Talavera, J. Yguerabide, *J. Phys. Chem. A*, 2001, **105**, 6320-6332.

[o] N. Klonis, A. H. A. Clayton, E. W. Voss, W. H. Sawyer, *Photochem. Photobiol.*, 1998, **67**, 500-510.

[p] M. F. Choi, P. Hawkins, *Spectros. Lett.*, 1994, **27**, 1049-1063.

[q] N. Klonis, W. H. Sawyer, *Photochem. Photobiol.*, 200, **72**, 179-185.

[r] N. O. Mchedlov-Petrossyan, N. A. Vodolazkaya, N. V. Salamanova, A. D. Roshal, D. Y. Filatov, *Chem. Lett.*, 2010, **39**, 30-31.