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Title: Structural Diversity in Luminescent MOFs Containing a Bent Electron-rich Dicarboxylate Linker and

a Flexible Capping Ligand: Selective Detection of 4-Nitroaniline in Water

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Abstract: A combination of a bent bis(naphthalene) and hydroxy-based dicarboxylate linker and a flexible

bis(tridentate)polypyridyl ligand has been employed to self-assemble with two different d10 metal centers, ZnII and CdII, to form structurally diversified luminescent metal-organic frameworks, $[Zn2(tpbn)(mbhna)2(H2O)2]\cdot 4\ H2O\cdot 1.5DMF\ (1)\ and\ \{[Cd2(tpbn)(mbhna)2]\cdot 2DMF\}n\ (2),$ $respectively\ (where,\ tpbn=N,N',N'',N'''-tetrak is (pyridine-2-ylmethyl) but an e-1,4-diamine\ and$ H2mbhna=4,4'-methylene-bis[3-hydroxy-2-naphthalene carboxylic acid]). Both 1 and 2 are characterized and analyzed by various analytical techniques including single-crystal X-ray diffractometry. Their excellent emissive nature is studied in different solvents and further utilized to selectively detect aromatic amines, particularly 4-nitroaniline in water with detection limits at subppm level. The difference in sensing activity of 1 and 2 toward 4-NA is corroborated well with their structures. The mechanism of action has been established through Stern-Volmer plot, spectral overlap, time-resolved lifetime studies and HOMO-LUMO energy calculations. In addition, 1 and 2

are found to be recyclable and display good stability after sensing experiments.

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