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Raman Spectroscopy-based Sensitive, Fast and Reversible Vapour Phase Detection of Explosives adsorbed on Metal-Organic Frameworks UiO-67

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Synthesis of UiO-67-dccpy, MOF 1: The MOF **1** used in this work was obtained from the work of Ghosh et al.[1] The synthesis protocol is discussed briefly where firstly the linker, 2-phenylpyridine-5,4' -dicarboxylic acid was synthesized by using the previoulsly reported method. [2]

Then, the MOF 1 was synthesized by taking $ZrCl_4$ and the linker in N,N-dimethylformamide (DMF, 4 mL) in a Teflon lined Parr stainless steel vessel (17 mL). The sealed vessed was placed in oven and heated at 120 °C for 24 h. The sample was cooled to room temperature, after which the white product was filtered and washed with DMF. The occluded solvent in MOF was then exchanged for methanol by dipping it in methanol for 3 days and replacing it with fresh methanol every 24 h. The guest free porous MOF **1** was obtained by heating the methanol exchanged MOF at 130 °C under vacuum for 24 h which was then used for further studies.

The powder XRD, TGA and fluorescence studies were done. The obtained MOF **1** showed fluorescence spectra when excited at 320 nm with the emission spectra in the range 330 nm-630 nm with maximum peak at 438 nm. The sizes of the pore windows as 11.5 Å × 23 Å were also mentioned.

Table S1. The comparison of different materials used for the vapour phase detection of explosives.

S. No.	Materials	Technique	Analyte detected	Time taken for the detection
1	Gold substrate	SERS	Triacetone triperoxide	40 s[3]
2	Fluorescent polymers	Fluorescence	2,4-Dinitrotoluene	10 min[4]
3	Gold nanoparticles	SERS	2,4-Dinitrotoluene	10 min[5]
4	Thiophene-based polymer films	Fluorescence	2,4-Dinitrotoluene	5 min[6]
5	Hetero-oligophenylene-Based Carbazole Derivatives	Fluorescence	Trinitrotoluene	30 min[7]
6	Pentacenequinone derivative	Fluorescence	Trinitrophenol	5 min[8]
7	$[Zn(ndc)(ted)_{0.5}]$	Fluorescence	Nitrobenzene	10 min[9]
8	$[NH_2(CH_3)_2][Cd_6(L)_4(DMF)_6(HCOO)]$	Fluorescence	Nitrobenzene	11 min[10]
9	Triphenylamine derivative	Fluorescence	Trinitrophenol	1 min[11]
10	$[Tb(L')(OH)].x(H_2O)]$	Fluorescence	Nitrobenzene	10 min[12]
11	[Zn(dcbpy)(DMF)].DMF	Fluorescence	2,3-Dimethyl-2,3-dinitrobutane	5 min[13]
12	Polysiloxane-Modified Tetraphenylethene	Fluorescence	Trinitrotoluene	10 min[14]
13	Silver nanocubes	SERS	2,4-Dinitrotoluene	3 min[15]
14	$Zr_6(sdba)_4(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(HCOO)_2(OH)_2(H_2O)_2$	Fluorescence	Nitrobenzene	30 min[16]
15	$Zr_6O_4(OH)_4(dcppy)_6$	Raman	Trinitrophenol	30 s (this work)

ndc = 2,6-naphthalenedicarboxylic acid; ted = triethylenediamine; DMF = N,N-dimethyl formamide; L= 2,4,6-tris[1-(3-carboxylphenoxy)methyl]mesitylene; L'= 5-(4-carboxyphenyl) pyridine-2-carboxylate; dcbpy= 2,2'-bipyridine-4,4'-dicarboxylate; sdba= 4,4'-sulfonyl dibenzoate; dcppy is 2-phenylpyridine-5,4'-dicarboxylate; SERS= surfaced-enhanced Raman spectroscopy

Table S2. The comparison of present work on the reversibility conditions with previously reported work.

S. No.	Materials	Analyte detected	Temperature for reusability	Time taken for heating
1	$[Zn_2(bpdc)_2(bpee)]$	2,4-Dinitrotoluene and 2,3-dimethyl-2,3-dinitrobutane	150 °C[17]	1 min
2	Polycarbazole polymer	Trinitrotoluene	45 °C[18]	3 h
3	$[NH_2(CH_3)_2][Cd_6(L)_4(DMF)_6(HCOO)]$	Nitrobenzene	50 °C[10]	30 min
4	$[Tb(L')(OH)].x(H_2O)]$	Nitrobenzene	150 °C[12]	30 min
5	Polysiloxane-Modified Tetraphenylethene	Trinitrotoluene	40 °C[14]	8 h
6	$Zr_6(sdba)_4(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(HCOO)_2(OH)_2(H_2O)_2$	Nitrobenzene	100 °C[16]	-
7	$Zr_6O_4(OH)_4(dcppy)_6$	Trinitrophenol	80 °C (this work)	5 min

bpdc=4,4'-biphenyldicarboxylate; bpee=1,2-bipyridylethene; DMF = N,N-dimethyl formamide; L'= 5-(4-carboxyphenyl) pyridine-2-carboxylate; sdba= 4,4'-sulfonyl dibenzoate; dcppy is 2-phenylpyridine-5,4'-dicarboxylate

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