Luminescent Coordination Polymer-Fullerene Composite as Highly Sensitive and Selective Optical Detector for 2,4,6-Trinitrophenol (TNP)

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ELECTRONIC SUPPLEMENTARY INFORMATION

medium.	ig based detect	ors for the detections of	or the in iiquid
Type of luminophore/Name/formula of sensor material	Solvent	$K_{SV}(M^{-1}) \times 10^{-4}$	Reference
$[Zn(L)_2(H_2O)_2] (L = 3-(3-pyridyl acrylate)-C_{60} composite$	Acetonitrile + Water)	37.5	Present work
BTPE grafted amine-modified mesoporous SBA-15 [BTPE = 1,2-bis[4-(bromomethyl) phenyl]-1,2-diphenylethene]	Water	25	7a
Fluoroalkylated poly(3,3,3-trifluoropropylmethylsilane)	THF	4.15	7b
Poly(tetraphenylsilole-vinylene), Poly(tetraphenylsilole- silafluorene-vinylene), Poly(silafluorene-vinylene)	Toluene	1.64, 1.56, 2.01	7c
π -conjugated fluoranthene derivative	Ethanol	9.9	7d
Supramolecular polymers of pyrene-based polycarboxylic acids	DMSO	2.3, 3.2, 3.8	7e
Anthracene-functionalized tris-imidazolium salts	CHCl ₃	3.3, 3.8	4b
Polydiacetylene (PDA) microtube	H ₂ O	1.3	7f
Poly(9,9-dioctylfluorene)	Water	10.2	7g
Cage based on Schiff base condensation of 1,3,5- tris(aminomethyl)-2,4,6-trimethylbenzene with 4,40-diformyltriphenylamine	DCM	22	7h
Bis(benzothieno)silole (BBTS) derivatives	Ethanol	8.2	7i
Two porous COPs synthesized using 1,4- Dibromobenzene (DB) with 2,4,6-Tris-(4-bromo- phenyl)-[1,3,5]-triazine (TBT) and 1,3,5-Tris(4- bromophenyl)benzene (TBB)	Methanol	8.3, 26	7ј
1,3,5-Tri(1H-benzo[d]imidazol-2-yl)benzene derivatives	THF	11.2	7k
7,10-Di([1,1'-biphenyl]-4-yl)-8,9-bis(4- (hexyloxy)phenyl)fluoranthene	Ethanol	24	71
Hexaphenylbenzene derivative-Hg ²⁺ assembly	Water + THF)	19.2	7m
N,N-dimethylaminocinnamaldehyde-Hg ²⁺ assembly	Water + THF)	9	7n
2,6-diamino pyridine functionalized graphene oxide	H ₂ O	13.2	70
MoS_2 quantum dot	Tris-HCl buffer	4.3	7p
Carbon nitride nanosheet	Tris-HCl buffer	24.8	7q
$[Tb_{0.2}Y_{0.18}(PDA)_{3}(H_{2}O)_{1}].2H_{2}O (PDA = 1,4-phenylenediacetate)$	Acetonitrile	7.09	3
$Fe_3O_4@Tb-BTC (BTC = 1,3,5-benzenetricarboxylate$	Ethanol	1.84	9a
$[Cd(ndc)_{0.5}(pca)].xG$ (G = guest molecules, ndc = 2,6-	Acetonitrile	3.5	9b

Table S1 Summary of state-of-art luminescence quenching based detectors for the detections of TNP in liquid

napthalenedicarboxylic acid, pca = 4-pyridinecarboxylic acid)			
$Zr_6O_4(OH)_4(L)_6$ (L = 2-phenylpyridine-5,4'-dicarboxylate	H ₂ O	2.9	9c
$[Cd_3(TPT_{)2}(DMF)_2] \cdot (H_2O)_{0.5}$ (TPT = p-terphenyl-3,4",5-tricarboxylate	Ethanol	6.56	9d
$[Zn_8(ad)_4(BPDC)_6O\cdot 2 Me_2NH_2]\cdot G$ (G=DMF and water, ad = adeninate, BPDC = biphenyl dicarboxylate)	Water	4.6	9e
$[Eu(L)_{1.5}(DEF)]_n$ (H ₂ L = 9,9-diethylfluorene-2,7-dicarboxylic acid)	DMF	6.24	9f
[Tb(1,3,5-BTC)]	Ethanol	3.4	9g
[Eu ₃ (bpydb) ₃ (HCOO)(μ ₃ - OH) ₂ (DMF)]·(DMF) ₃ (H ₂ O)	Water, DMF	2.1, 1.5	9h



Fig. S1: Powder XRD (CuK_a) patterns: (a) simulated from single crystal X-ray data of CP, $[Zn(L)_2(H_2O)_2]$ (L = 3-(3-pyridyl acrylate) [CCDC: 245503], (b) solvothermally synthesized CP (X. Li, R. Cao, Y. Sun, W. Bi, X. Li and Y. Wang, *Eur. J. Inorg. Chem.*, 2005, 321-329).



Fig. S2: Emission spectra of CP-C₆₀ composite solution ($\lambda_{ex} = 314$ nm). Note the emission peak centered at 394 nm. The spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S3: (a) Emission spectra of 1 mM CP in water ($\lambda_{ex} = 314$ nm). (b) Emission spectra of 0.5 μ M C₆₀ in acetonitrile ($\lambda_{ex} = 314$ nm). Both the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S4. Emission spectra of the composite solution upon incremental addition of acetonitrile solution of TNP ($\lambda_{ex} = 314$ nm). Final concentration of TNP in the medium is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



(a)



(b)

Fig. S5. (a) Emission spectra of 1 mM CP in water upon incremental addition of water solution of TNP ($\lambda_{ex} = 314$ nm). (b) Emission spectra of 0.5 μ M C₆₀ in acetonitrile upon incremental addition of acetonitrile solution of TNP ($\lambda_{ex} = 314$ nm). Both the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer. Final concentration of TNP in the medium is indicated in the legend.



Fig. S6. Emission spectra of the composite solution upon incremental addition of acetonitrile solution of 1,3-DNB ($\lambda_{ex} = 314$ nm). Final concentration of 1,3-DNB in the medium is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S7. Emission spectra of the composite solution upon incremental addition of acetonitrile solution of 1,4-DNB ($\lambda_{ex} = 314$ nm). Final concentration of 1,4-DNB in the medium is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S8. Emission spectra of the composite solution upon incremental addition of acetonitrile solution of DNT ($\lambda_{ex} = 314$ nm). Final concentration of DNT in the medium is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S9. Emission spectra of the composite solution upon incremental addition of acetonitrile solution of NT ($\lambda_{ex} = 314$ nm). Final concentration of NT in the medium is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S10. Emission spectra of the composite solution upon incremental addition of acetonitrile solution of NB ($\lambda_{ex} = 314$ nm). Final concentration of NB in the medium is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S11. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M acetonitrile solution of 1,3-DNB sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (1,3-DNB and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S12. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M acetonitrile solution of 1,4-DNB sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (1,4-DNB and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S13. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M acetonitrile solution of DNT sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (DNT and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S14. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M acetonitrile solution of NT sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (NT and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S15. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M acetonitrile solution of NB sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (NB and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S16. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M water solution of NaCl sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (NaCl and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S17. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M water solution of KCl sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (KCl and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S18. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M water solution of MgCl₂ sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (MgCl₂ and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S19. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M water solution of CaCl₂ sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (CaCl₂ and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S20. Emission spectra of the composite solution upon addition of 1 μ L of 0.01 M water solution of FeCl₃ sequentially in two equal portion (0.5 μ L in each portion) followed by 1 μ L of 0.01 M actonitrile solution of TNP in similar way ($\lambda_{ex} = 314$ nm). The addition cycles were repeated for two more times. The final added volume of analytes solution (FeCl₃ and TNP) is indicated in the legend. All the spectra measured using Fluorolog Horiba Jobin-Yvon spectrofluorometer.



Fig. S21: Absorption spectra of all the six analytes in mixed solvent (acetonitrile and water in 1:2 volume ratio) (Conc. of analyte. = 50μ M).



Fig. S22. Orange curve is absorption spectra of TNP in mixed solvent (acetonitrile and water in 1:2 volume ratio) (Conc. of analyte. = 50μ M). Blue is the emission spectrum of composite solution which is nicely overlapped with the absorption band of TNP.