Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Fluorescent metal-organic framework for highly selective detection of nitro explosive in aqueous phase

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Experimental Section

Caution! TNT, RDX and TNP are highly explosive and should be handled carefully and in small amounts. The explosives were handled as dilute solutions and with safety measures to avoid explosion.

Materials: TNT and RDX were obtained from HEMRL Pune (India). TNP, 2,4-DNT, 2,6-DNT, DMNB, NM were purchased from Aldrich, 1,3-DNB, NB from local company and used as received. Dry solvents were used during complete analysis and were obtained locally.

Physical Measurements: Powder X-ray diffraction patterns (PXRD) were measured on Bruker D8 Advanced X-Ray diffractometer using Cu Kα radiation (λ= 1.5406 Å) with a tube voltage of 40 kV and current of 40 mA in 5 to 40° 2θ range. Thermogravimetric analyses were recorded on Perkin-Elmer STA 6000 TGA analyzer under N_2 atmosphere with a heating rate of 10 °C min^{-1}. Fluorescence measurements were done using Horiba FluoroMax 4 with stirring attachment. ^1H and ^{13}C NMR was recorded in 400 MHz Jeol ECS-400 Instrument. The UV-Vis measurements were performed using Chemito SPECTRASCAN UV-2600.

Synthesis of UiO-67@N (1): The ligand 2-phenylpyridine-5,4'-dicarboxylic acid (**LH₂**) was synthesized using procedure previously reported.[1] For synthesis of **1** $ZrCl_4$ (60 mg), **LH_2** (60 mg) were dissolved in N,N-dimethylformamide (DMF, 4 mL) in a Teflon lined Parr stainless steel vessel (17 mL). The vessel was sealed and placed in oven and heated at 120 °C for 24 h. After cooling to room temperature, the white crystalline product was isolated by filtration the solid was washed with DMF. The occluded solvent in MOF was then exchanged for MeOH by dipping it in MeOH for 3 days and replacing it with fresh MeOH every 24 h. The guest free porous MOF (**1'**) was obtained by heating the MeOH exchanged MOF at 130 °C under vacuum for 24 h which was then used for fluorescence measurements.

Fluorescence study: In typical experimental setup, 1 mg of **1'** is weighed and added to cuvette (path length of 1cm) containing 2 mL of water under stirring. The fluorescence response in 330-630 nm range upon excitation at 320 nm was measured *in-situ* after incremental addition of freshly prepared aqueous analyte solutions (1 mM or Saturated) and corresponding fluorescence intensity was monitored at 438 nm. The solution was stirred at constant rate in fluorescence instrument with stirring attachment during experiment to maintain homogeneity of solution. All the experiments were performed in triplicate and consistent results were reported.

Figures:-

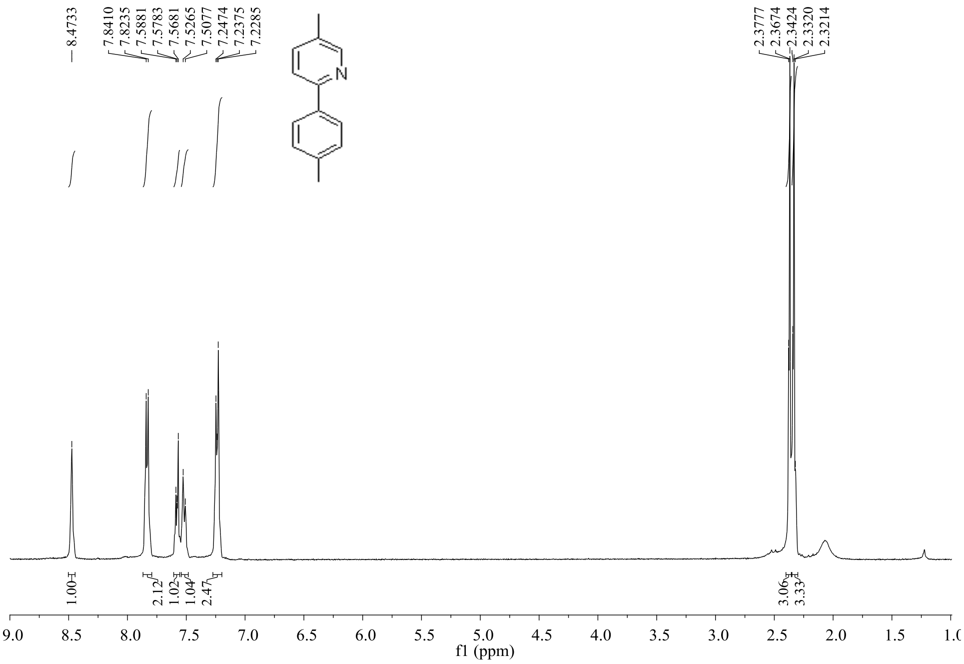

Figure S1: ^{1}H NMR in CDCl$_3$.

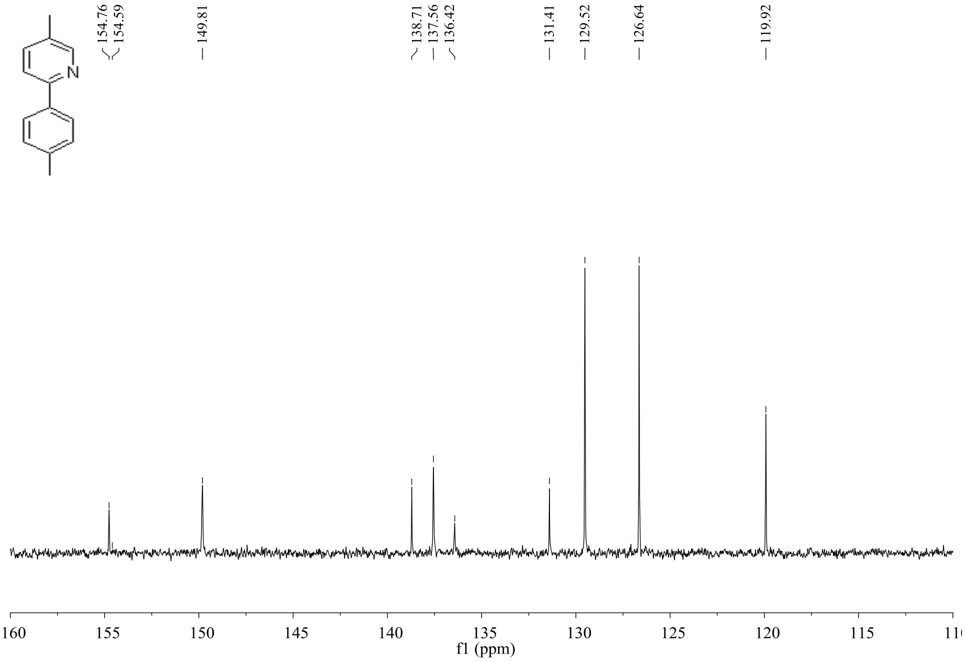

Figure S2: ^{13}C NMR in CDCl$_3$.

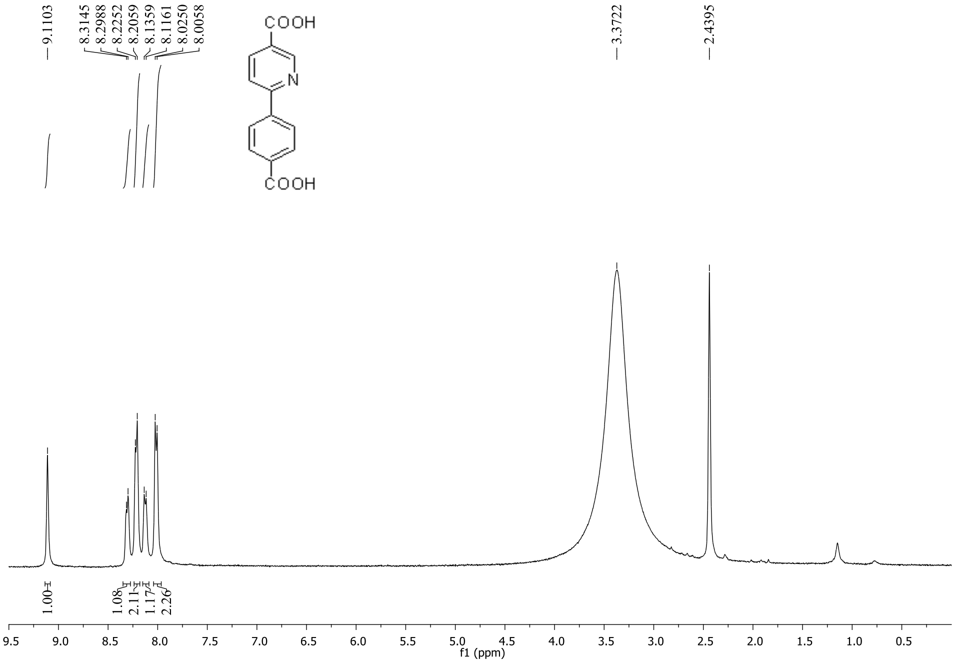

Figure S3: ^{1}H NMR in DMSO-d6.

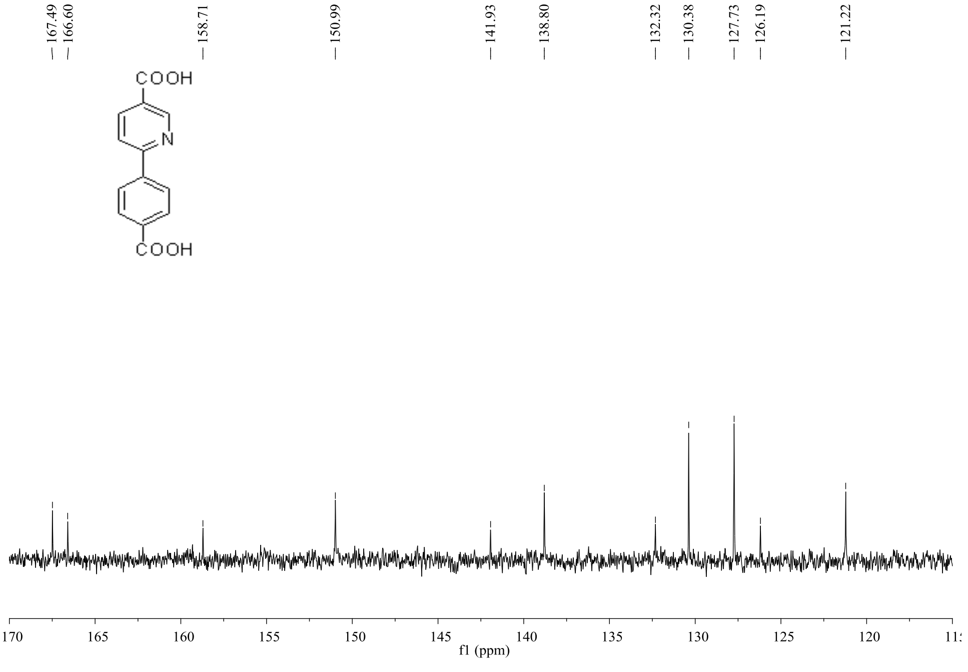

Figure S4: ^{13}C NMR in DMSO-d6.

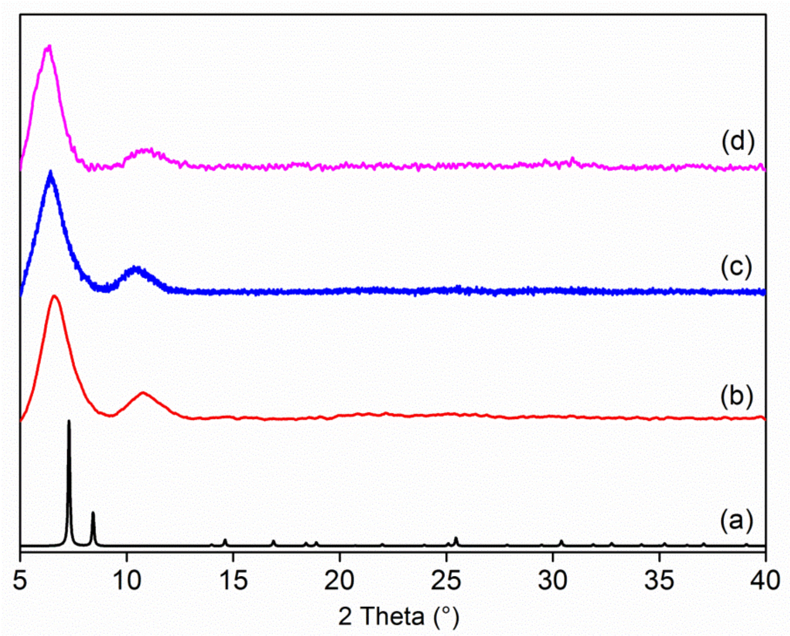

Figure S5: Powder X-ray diffraction patterns (PXRD) of (a) Simulated; (b) Assynthesized compound; (c) MeOH exchange MOF; (d) Desolvated MOF (**1'**).

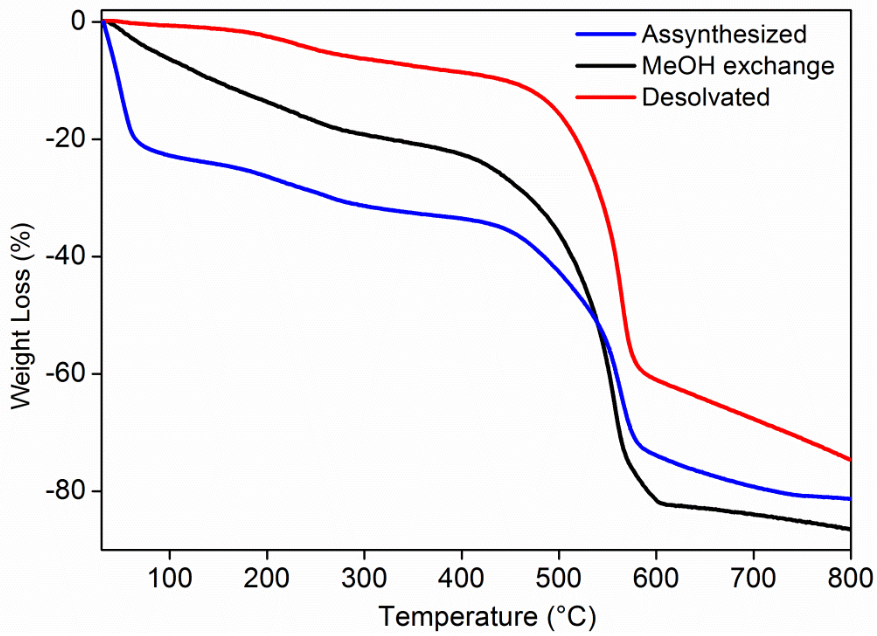

Figure S6: Thermo gravimetric analysis of MOF.

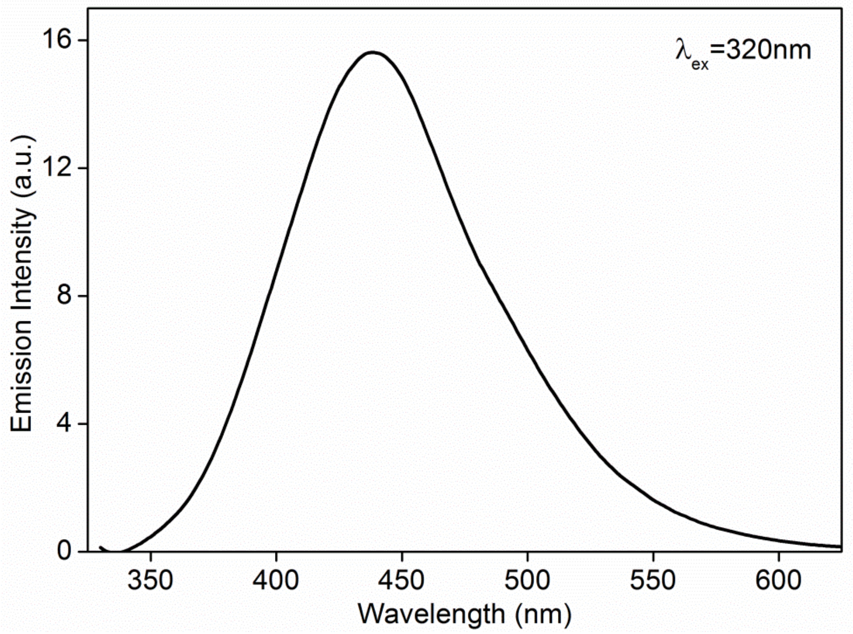

Figure S7: Emission spectra of MOF (**1'**) dispersed in water upon excitation at 320 nm.

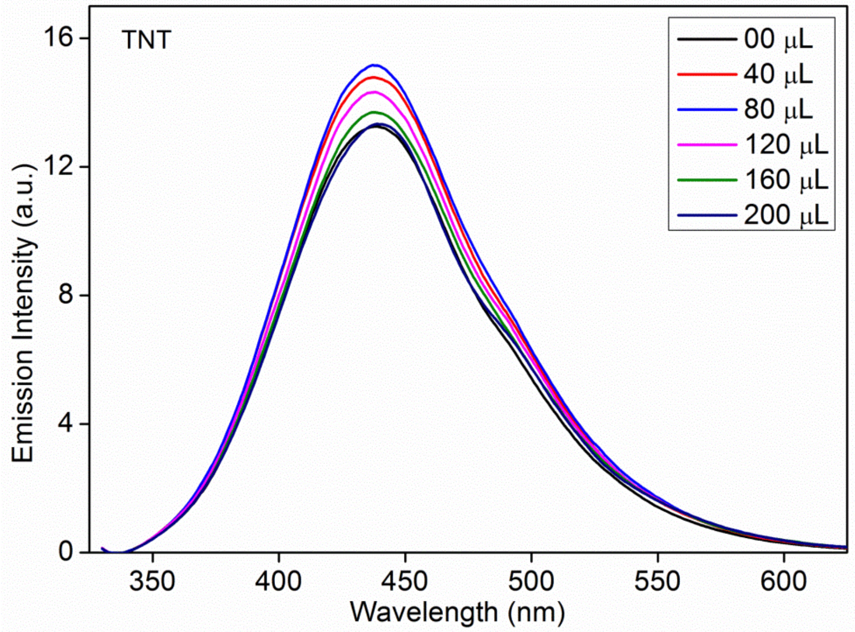

Figure S8: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of TNT solution (1mM) in water.

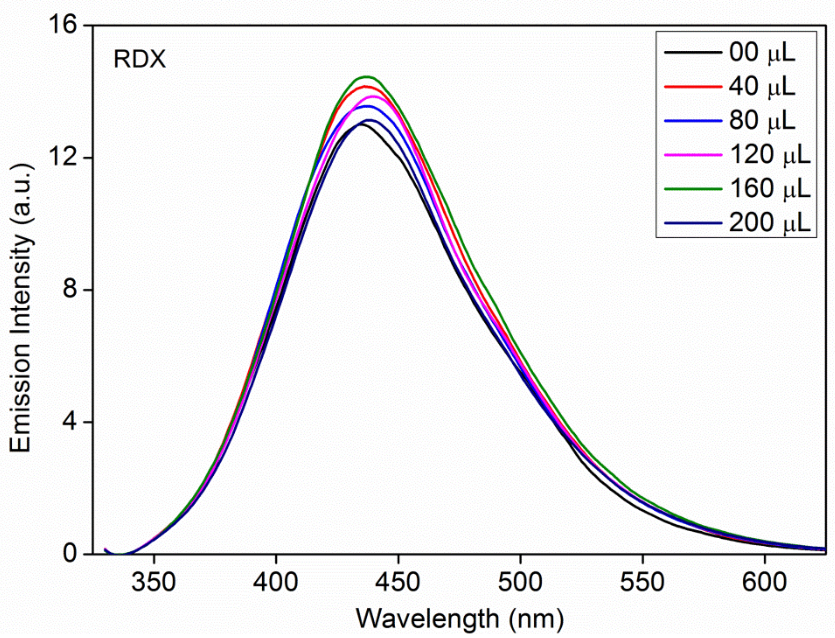

Figure S9: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of RDX solution (1mM) in water.

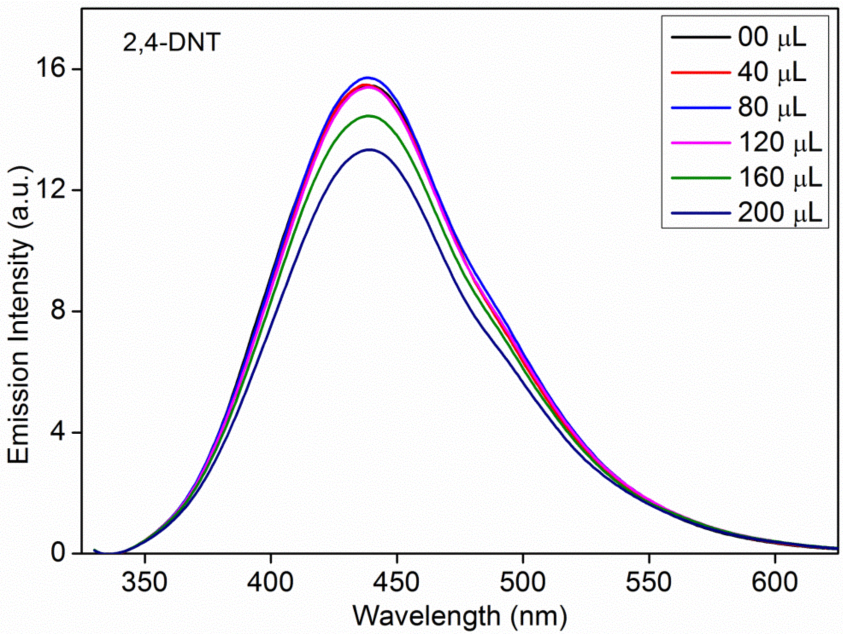

Figure S10: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of 2,4-DNT solution (1mM) in water.

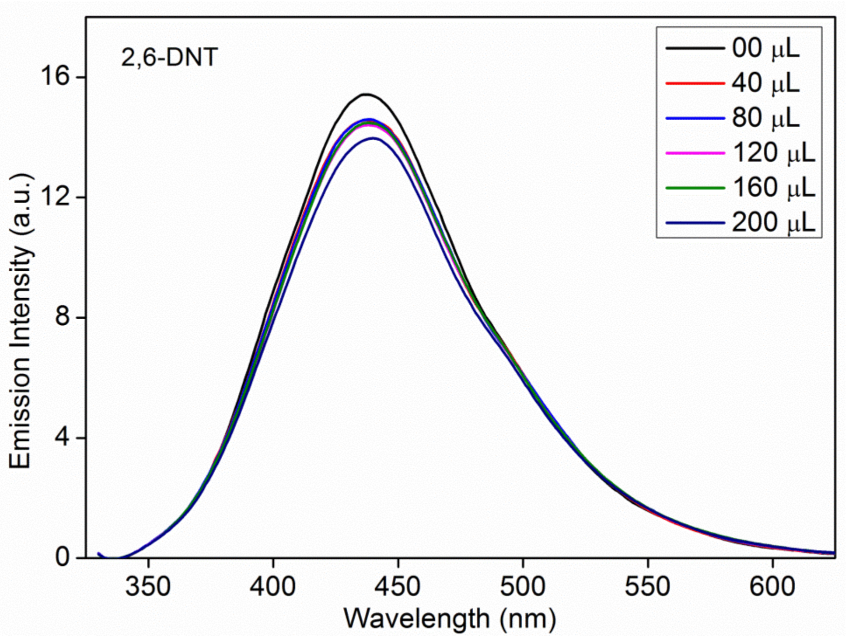

Figure S11: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of 2,6-DNT solution (1mM) in water.

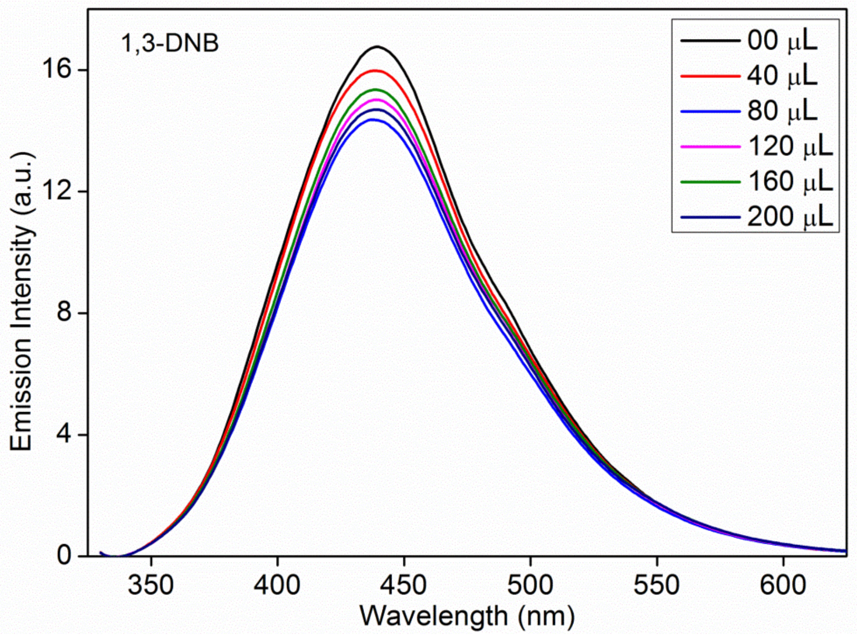

Figure S12: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of 1,3-DNB solution (1mM) in water.

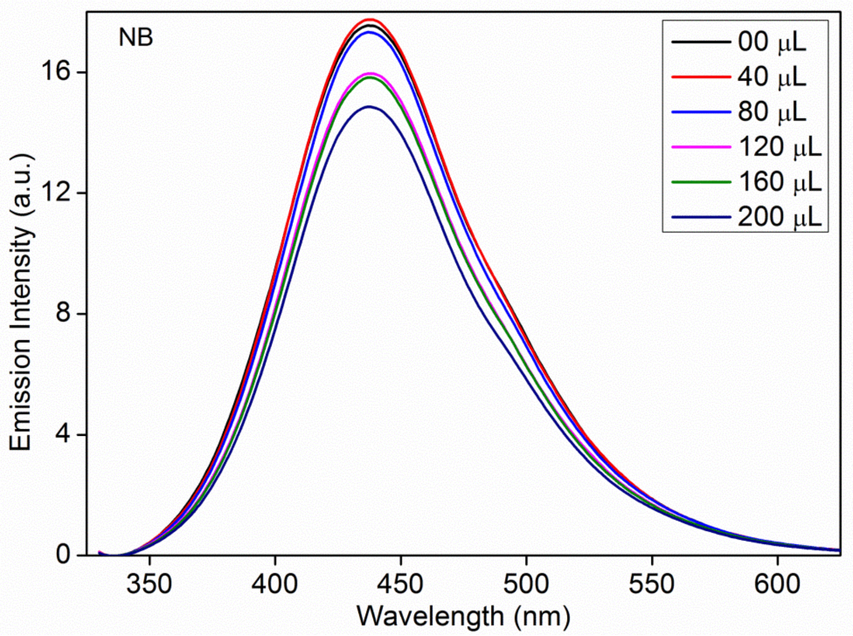

Figure S13: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of NB solution (1mM) in water.

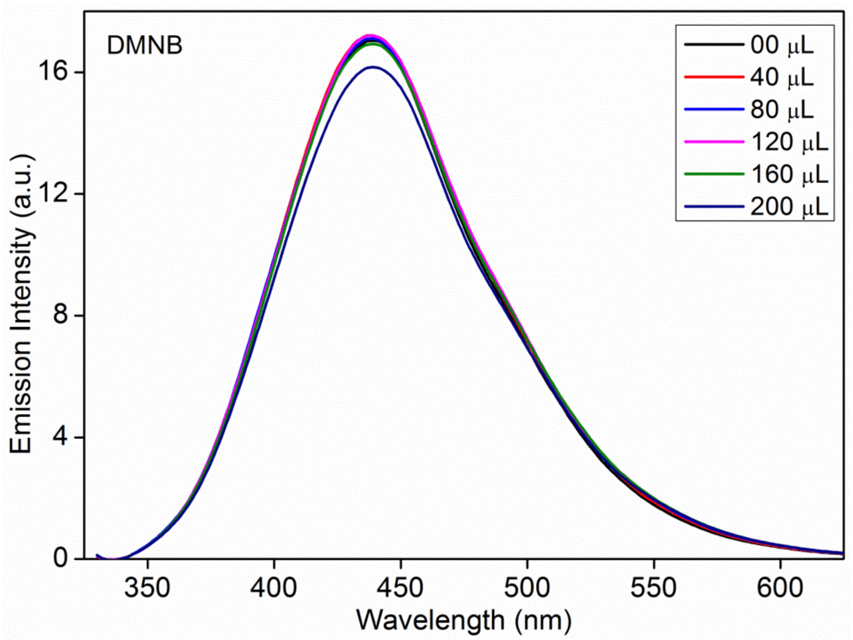

Figure S14: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of DMNB solution (1mM) in water.

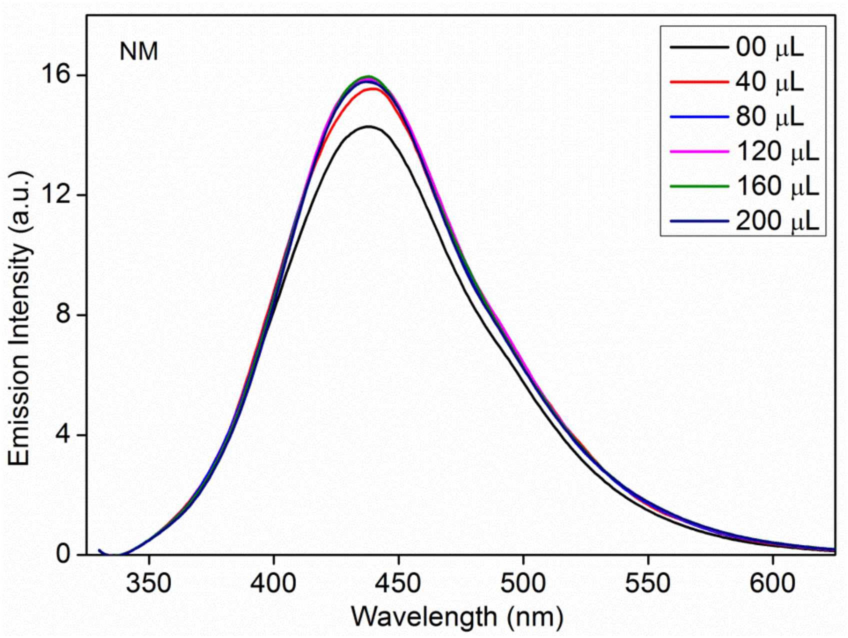

Figure S15: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of NM solution (1mM) in water.

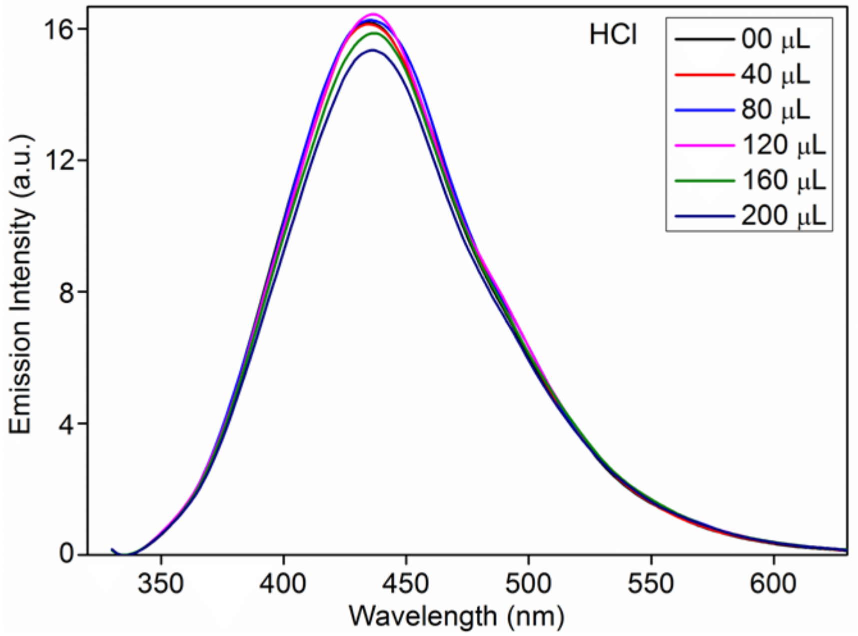

Figure S16: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of HCl solution (1mM) in water.

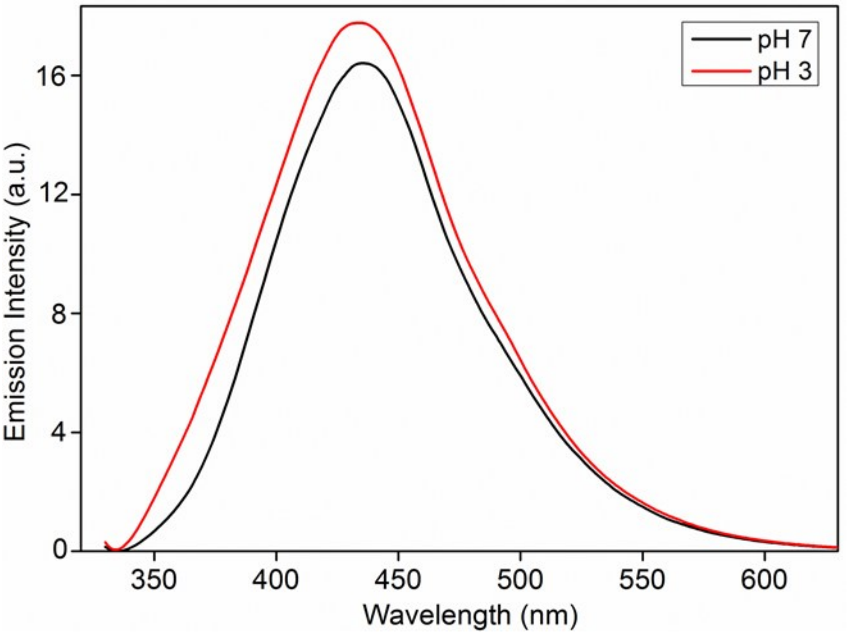

Figure S17: Effect of pH on fluorescence intensity of MOF (**1'**) dispersed in water.

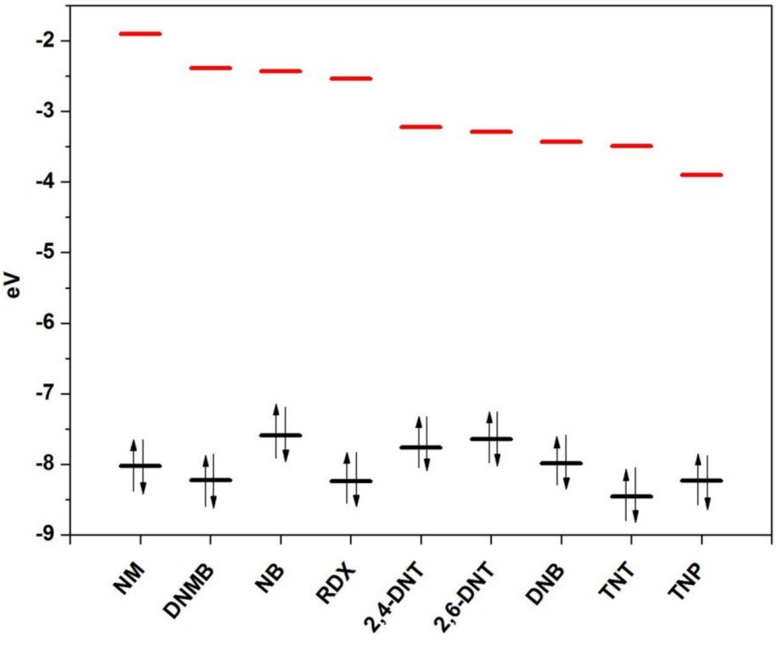

Figure S18: HOMO and LUMO energies of electron deficient nitro explosives.[2]

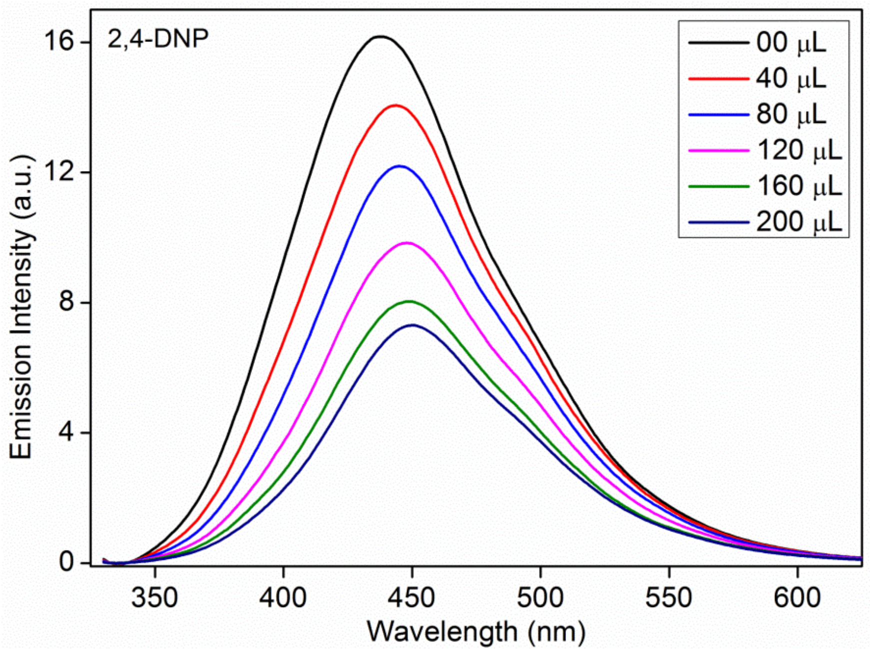

Figure S19: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of 2,4-DNP solution (1mM) in water.

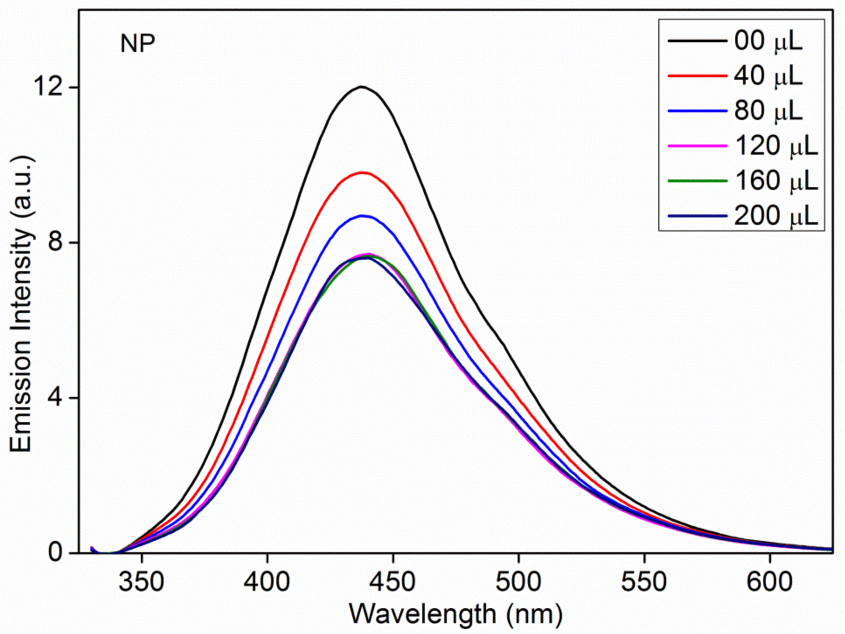

Figure S20: Emission spectra of MOF (**1'**) dispersed in water upon incremental addition of NP solution (1mM) in water.

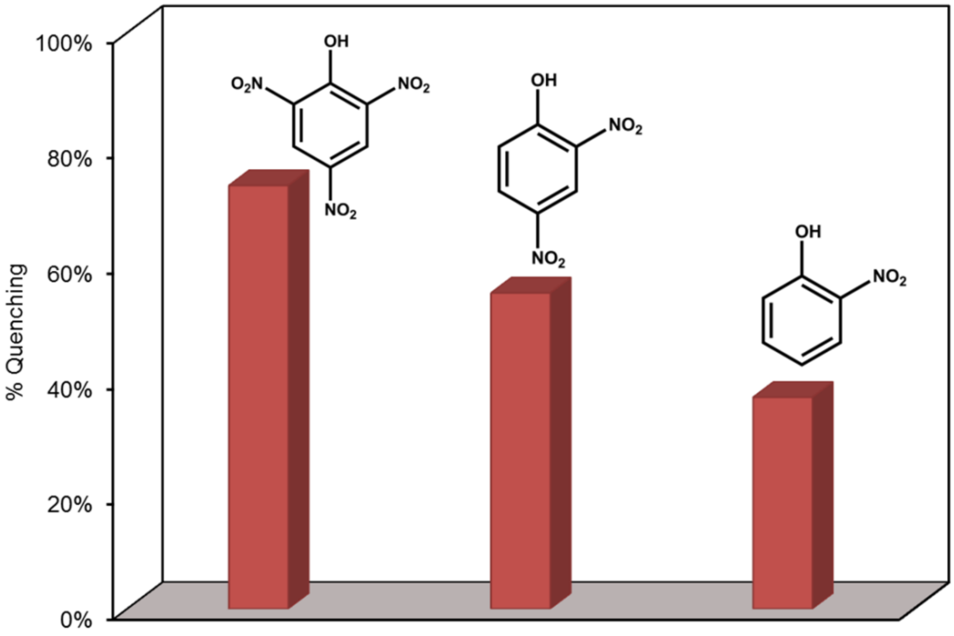

Figure S21: Comparison of percentage fluorescence quenching obtained upon addition of NP, 2,4-DNP, TNP to **1'** dispersed in water.

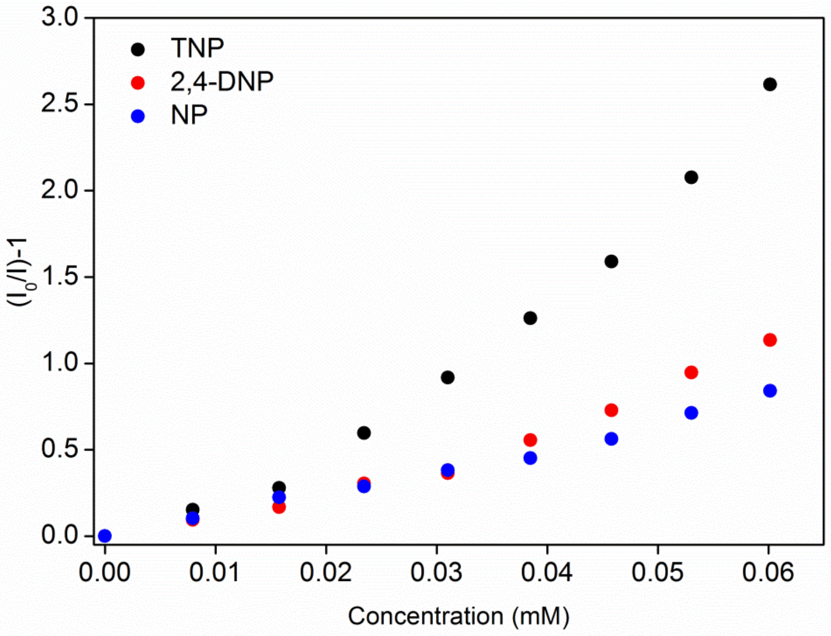

Figure S22: Comparison between Stern-Volmer (SV) plots for TNP, 2,4-DNP and NP in water.

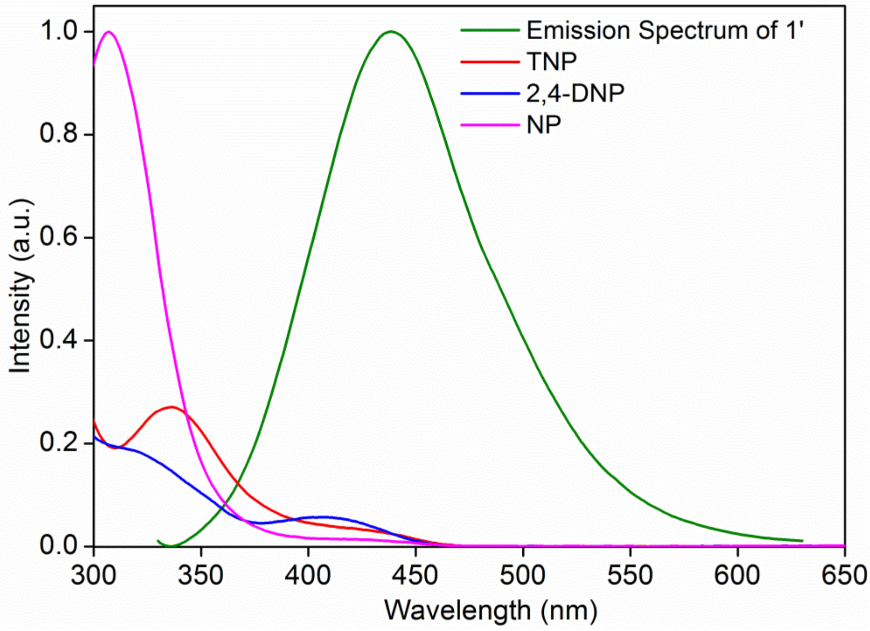

Figure S23: Spectral overlap between normalized absorbance spectra of phenolic nitro analytes and normalized emission spectra of **1'** in water.

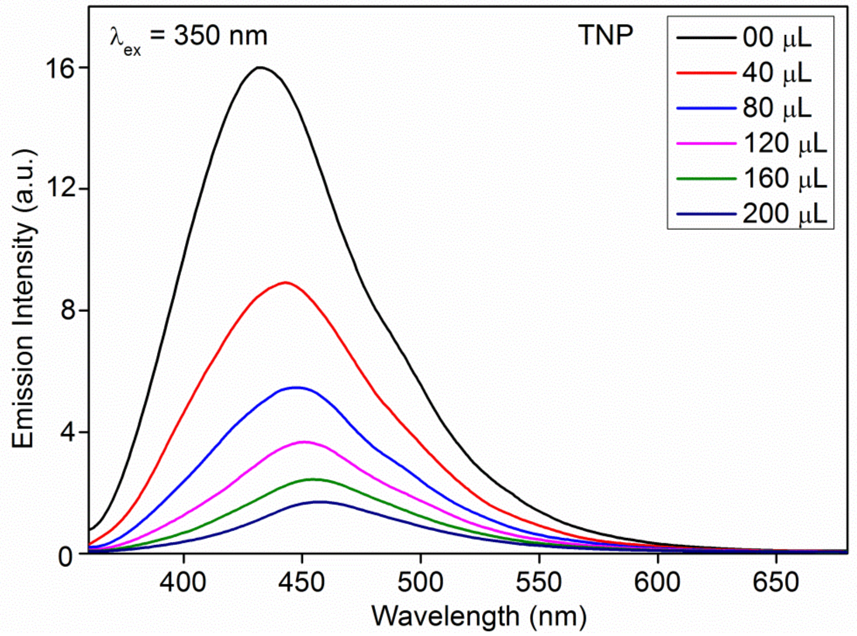

Figure S24: Change in the fluorescence intensity of **1'** in water upon incremental addition of aqueous TNP solution 1 mM. (λex= 350, [**1'**] = 0.5 mg/mL).

References:

1) P. V. Dau, M. Kim, S. J. Garibay, F. H. L. Munch, C. E. Moore and S. M. Cohen, *Inorg. Chem.,* 2012, **51,** 5671.
2) S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee and S. K. Ghosh, *Angew. Chem.,* 2013, **125,** 2953-2957; *Angew. Chem. Int. Ed.*, 2013, **52,** 2881.