



Amine and Imine-Functionalized Mn-based MOF as Unusual Turn-on and Turn-off Sensor for d¹⁰ Heavy Metal Ions and Efficient Adsorbent to Capture Iodine

Samrah Kamal,^a M. Khalid,^{a*} M. Shahnawaz Khan,^a M. Shahid,^a Musheer Ahmad,^b

^aFunctional Inorganic Materials Lab (FIML), Department of Chemistry, Aligarh Muslim University, Aligarh, 202002, India

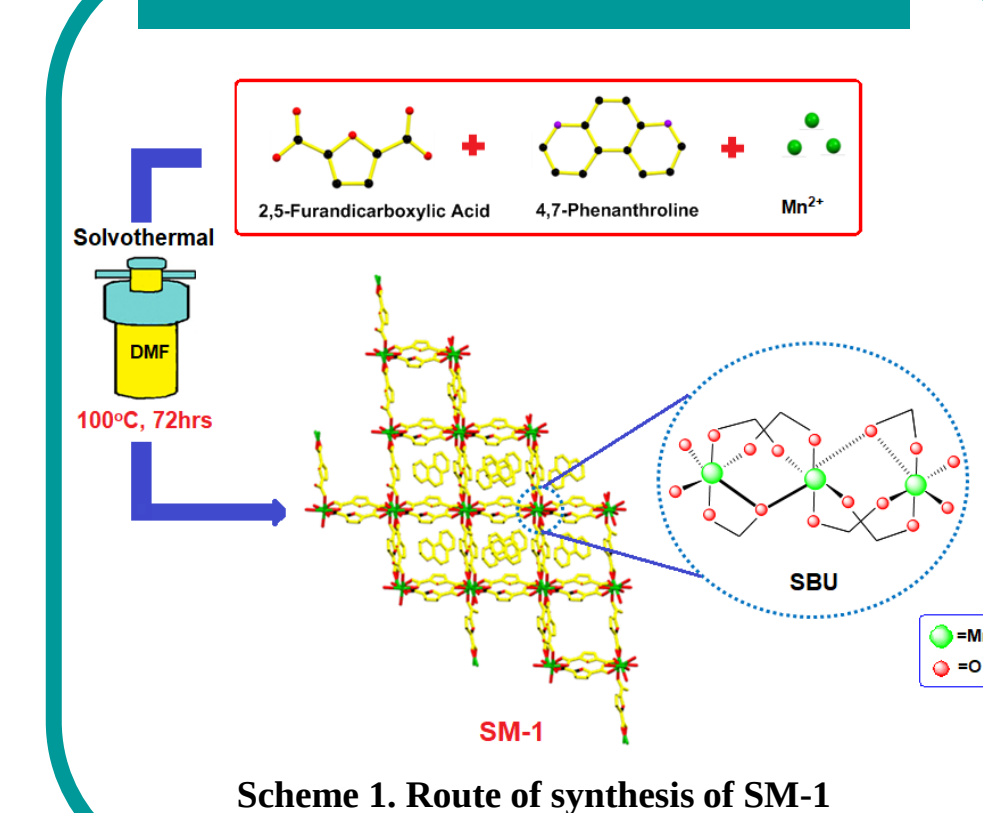
^bZHCET Aligarh Muslim University, Aligarh, 202002, India

*Email: khalid215@gmail.com

ABSTRACT

In this work an Mn-based metal-organic framework (MOF), {[H-Phen]₂[Mn₃(FDA)₄(H₂O)₂]·2H₂O}_n (SM-1) has been synthesized solvothermally using 2,5-Furandicarboxylic acid (2,5-FDA) as linker and 4,7-Phenanthroline (4,7-Phen) as coligand. The SM-1 was characterized by elemental analysis, FTIR, PXRD and crystallographic studies. Single crystal X-ray data reveal that SM-1 framework is constituted by trinuclear Mn-SBUs as dianion ([Mn₃(COO)₆]²⁻), 2,5-FDA and free 4,7-Phenanthroline cation [H-Phen]⁺ rings containing uncoordinated amino and imino moieties which provides extra stability to the framework as well as feasible recognition sites to interact with analytes. Overall, the MOF is anionic in nature which is counter balanced by two protonated phenanthroline cations thus giving rise to +2 oxidation states to all three Mn ions. SM-1 is an excellent fluorescent sensor for d¹⁰ heavy metal ions in an aqueous environment, exhibits fluorescence “turn-on” response for Ag⁺ and Cd²⁺ ions while fluorescence “turn-off” response in case of Hg²⁺ ion with much lower LOD values. Moreover, SM-1 also serve as an adsorbent to capture hazardous substances, SM-1 captures iodine reversibly in cyclohexane solution with high adsorption capacity within 36 h. Further, a plausible mechanism of sensing and iodine adsorption was also discussed briefly. So far as we know, it is the first example of Mn-based anionic MOF functioning as fluorescent sensor to simultaneously detect d¹⁰ heavy metal ions in water and as an adsorbent to trap iodine.

SYNTHESIS OF SM-1



Turn-ON Sensing of Ag⁺ and Cd²⁺

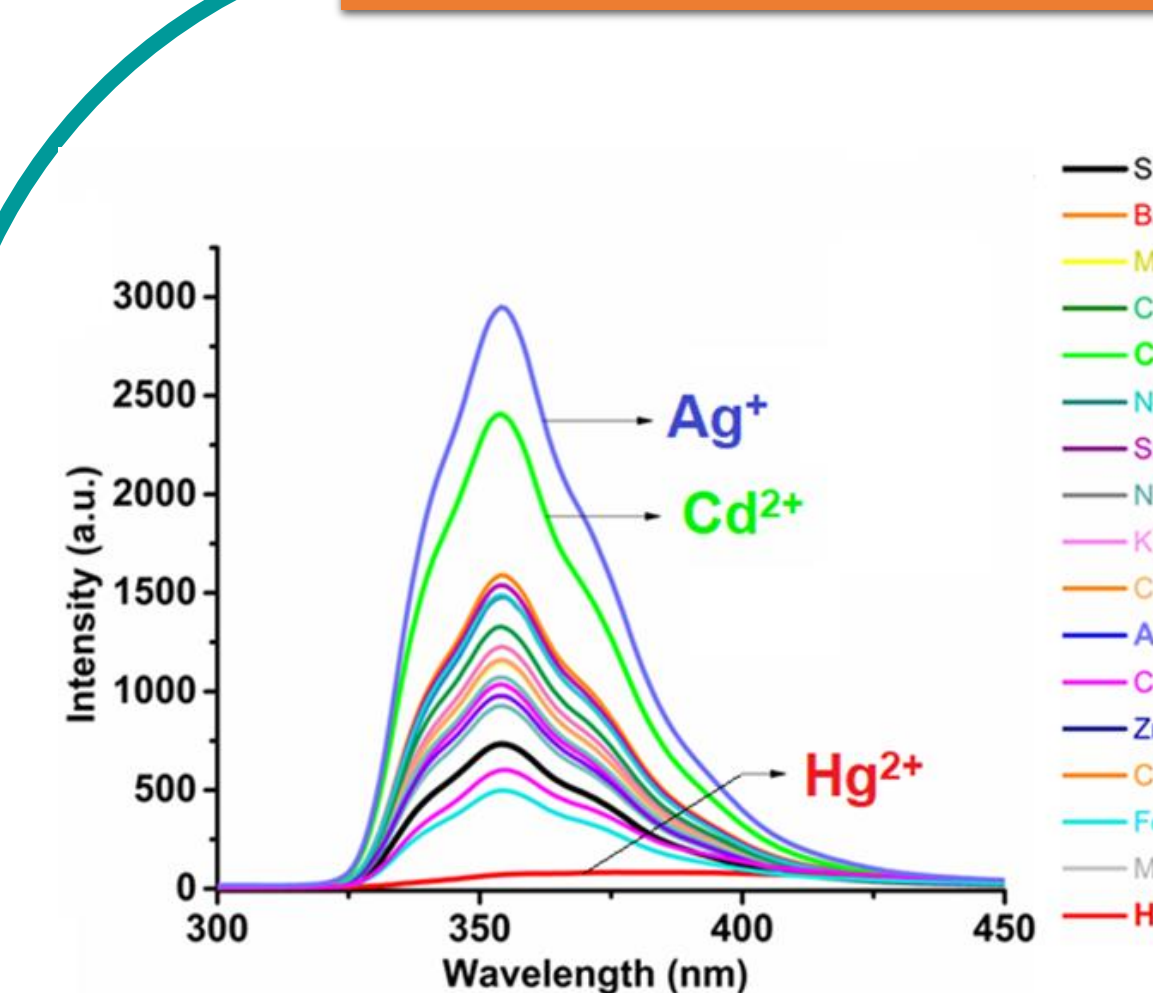


Fig. 2. The change in fluorescence intensity of SM-1 upon addition of aqueous solution of different metal cations (50 μ L each, 1mM stock solution).

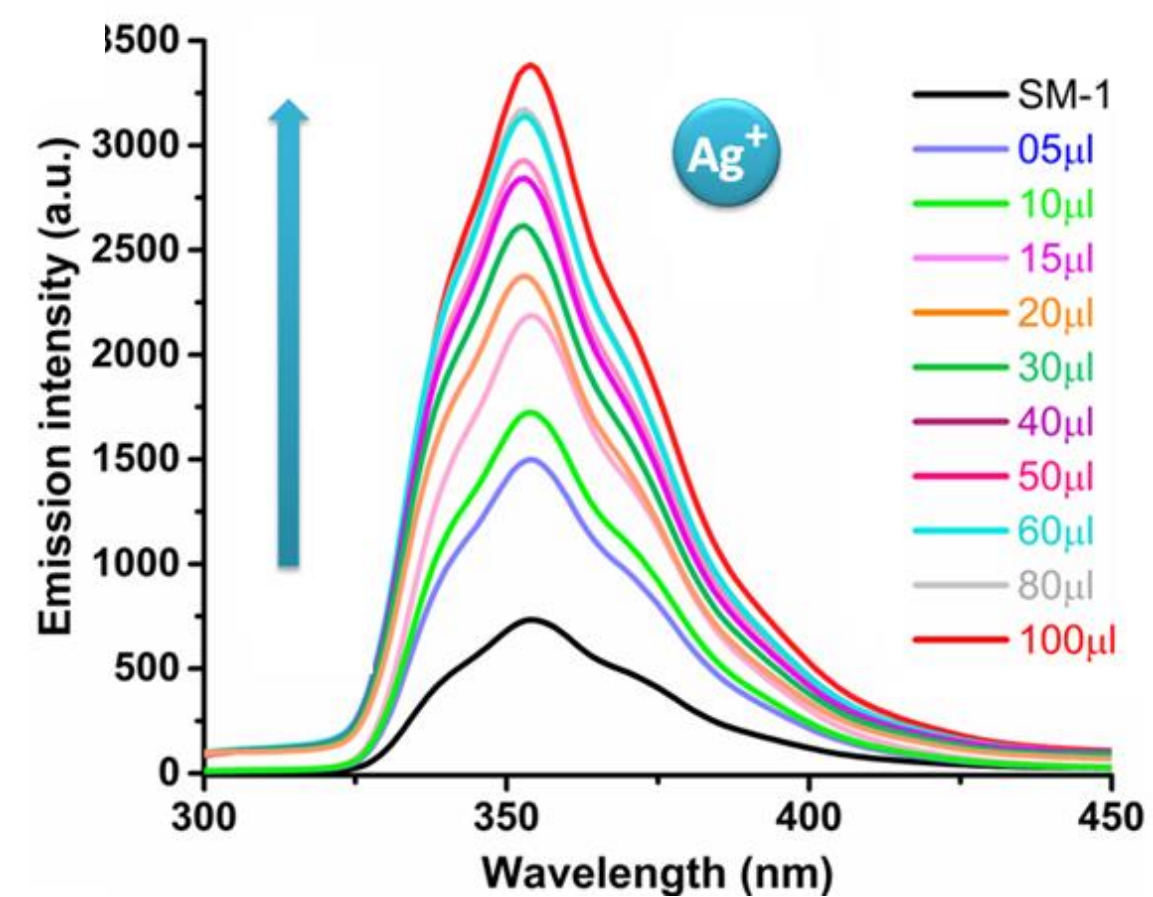


Fig. 3. The Fluorescence spectra of SM-1 with different concentrations (0.5 to 100 μ L) of Ag⁺ (1mM) solution in water.

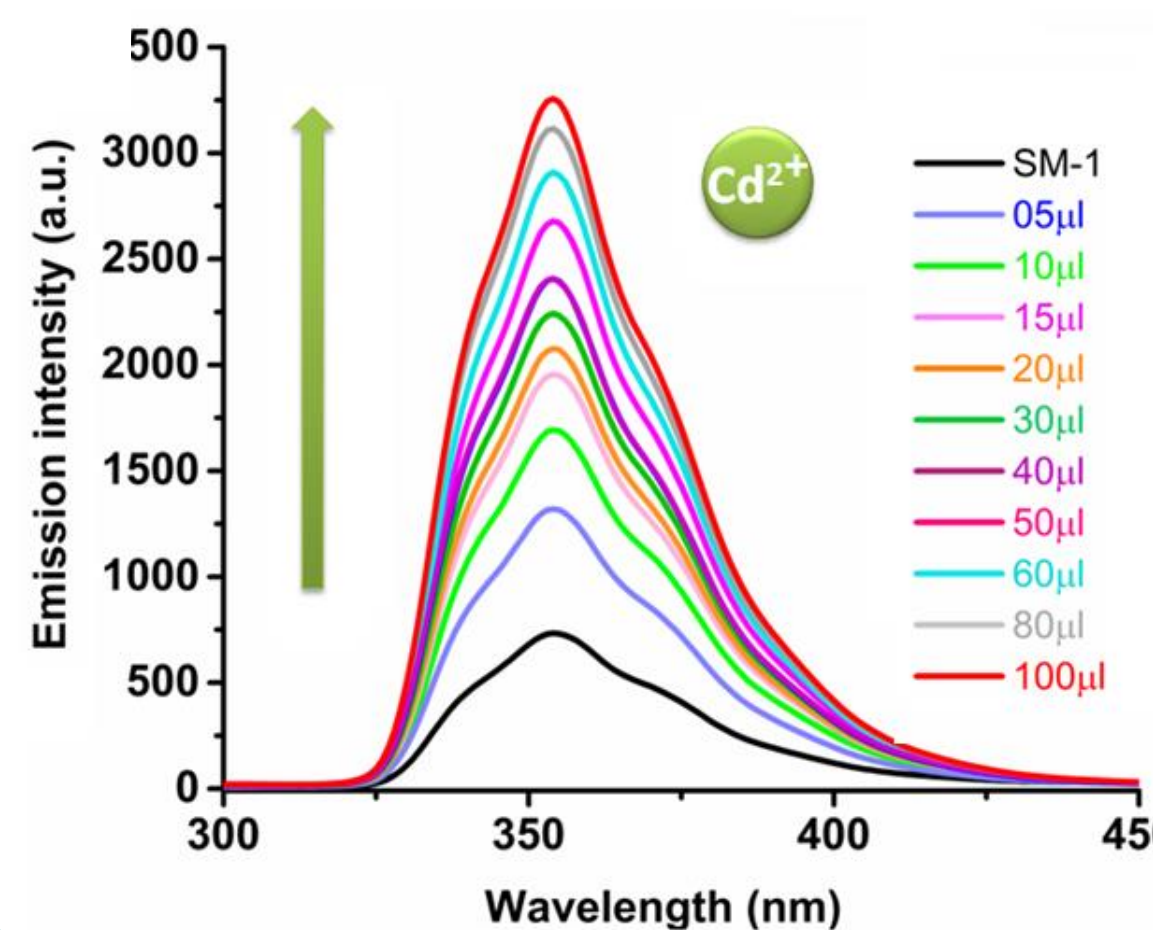


Fig. 4. The Fluorescence spectra of SM-1 with different concentrations (0.5 to 100 μ L) of Cd²⁺ (1mM) solution in water.

SENSING OF d¹⁰ HEAVY METAL IONS IN WATER

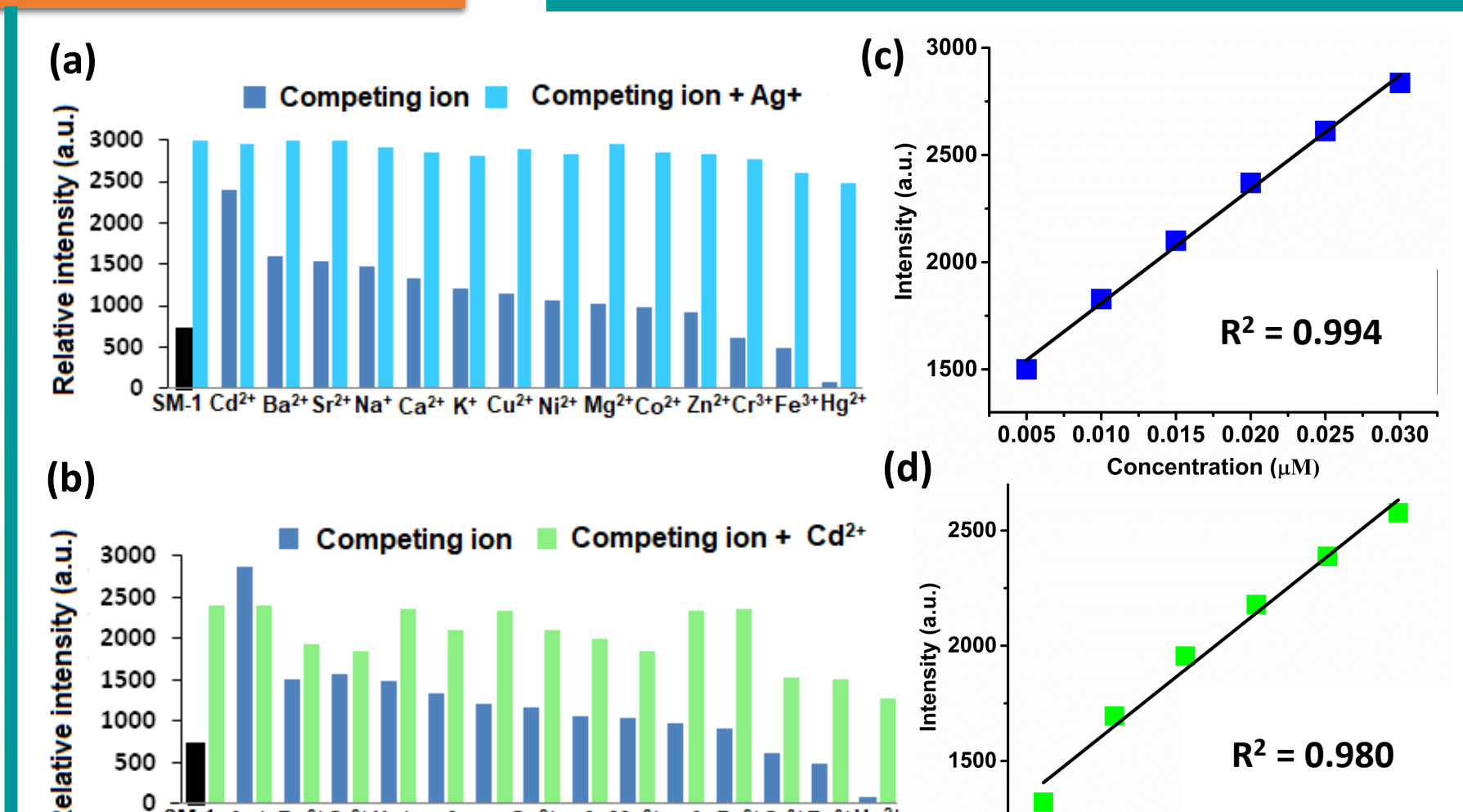


Fig. 5. Changes in fluorescence intensity of SM-1 upon addition of different metal ion solutions followed by (a) Ag⁺ and (b) Cd²⁺ solution respectively (50 μ L each, 1mM) in water (c) Linear region of fluorescence intensity of SM-1 upon addition of Ag⁺ and (d) Cd²⁺ in water.

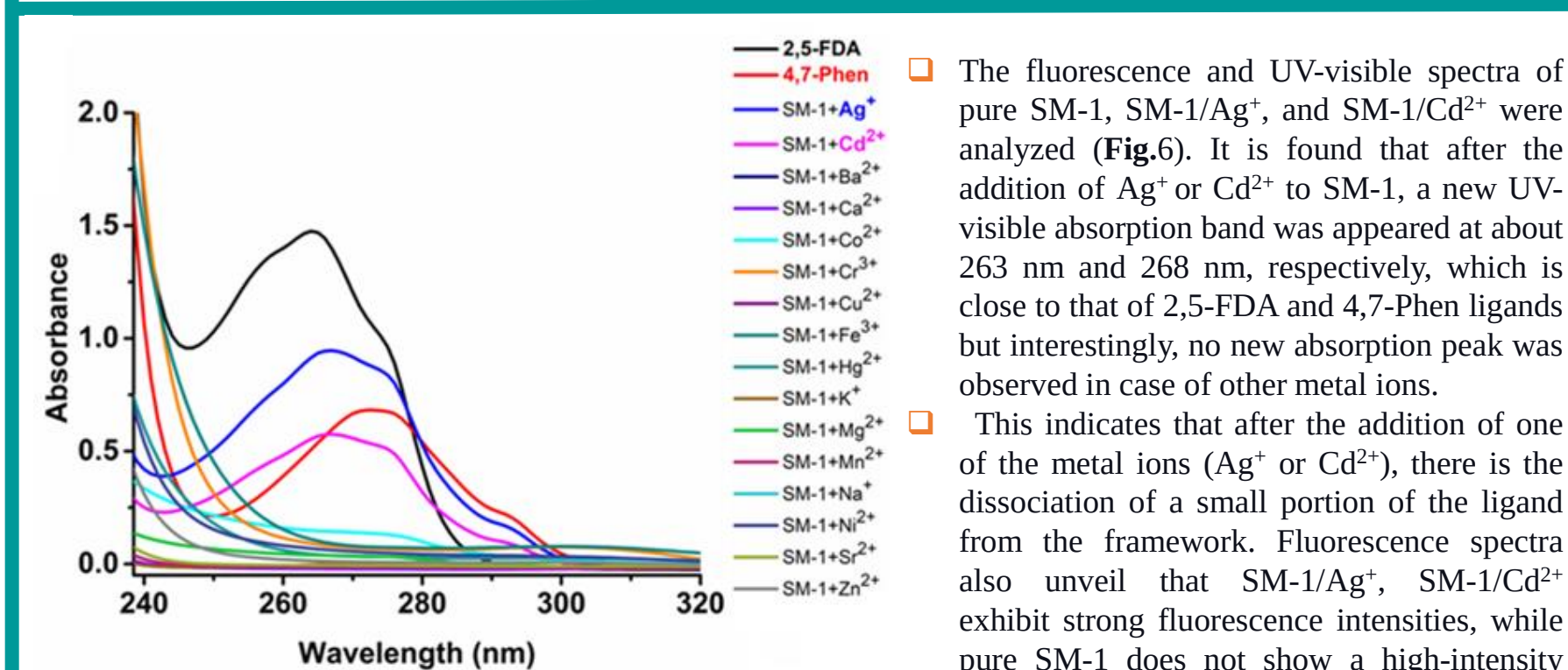


Fig. 6. UV-visible absorption spectra of 2,5-FDA, 4,7-Phen ligand, aqueous solution of SM-1/Ag⁺, SM-1/Cd²⁺ and SM-1/M²⁺ (M = different metal ions) were analyzed.

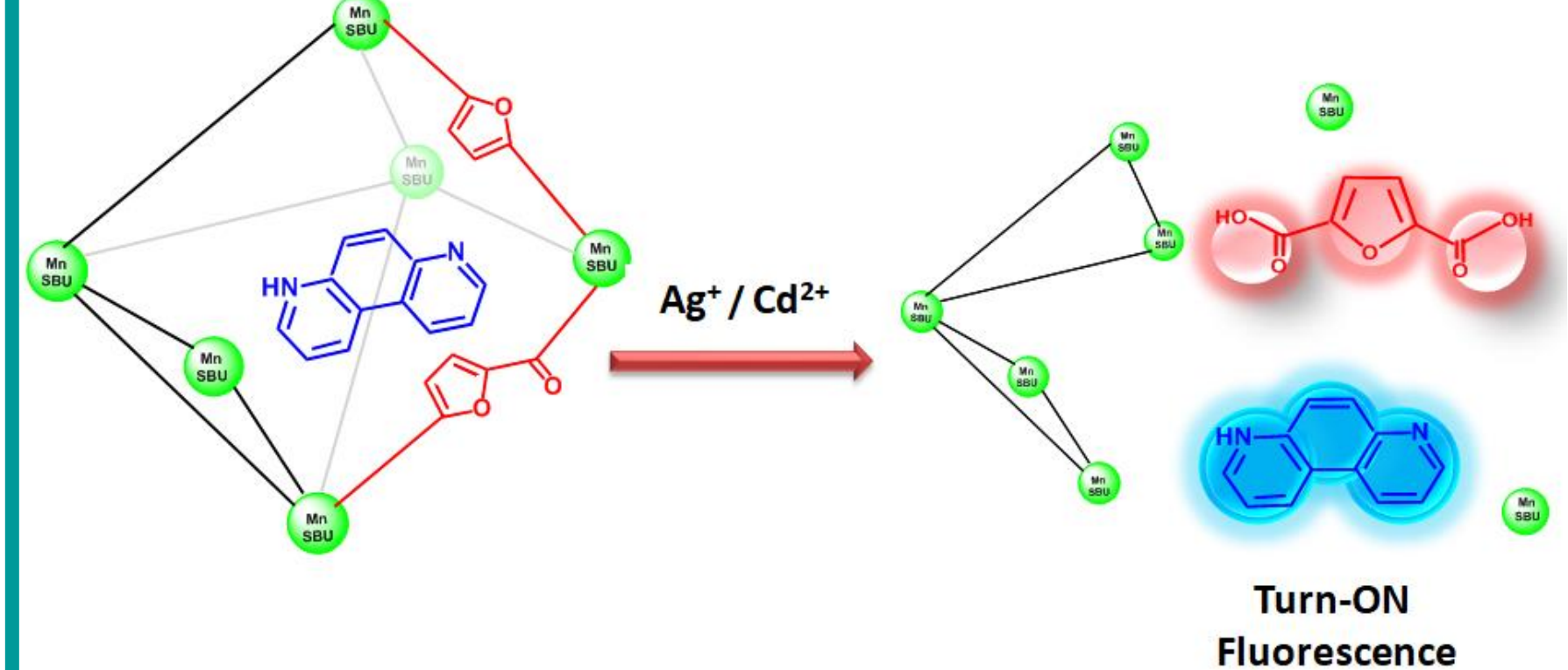


Fig. 7. Framework collapse mechanism of SM-1 as Turn-On fluorescent probe for the aqueous phase detection of Ag⁺ and Cd²⁺ ions.

- The “turn-on” fluorescence enhancement mechanism of SM-1 is most likely assigned to the collapse of the framework and aggregation of the ligands with the Ag⁺ or Cd²⁺ ion.
- Limits of detections (LODs) for Ag⁺ and Cd²⁺ were determined to be ~0.023 ppb and ~0.05 ppb, respectively, which is quite lower as compared to the maximum concentration of Ag⁺ (0.93 μ M), and Cd²⁺ (5 ppb) ion in drinking water, in accordance to the standards of the U.S. Environmental Protection Agency (EPA).

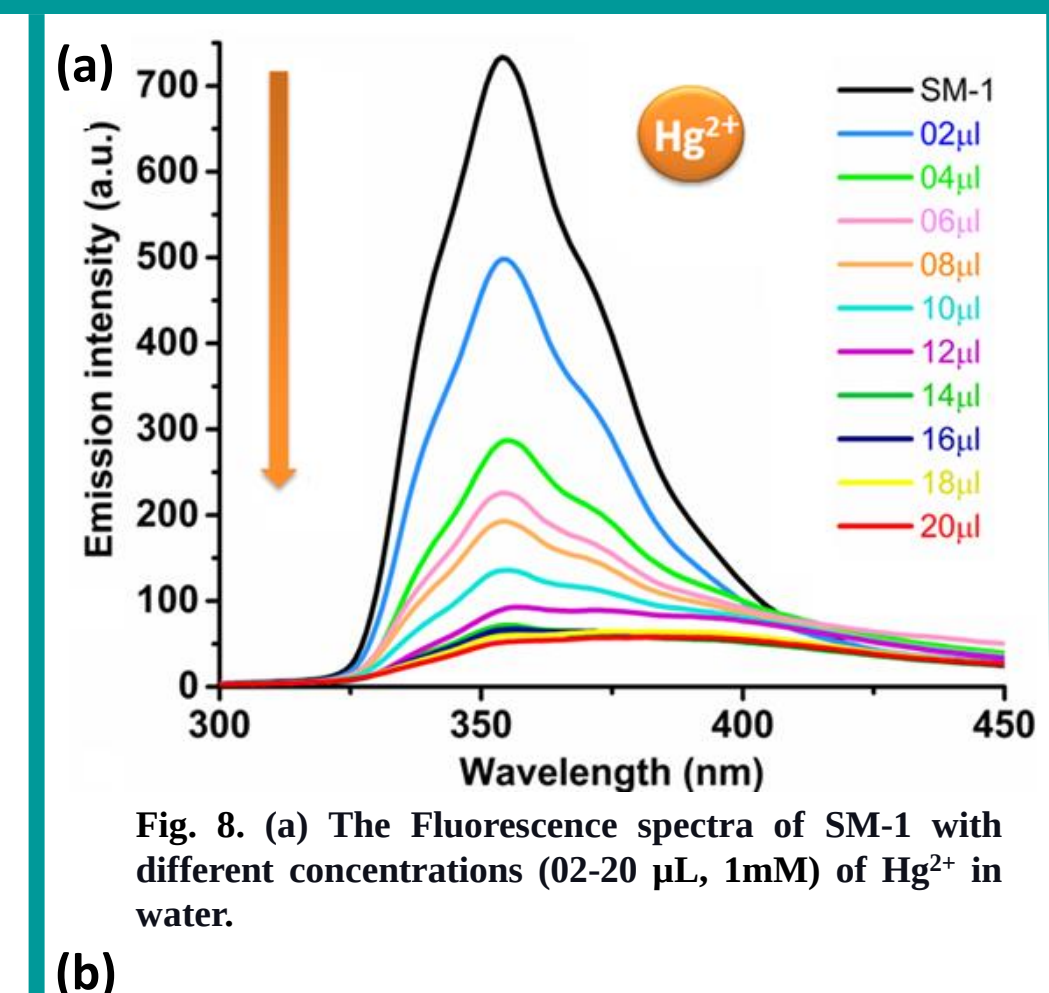


Fig. 8. (a) The Fluorescence spectra of SM-1 with different concentrations (0.2-20 μ L, 1mM) of Hg²⁺ in water.

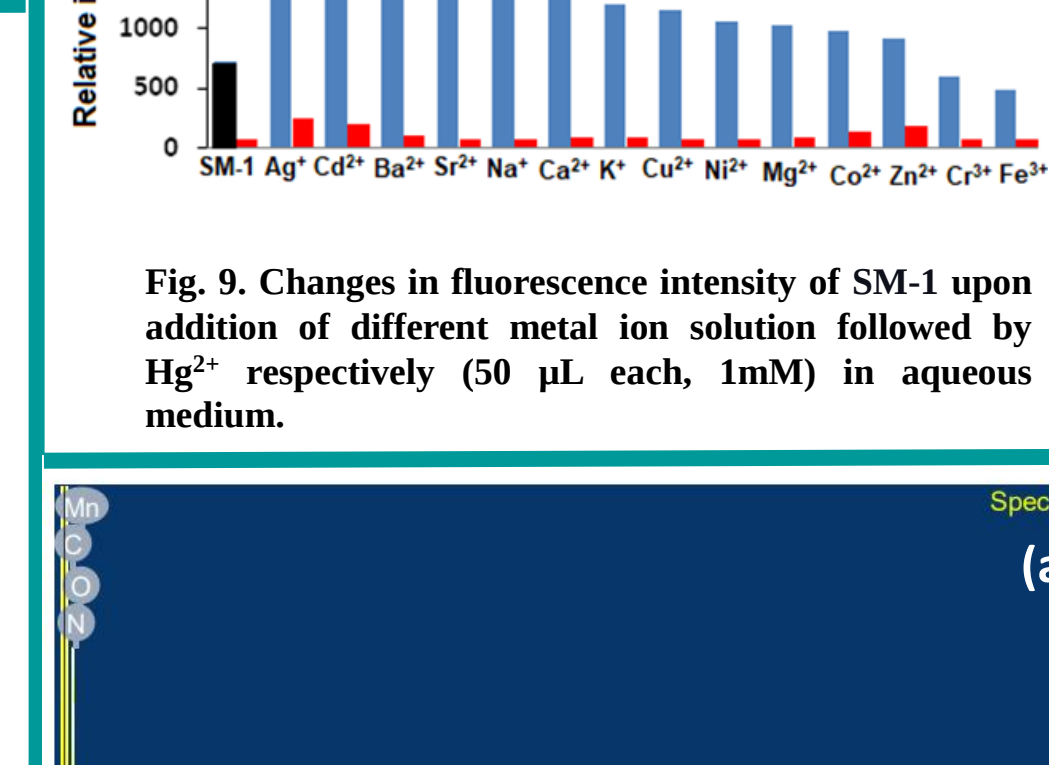


Fig. 9. Changes in fluorescence intensity of SM-1 upon addition of different metal ion solution followed by Hg²⁺ respectively (50 μ L each, 1mM) in aqueous medium.

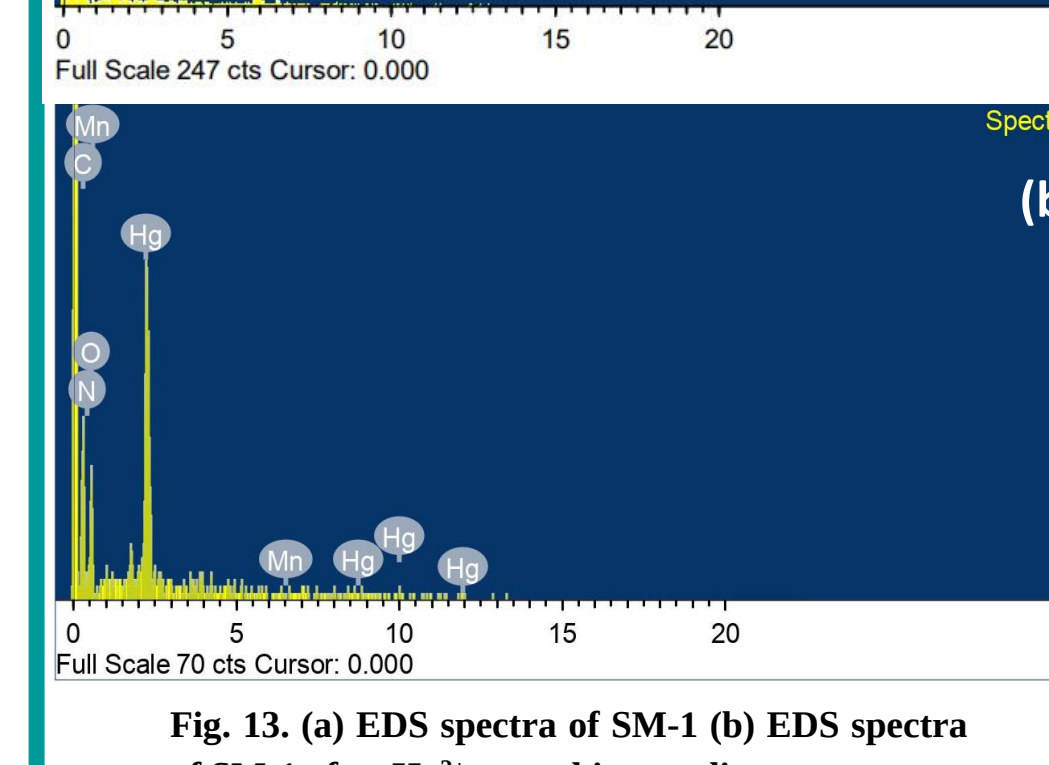


Fig. 10. Linear region of fluorescence intensity of SM-1 upon addition of Hg²⁺ in water.

- Limit of detection (LOD) SM-1 towards Hg²⁺ was calculated to be ~0.10 ppb which is considerably lower than the maximum permitted range in drinking water (6 ppb), set by the World Health Organization (WHO), and the limit of 2 ppb according to the U.S. Environmental Protection Agency (EPA).
- Owing to the electrostatic interaction occur between anionic framework and cationic-guest and strong affinity to bind with N and O donor atoms, thereby restricts the transfer of energy from π to π^* orbital of the chromophore and resulting in quenching of fluorescence intensity.
- The coordination of Hg²⁺ ions with imino group i.e., sp² hybridized -N of 4,7-Phen ligand possibly increases the sp³ character of Nitrogen, which can cause deviation of imino moiety from the plane of the benzene ring may reduce the degree of delocalization in SM-1, and hence overall quenches the emission intensity of SM-1.

Turn-OFF Sensing of Hg²⁺

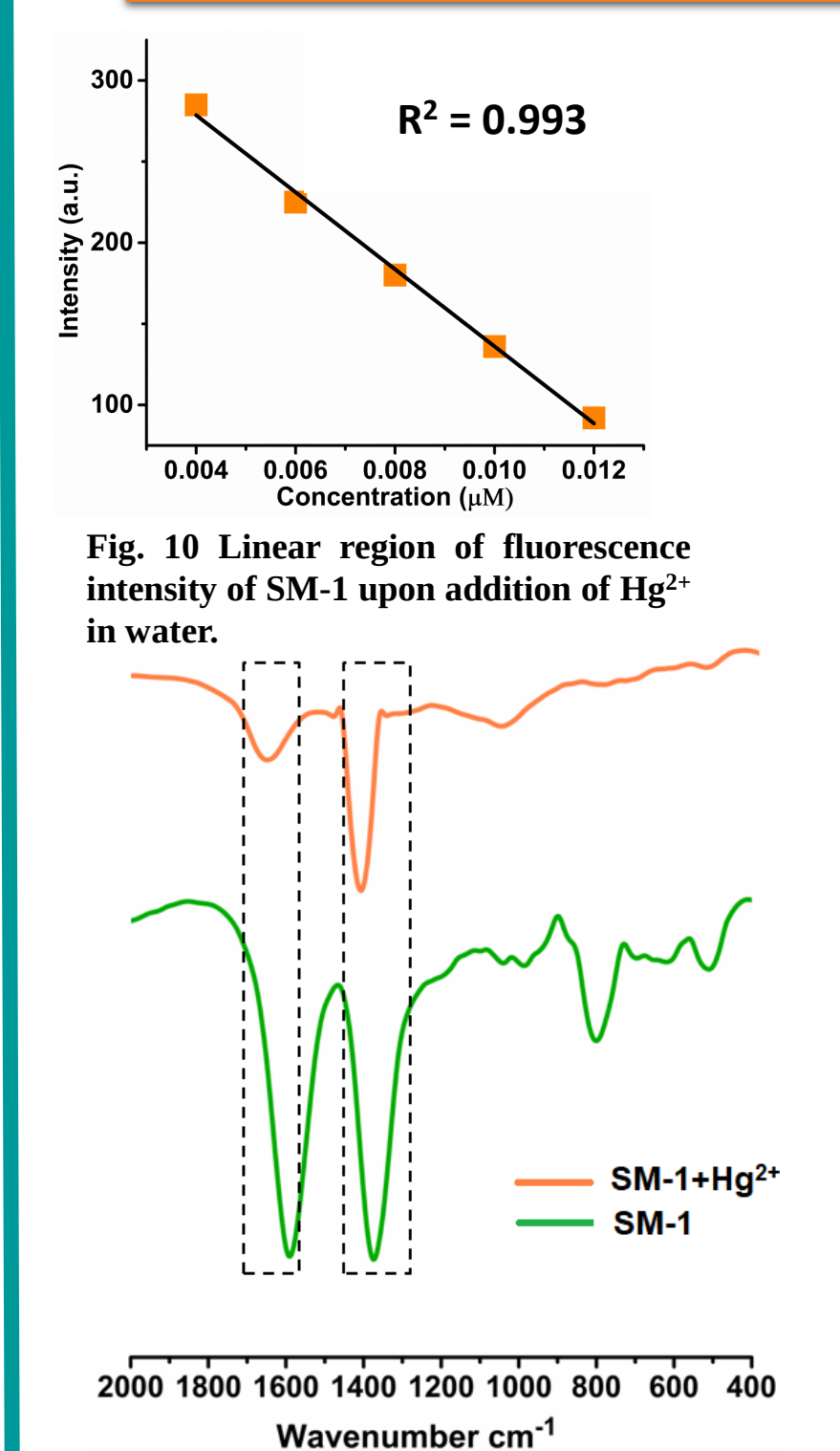


Fig. 11. FTIR spectra of SM-1 before and after the addition of Hg²⁺.

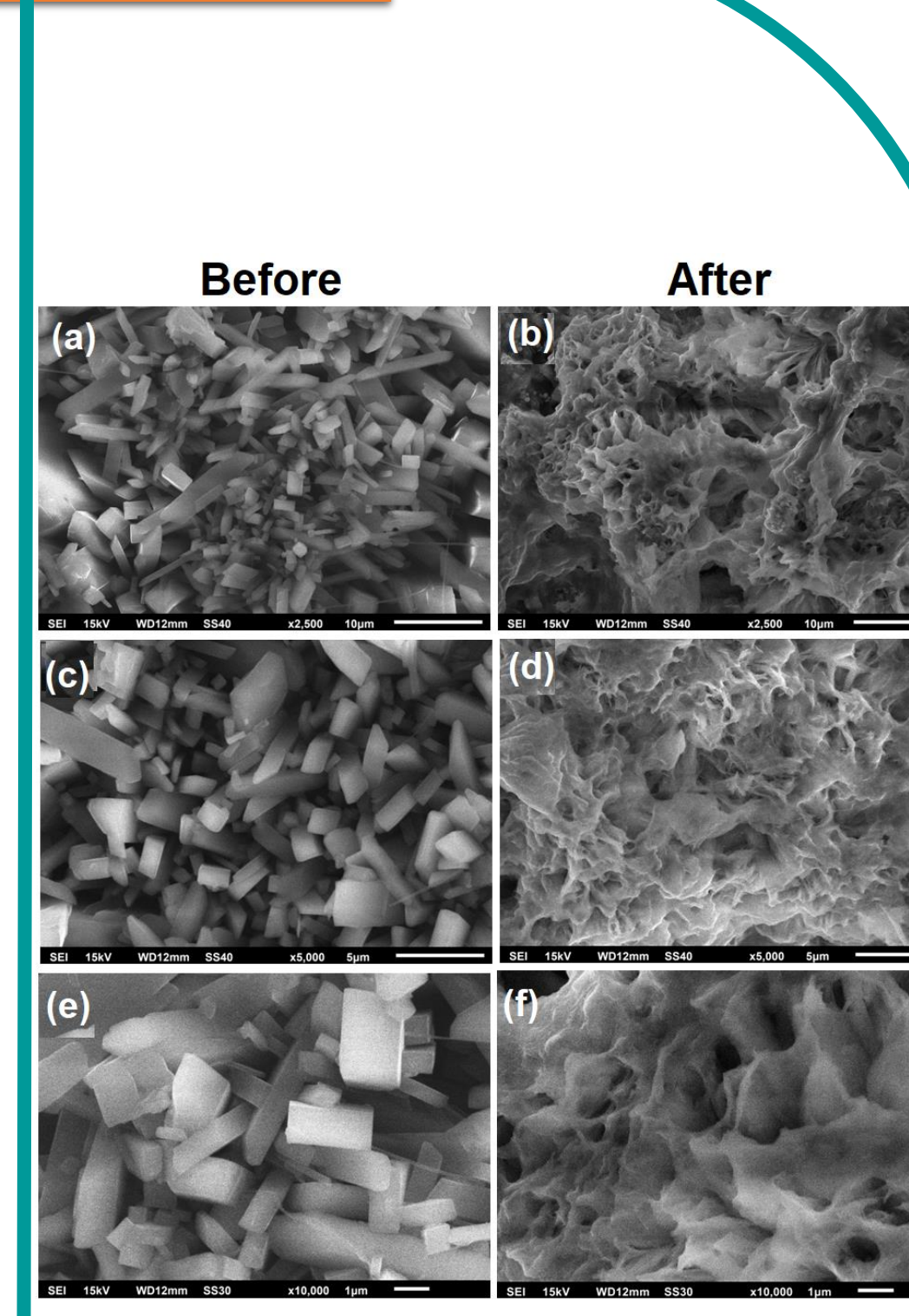


Fig. 12. SEM images of SM-1 before (a,c,e), and after Hg²⁺ sensing (b,d,f).

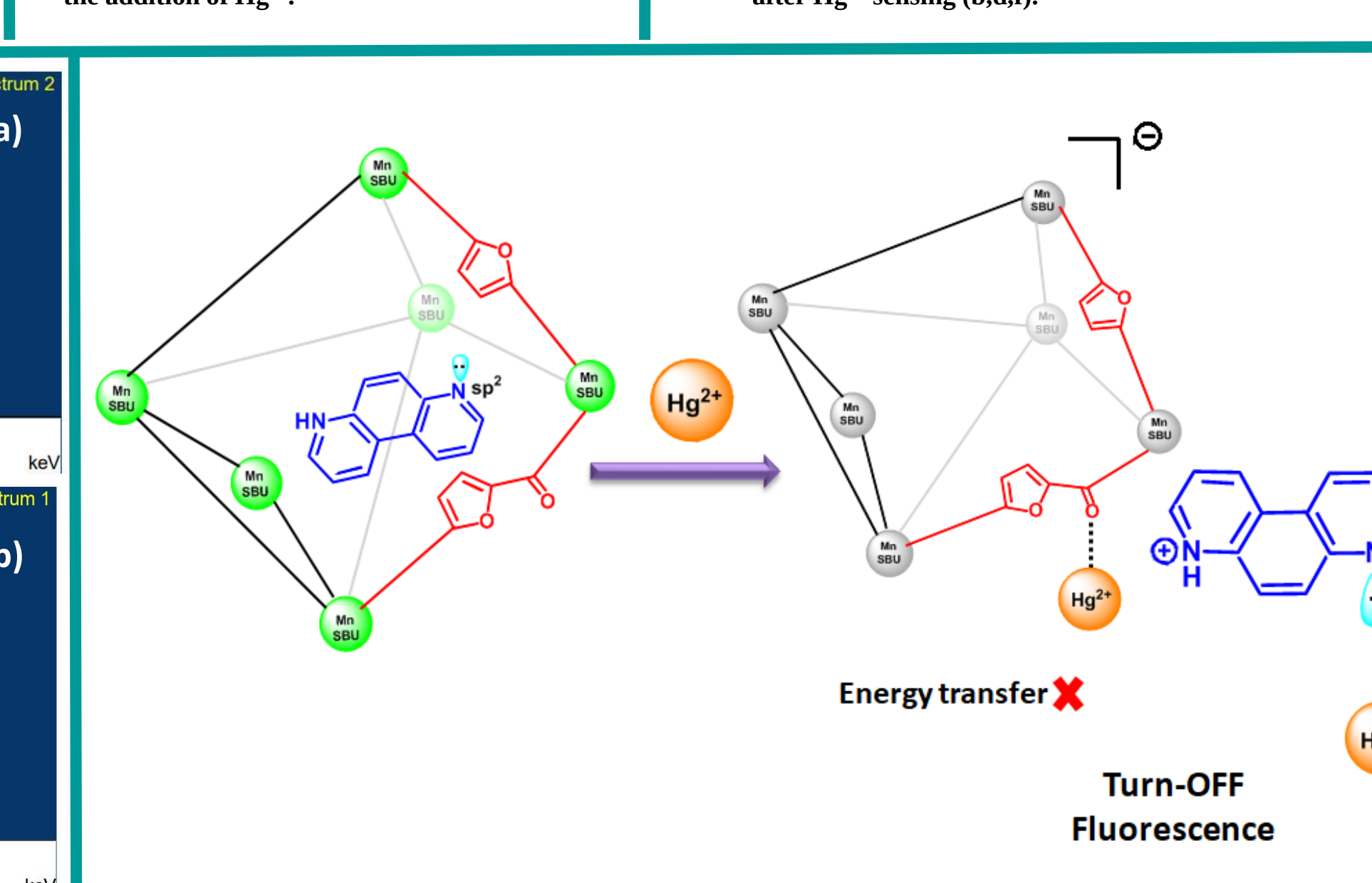


Fig. 13. Possible mechanism of SM-1 as Turn-OFF fluorescent probe for the aqueous phase detection of Hg²⁺ ions.

- Limit of detection (LOD) SM-1 towards Hg²⁺ was calculated to be ~0.10 ppb which is considerably lower than the maximum permitted range in drinking water (6 ppb), set by the World Health Organization (WHO), and the limit of 2 ppb according to the U.S. Environmental Protection Agency (EPA).
- Owing to the electrostatic interaction occur between anionic framework and cationic-guest and strong affinity to bind with N and O donor atoms, thereby restricts the transfer of energy from π to π^* orbital of the chromophore and resulting in quenching of fluorescence intensity.
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IODINE ADSORPTION

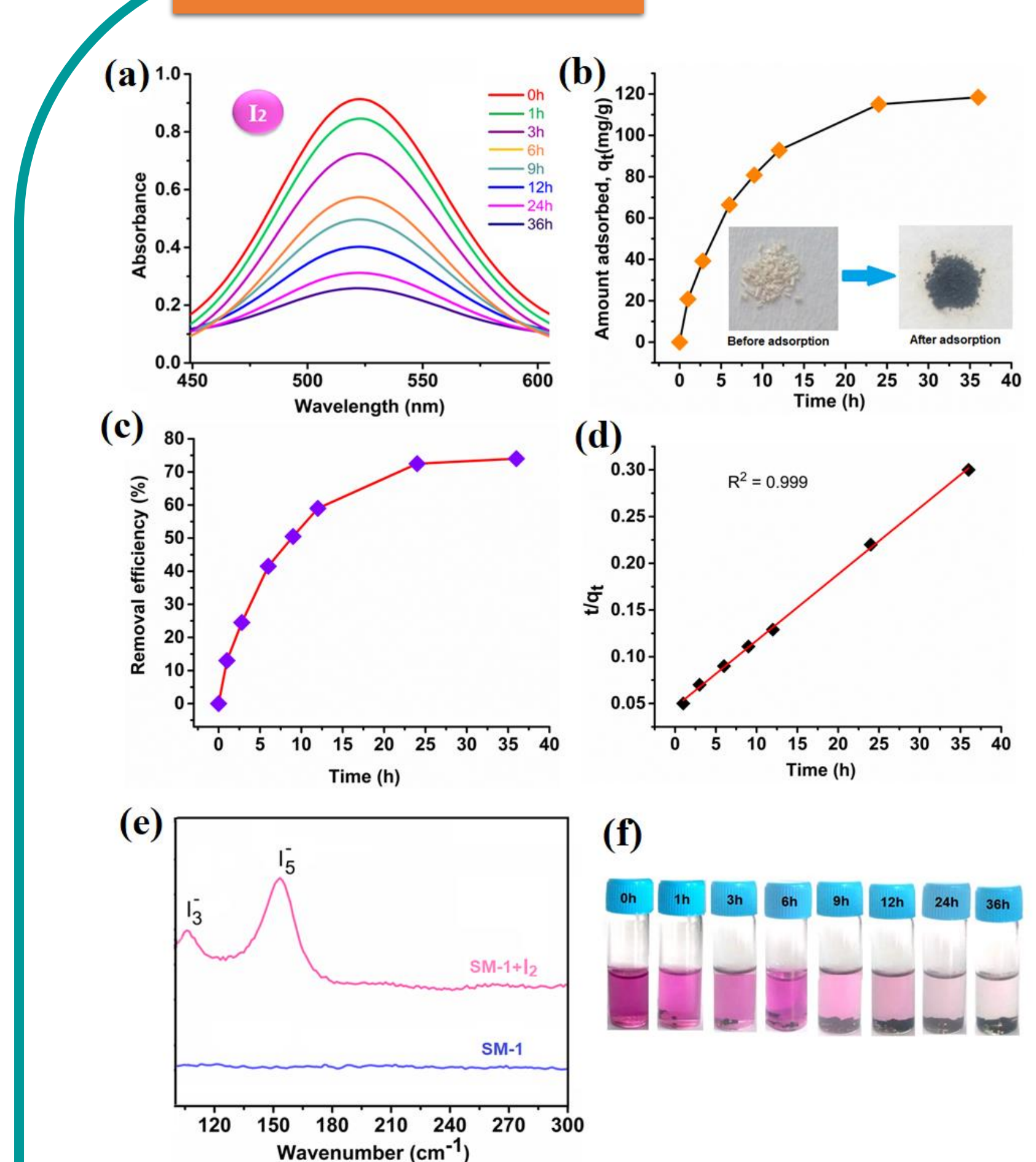


Fig. 14. (a) UV-Vis spectra of SM-1 adsorbing iodine over time in a cyclohexane solution of iodine (b) Adsorption amounts of SM-1 toward iodine in a cyclohexane solution of iodine when 30 mg of SM-1 is added (inset: images of the sample before and after I₂ adsorption) (c) Removal efficiency of SM-1 toward iodine in a saturated cyclohexane solution of iodine when 30 mg of SM-1 is added (d) Pseudo-second-order kinetics for the adsorption process of iodine by SM-1 in cyclohexane solution (e) Raman spectra of SM-1 before and after iodine loading (f) Photographs of time-dependent I₂ adsorption process by SM-1 in cyclohexane.

- At 36 h, the adsorption rate of SM-1 for iodine was slowed down and reached equilibrium, an optimum iodine removal efficiency of 75.4% was reached by SM-1 and the adsorption amount can reach 118.4 mg/g.
- Abundant π -electron rich moieties and free N-functionalized groups (-N, -NH) in SM-1 framework provide more accessible adsorption sites, hence strong charge-transfer complex is established between SM-1 and iodine, consequently facilitating the high iodine uptake.

CONCLUSION

- We successfully designed an anionic Mn-MOF (SM-1), assembled by trinuclear clusters ([Mn₃(COO)₆]²⁻), which provides additional stability to the framework.
- SM-1 exhibits dual-functional behavior due to the presence of fluorescent ligands, π -electron rich moieties, uncoordinated oxygen atoms and free 4,7-Phen rings composed of amino and imino groups.
- SM-1 works as a tremendous “turn-on” and “turn-off” sensor for Ag⁺, Cd²⁺ and Hg²⁺ ions, respectively, which has a harmful effect on human health.
- SM-1 can also capture radioactive iodine, which is considered one of the major sources of environmental pollution.
- This work gives beneficial hints to design multifunctional MOFs, which can be employed in fluorescent metal ion sensing and adsorption of iodine by utilizing distinct tailorable building blocks.

IODINE CAPTURE BY SM-1

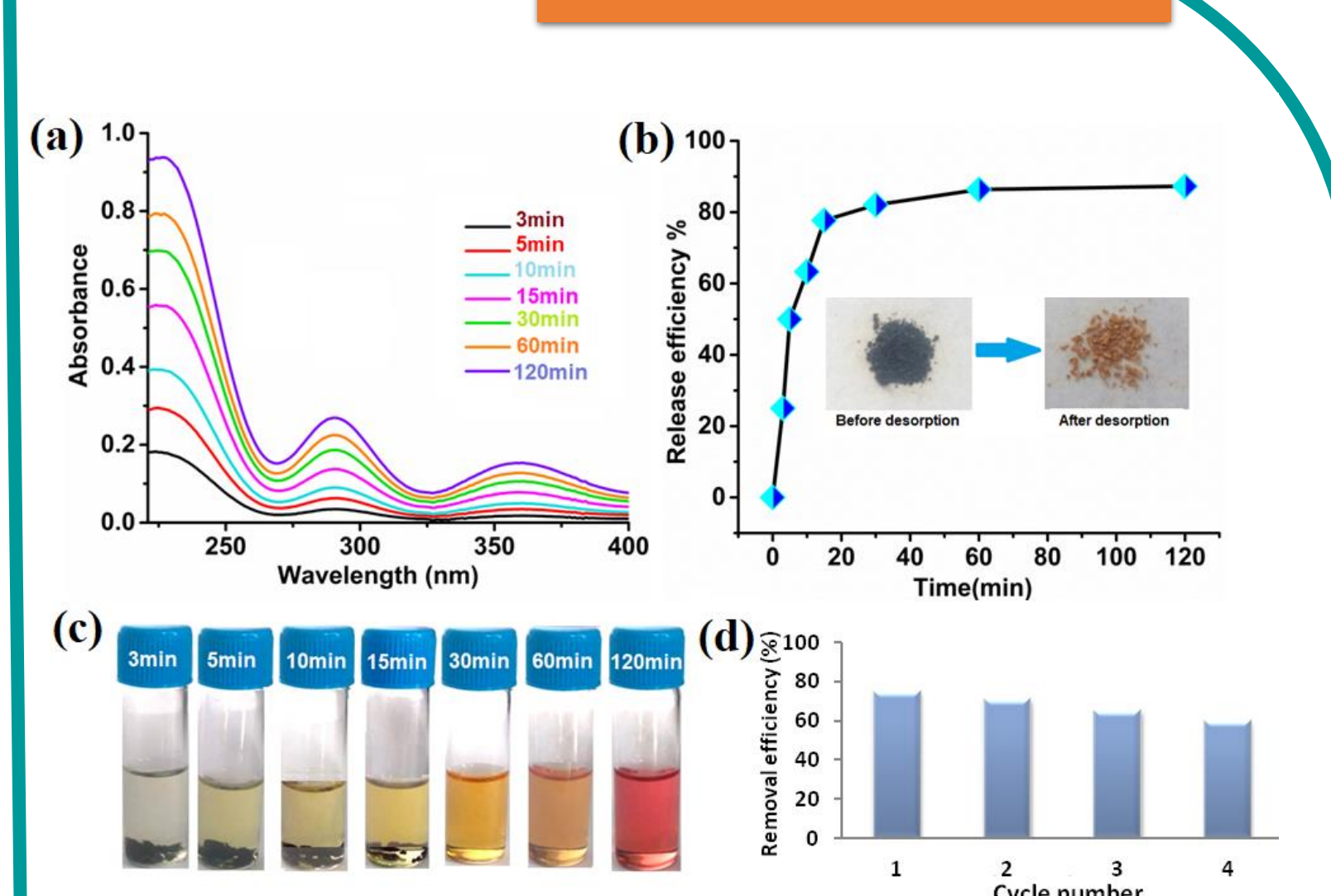


Fig. 15. (a) UV-Vis spectra for I₂ release from SM-1@I₂ in ethanol (b) Kinetic studies of iodine release from SM-1@I₂ in ethanol (c) Photographs of time-dependent I₂ desorption process by SM-1 in ethanol (d) Recyclability of SM-1 up to 4 cycles.

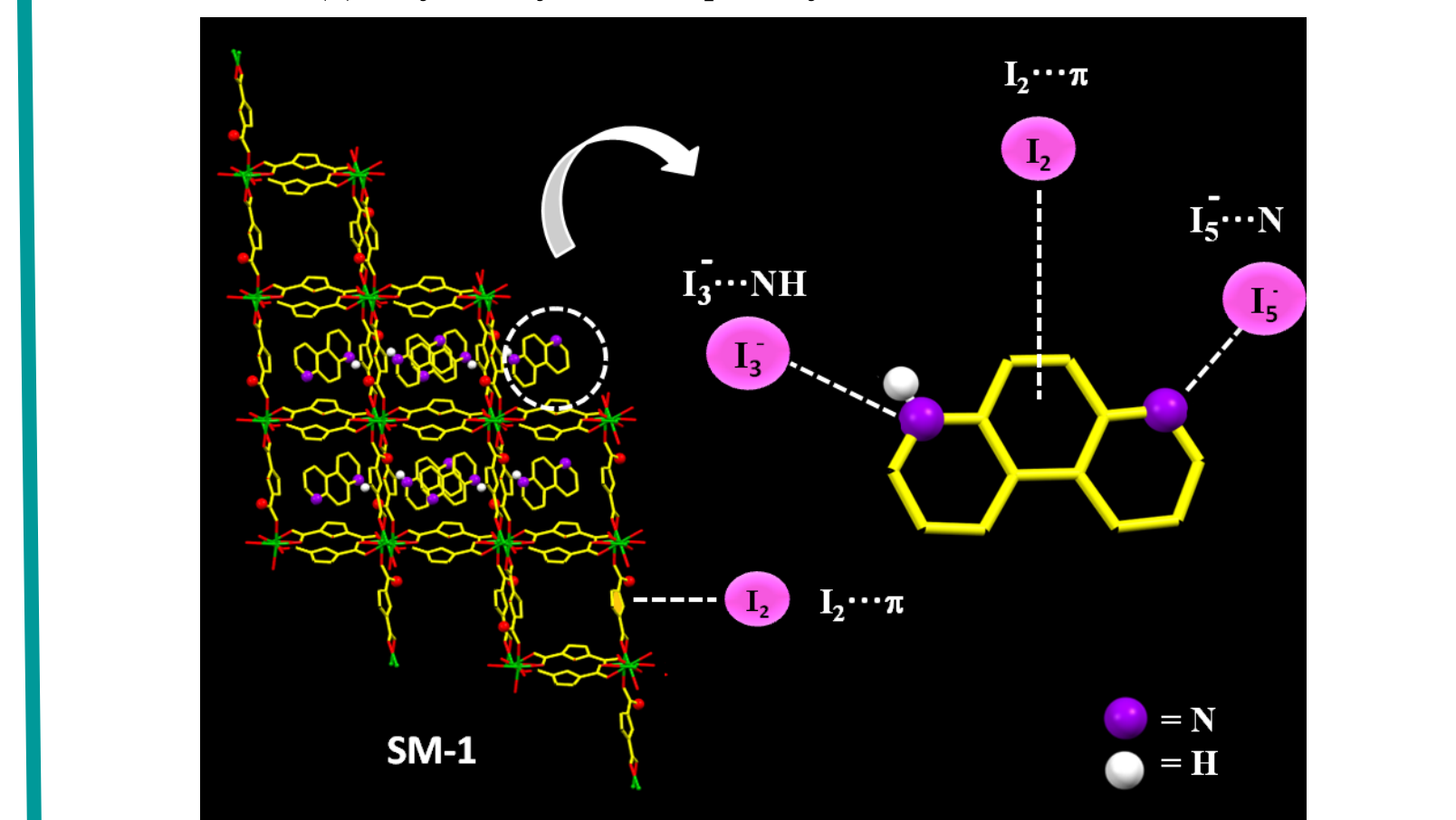


Fig. 16. Plausible mechanism of iodine adsorption by SM-1.

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