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Electronic Supporting Information to:

Fluorescent polymer film with self-assembled three-dimensionally ordered nanopores: preparation, characterization and its application for explosives detection

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SUPPLEMENTARY RESULTS

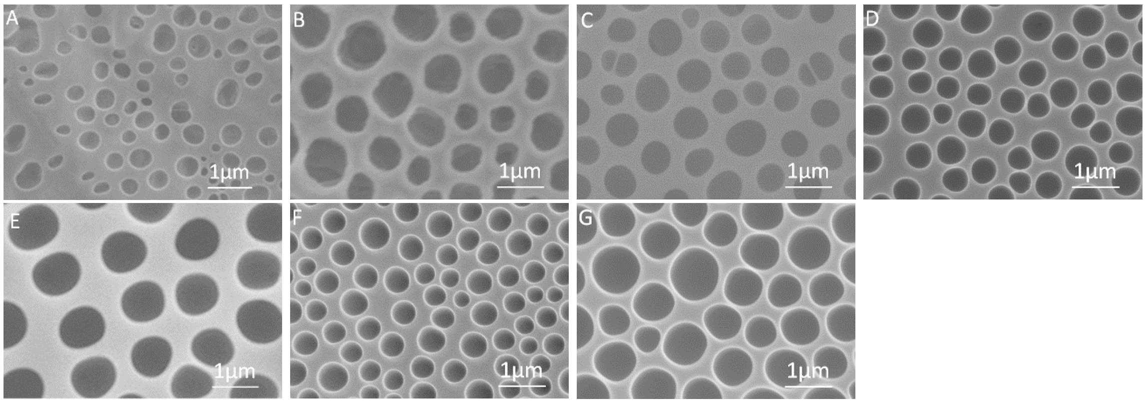

Figure S1. SEM images of a series of $PS_xPY_{0.1}$ and PS_4PY_z fluorescent films. A) $PS_{0.5}PY_{0.1}$, B) $PS_1PY_{0.1}$, C) $PS_2PY_{0.1}$, D) $PS_4PY_{0.1}$, E) $PS_6PY_{0.1}$, F) $PS_4PY_{0.05}$, and G) $PS_4PY_{0.2}$.

Table S1 | Calculated pore density (percentage of film surface area calculated from corresponding SEM images) of a series of $PS_xPY_{0.1}$ and PS_4PY_z fluorescent films.

Py-PES Films	Pore density (%)
$PS_{0.5}PY_{0.1}$	20.8±5.4
$PS_1PY_{0.1}$	41.1±2.0
$PS_2PY_{0.1}$	42.1±1.1
$PS_4PY_{0.1}$	43.4±2.0
$PS_6PY_{0.1}$	38.1±2.5
$PS_4PY_{0.05}$	30.8±1.3
$PS_6PY_{0.2}$	55.4±2.6

Table S2 | Saturated vapor concentrations, HOMO and LUMO energies of representative analytes and interferences[1]

Compound	Vapor concentration, ppb	HOMO, eV	LUMO, eV
Pyrene[2]	/	-5.33	-1.48
4-NT	6×10^4	/	/
1,3-DNB[3,4]	59.9	-7.9855	-3.4311
2,4-DNT	144	-7.7645	-3.2174
Chloranil[5]	1.001×10^4	/	-5.617

Previous studies have revealed that the efficiency of the fluorescence quenching of the solid film would depend on analyte's electronic structure, vapor pressure, diffusion of analytes in the films and the adsorptive affinity of the film to explosive molecules.[6-8] Table S2 summarizes the calculated orbital energies (at B3LYP/6-31G* level) as well as saturated vapor concentration of representative analytes investigated in this study. For nitro explosives, the low LUMO energies can accept the electron from the excited state of pyrene, and thus the nanoporous Py-PS film could be effectively quenched. Nitroaromatic explosives have π-electrons to facilitate their intercalative bindings with pyrene-PS film and also possess relative higher volatility. DNB has a slightly lower LUMO level compared to that of DNT (-3.4311 eV vs. -3.2174 eV), but it displays a lower quenching efficiency than that of DNT, which may be ascribed to its much lower vapor concentration compared to that of DNT (59.9 ppb vs. 144 ppb). 4-NT shows the highest fluorescence quenching efficiency in the study, possibly attributed to its highest vapor concentration (60 ppm) among the investigated nitroaromatic explosives. In contrast, It is surprising to note that, although chloranil has substantially lower LUMO energies and higher vapor concentrations than nitroaromatic explosives, much lower quenching efficiency was observed, which might be attributed to their weaker electrostatic interactions with sensing materials and a lower surface binding constant compared with that of nitro explosives. Not surprisingly, electron-rich compounds (aniline) or the mixture of organic compounds in perfume fail to provide quenching response since they are not favorable for PET process.

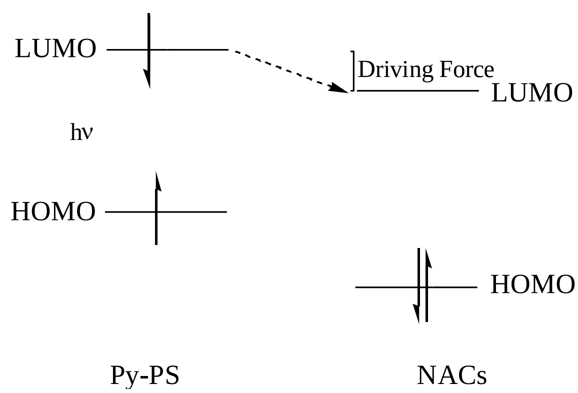

Figure S2. Photo-induced electron transfer mechanism for Py-PS films by NACs.

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