Electronic Supplementary Information (ESI) for

Enhanced Fluorescence of Functionalized Silica Microsphere based on Whispering Gallery Mode for Nitrate Ester Explosives and Hexogen Vapour Detection

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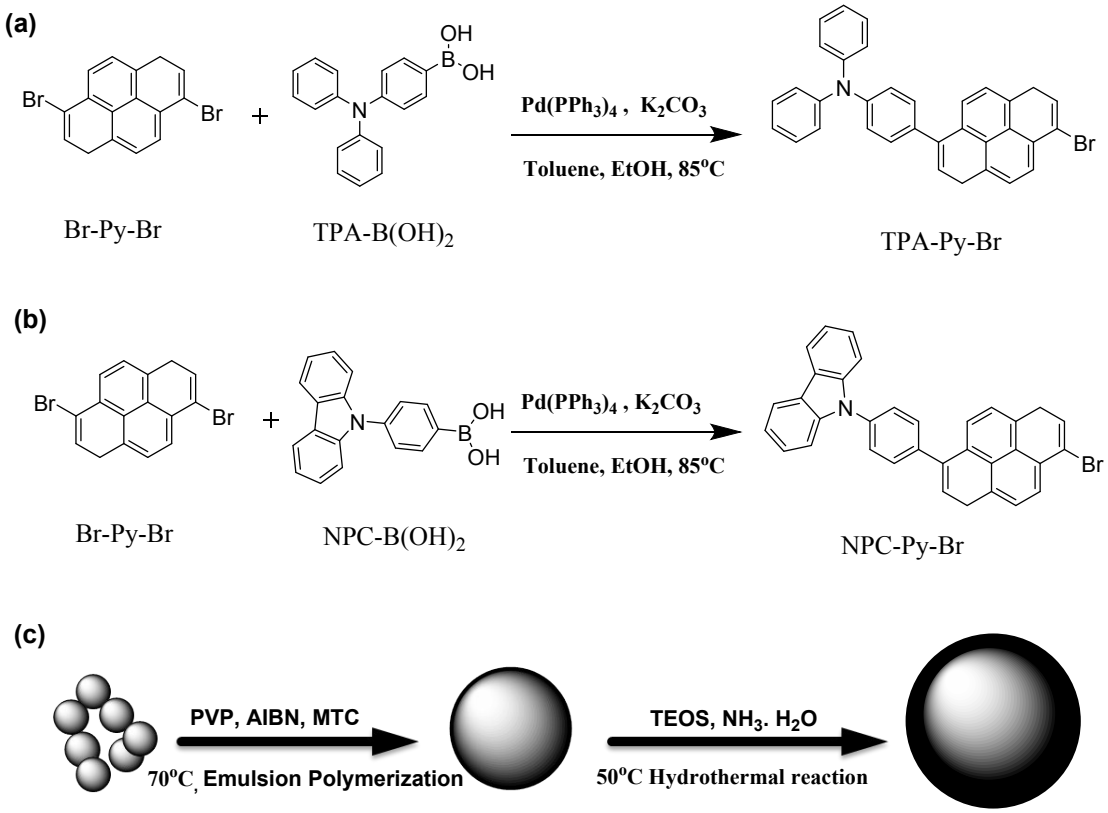
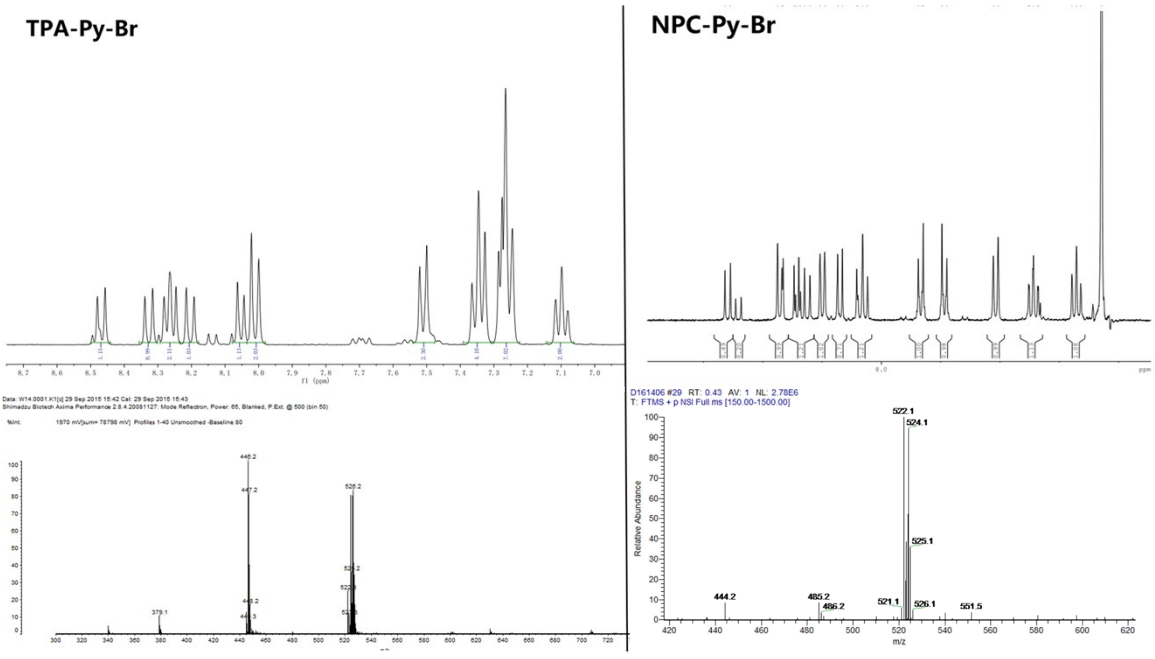
Catalogue

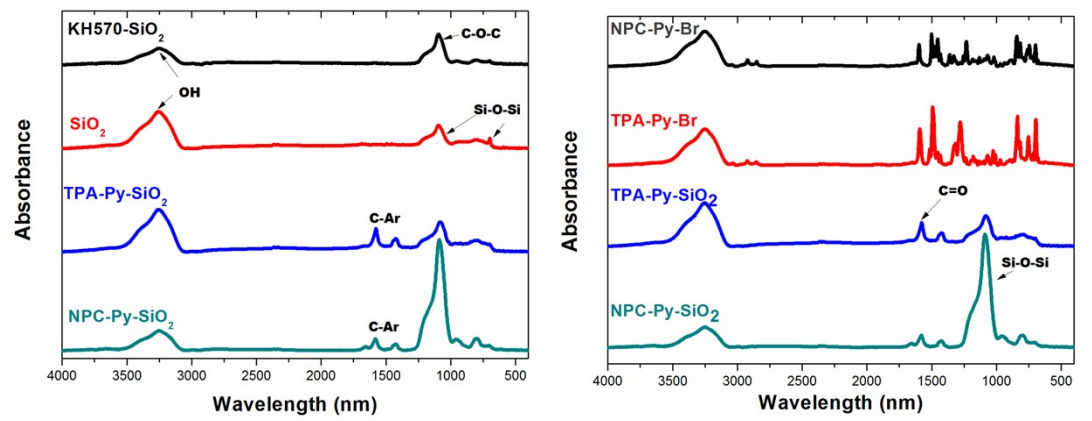
1. Synthesis of fluorophore sensing units and hollow-shell silica microsphere



2. NMR and mass spectrum of two fluorophores TPA-Py-Br and NPC-Py-Br

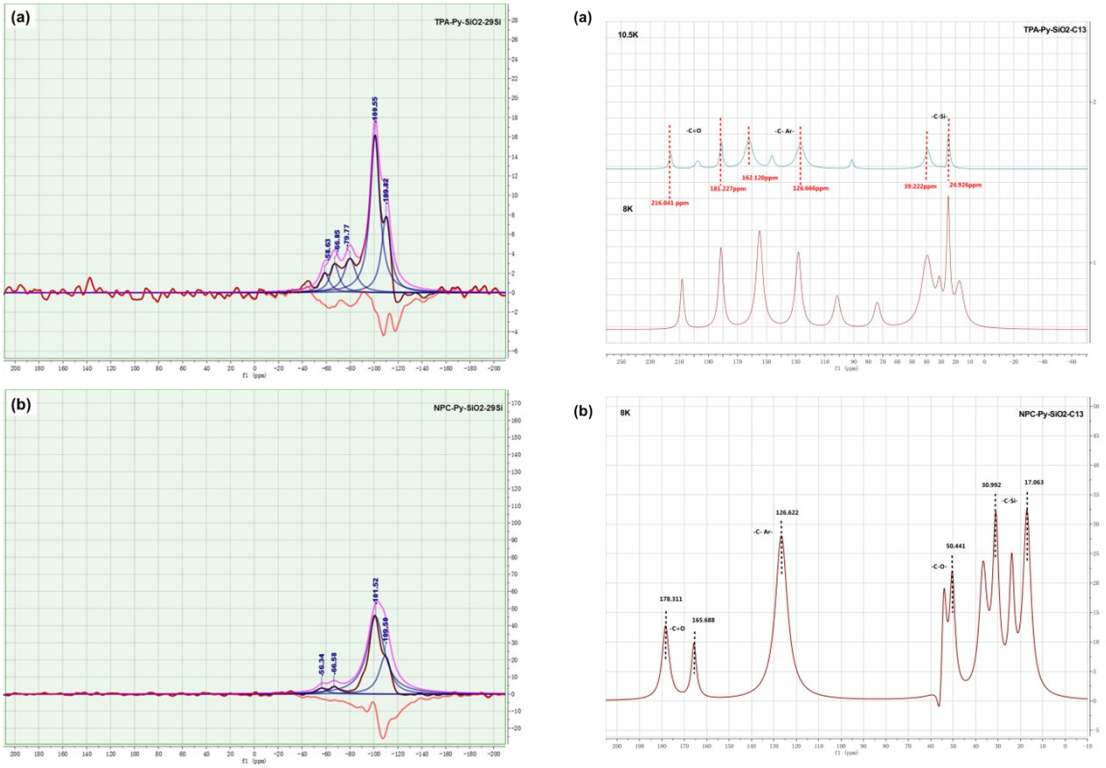


3. Fourier transforms infrared spectra of the hybrid silica microsphere



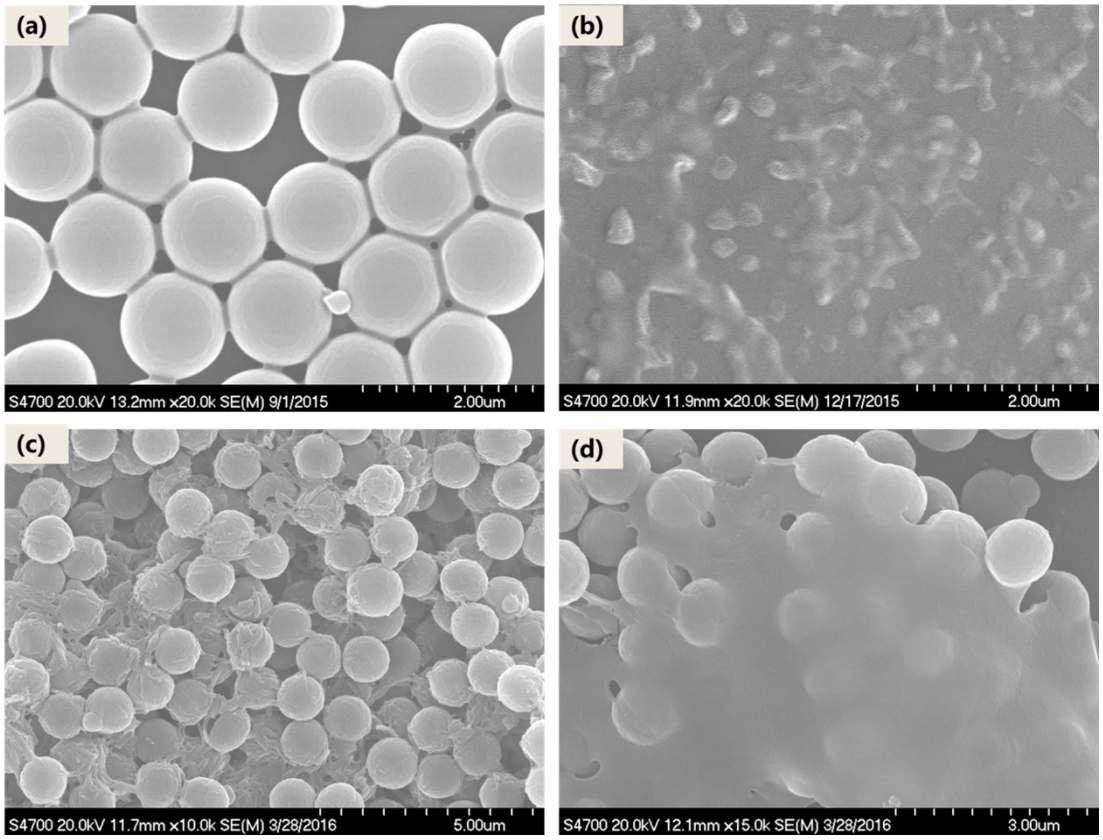
FT-IR was performed to prove the surface functional groups binding of the two hybrid microspheres, with the unmodified silica microsphere and KH-570-SiO_2 as contrast group. Compared with the spectrum of SiO_2, that of KH-570-SiO_2 displays small absorbance peaks at 1657 cm^{-1} and 950 cm^{-1}, attributing to stretching and bending vibrations of -C═O group of KH-570.[1, 2] This indicates the silica microsphere is modified with reactive vinyl groups at the first step. Secondly, the two fluorescent silica microspheres show similar absorption peak position and appearance of the major bands. It is observed that the peaks of aromatic ring vibrations at 1450 cm^{-1} and 1650 cm^{-1} confirm the existence of corresponding fluorophores (TPA-Py and NPC-Py) in the hybrid materials. The band at 3256 cm^{-1} is assigned to O-H stretching vibration on the surface of SiO_2. The peak at 1080 cm^{-1} is overlapped by the Si-O-Si and C-O-C stretching vibrations.[2, 3] All these results prove that TPA-Py and NPC-Py were grafted onto the surface of silica microsphere via covalent binding.

4. Solid-state ^{29}Si and ^{13}C cross-polarization magic-angle spinning NMR spectrum of (a) TPA-Py-SiO_2 and (b) NPC-Py-SiO_2 (using line fitting method with default parameters)

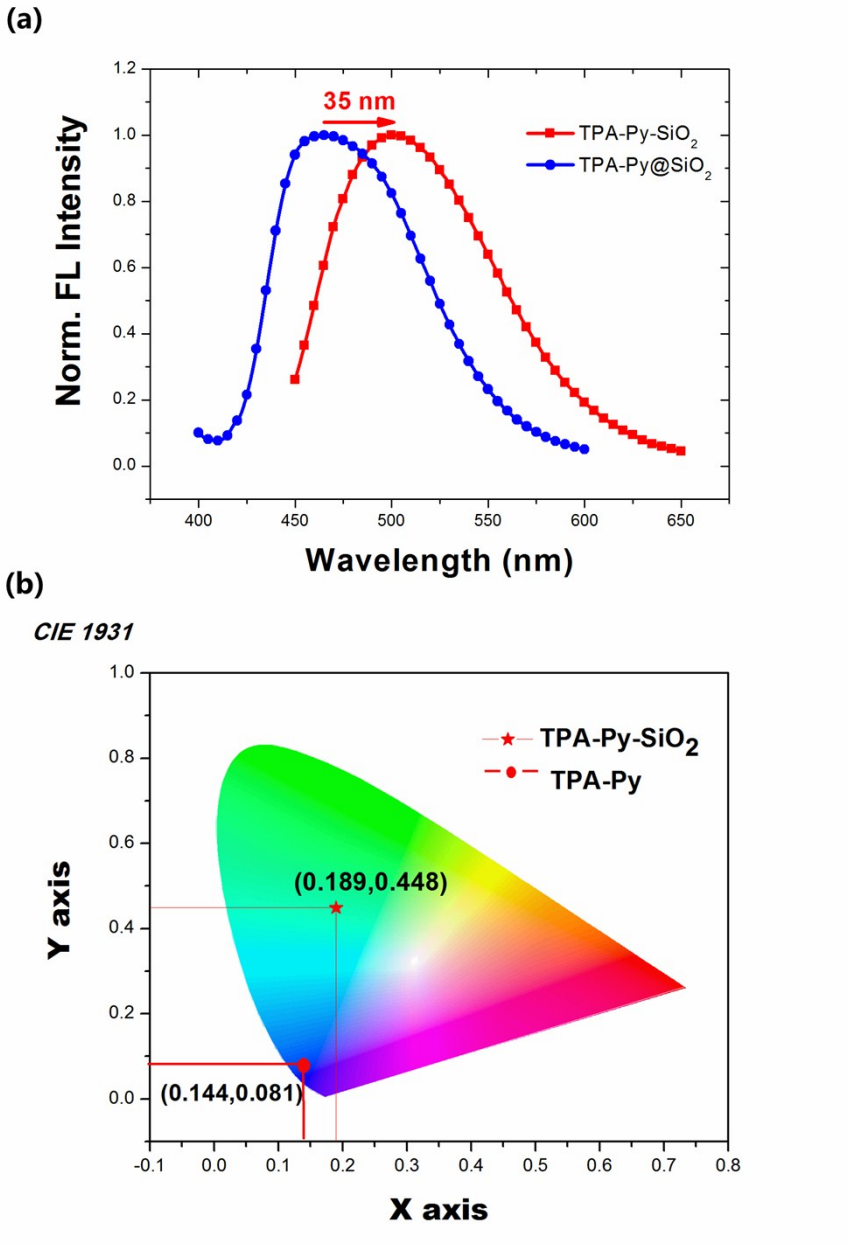


A further direct demonstration for the incorporation of TPA-Py and NPC-Py onto the surface of silica microsphere is given by the solid-state CP/MAS ^{13}C NMR and ^{29}Si NMR spectroscopy. As shown in Figure, signal peaks ranging from ca.162 to 126 ppm indicate the presence of structural units TPA-Py and NPC-Py. Both ^{13}C NMR spectra show the peaks at 181.127 and 178.311 ppm are assigned to the C═O group[4, 5]. Besides, the formation of -C-Si bond is confirmed by the signal peaks at 39.22 and 24.92 ppm (right figure) and ^{29}Si resonance peaks at δ -58.63, -68.65 and -79.77 ppm (Left figure). [5] Similarly, two broad and overlapping peaks at δ -56.34 and -66.58 ppm are assigned to the R-Si(HO)$(OSi)_2$ (T^2) and R-Si$(OSi)_3$ (T^3) organosiloxane species, respectively.[3, 4] These results are consistent with those obtained by means of FT-IR spectrum and certainly confirm the dye-functionalization of silica microspheres TPA-Py-SiO_2 and NPC-Py-SiO_2 is successful.

5. Sensing films of silica microspheres and their corresponding fluorophores by different preparation methods: (a) unmodified intact silica microsphere; (b) small fluorophores (TPA-Py); (c) dye-functionalized microsphere (TPA-Py-SiO_2); (d) vinyl-modified microsphere with fluorophores

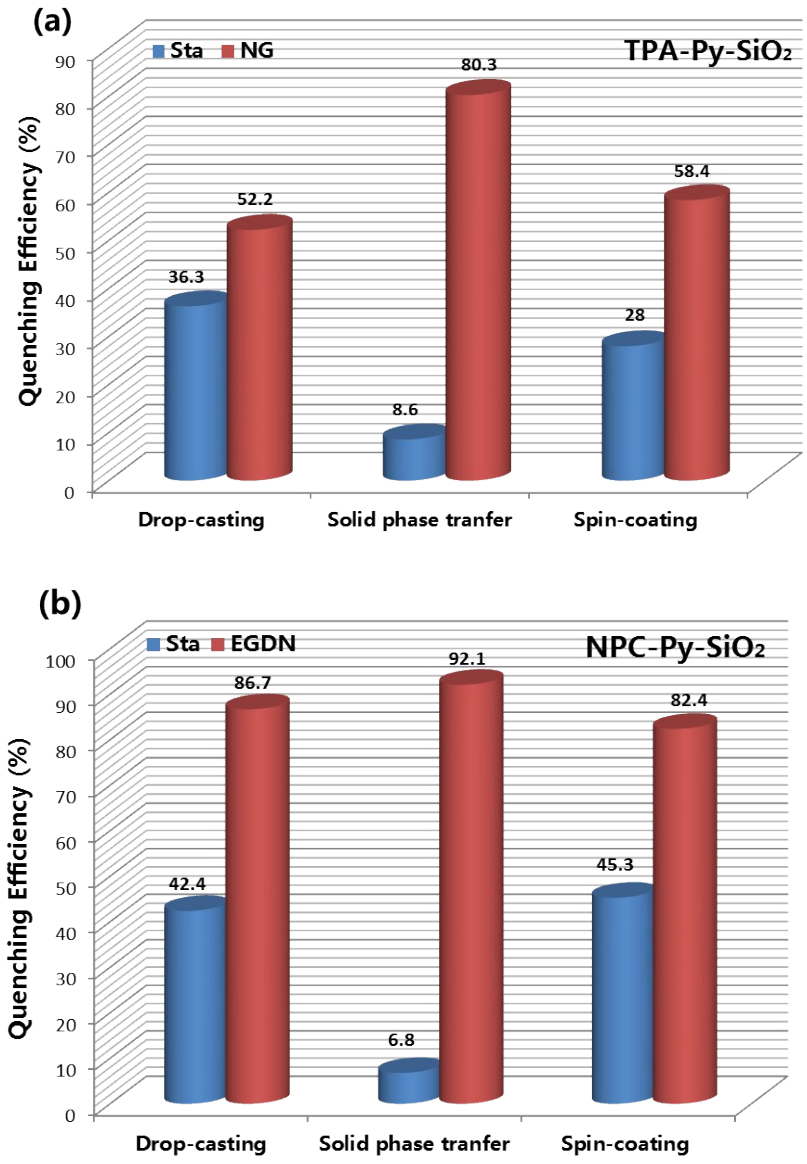


6. Comparison between dye-functionalized microsphere and vinyl-modified microsphere spin coated with fluorophore: (a: Normalized fluorescence spectrum (red: λex=379nm; blue: λex=374nm); b: Chromaticity diagram)



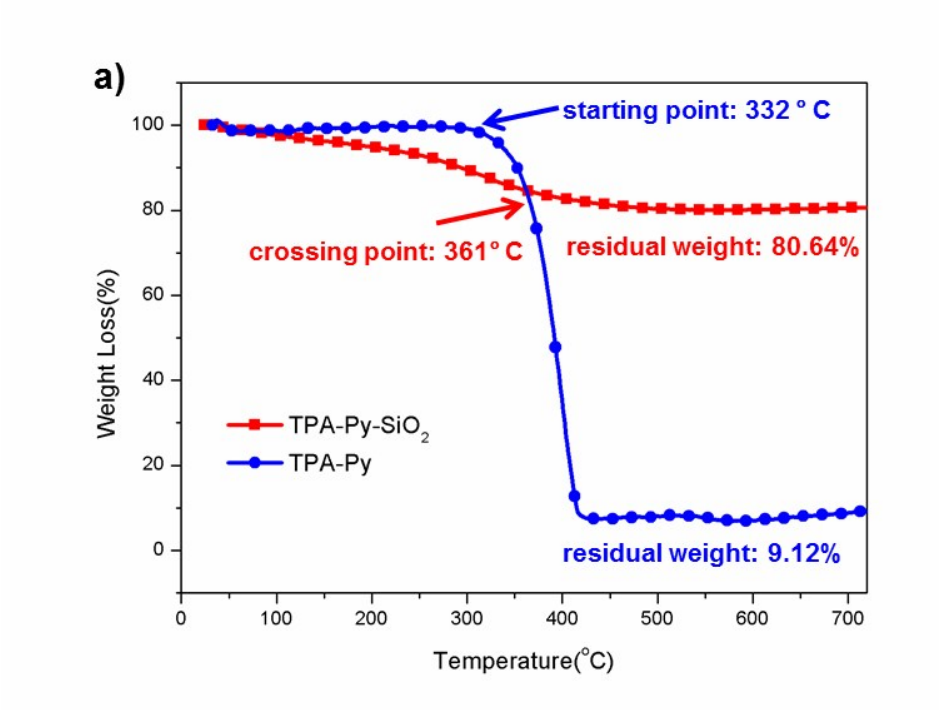
The fluorophore was proved to be covalently grafted on the surface of microsphere by the emission spectral shift compared with physically coated microsphere. It is because the fluorophores covalently linked with the vinyl group on the surface of silica may expand their conjugation length, thus contributing to the spectral shift[6].

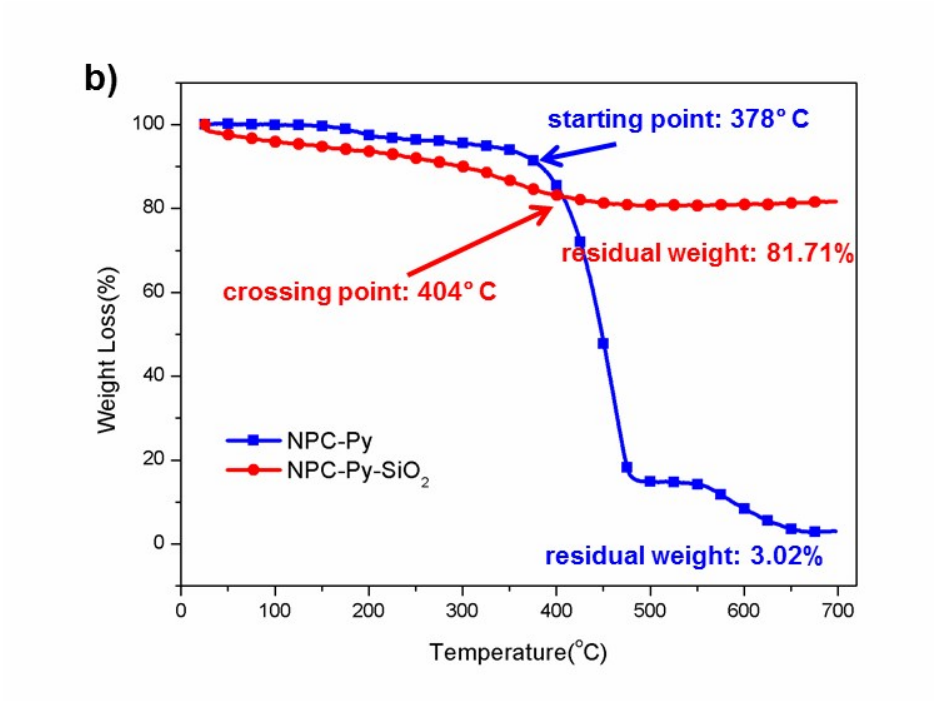
7. Fluorescent quenching efficiency (Red) and photobleaching behavior (Blue) of the silica-based sensing films: (a) TPA-Py-SiO_2 and (b) NPC-Py-SiO_2 by different film preparation methods.



The films made by solid phase transfer are experiment group and those by drop-spin coating and spin coating methods serve as contrast group to prove the influence of chemical binding to the sensing properties of hybrid microsphere.

8. TGA curve of the hybrid silica-based microspheres (a) TPA-Py-SiO_2 and (b) NPC-Py-SiO_2 and their corresponding fluorophores under oxygen condition

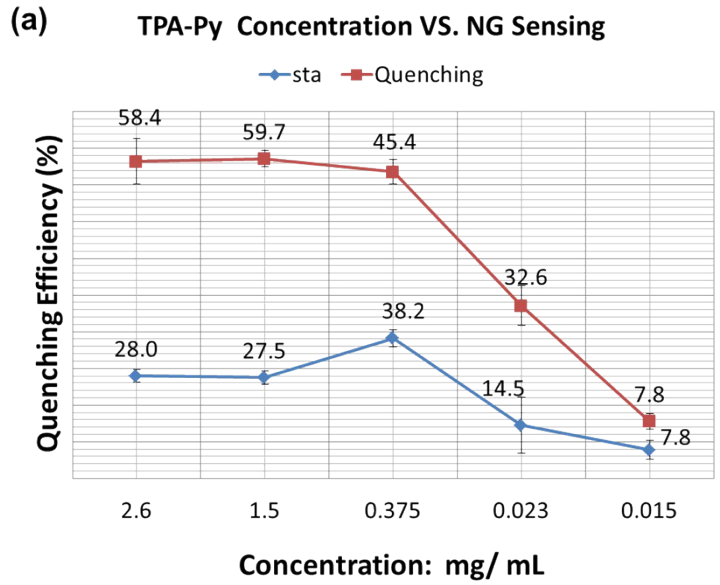


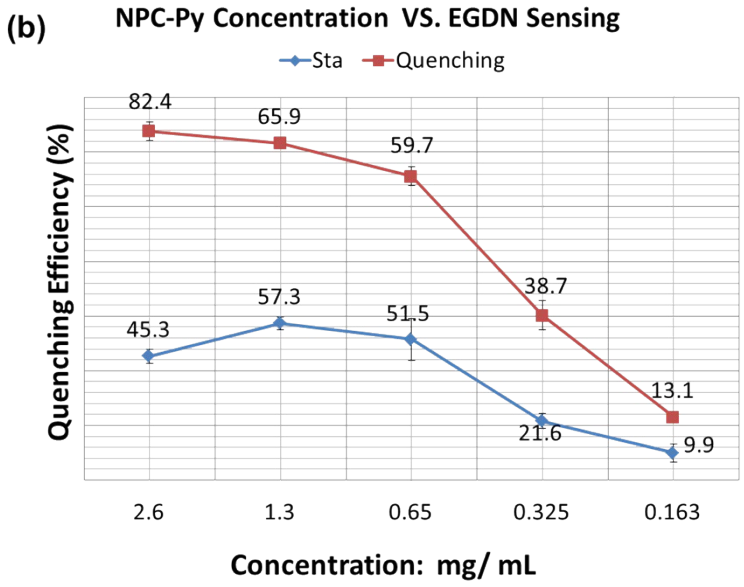


9. Simulation Parameters of finite-different time-domain (FDTD) method using the perfectly matched layer (PML) absorbing boundary condition for the theoretical analysis of field distribution and resonance spectrum of the optical hybrid silica resonator microsphere

Computation parameters	Optimized value	
Diameter	1.9 µm	1.4 µm
Wall Thickness	150 nm	100 nm
Refractive Index[7]	1.7	1.7
Dielectric Constant[7]	2.3716	2.3716
Extinction Coefficient[8]	4.54	5.00
Resonance Wavelength	513 nm	483 nm
Excitation Wavelength	393 nm	372 nm
Space Interval	30 nm	30 nm
Peak Shift	50 nm	20 nm

10. The photobleaching (blue) of two sensing fluorophores films made from different concentration of tetrahydrofuran solvents and their fluorescence quenching behavior (red) upon explosive vapours





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