

ELECTRONIC SUPPLEMENTARY INFORMATION

S1. Reagents and Instrumentation Techniques

All the chemicals used for azo receptor and silica monolith synthesis were of analytical grade and used without any purification process. The azo receptor, (E)-4-((4,5-dimethylthiazol-2-yl)diazenyl)-6-hexylbenzene-1,3-diol (DMTHBD), was synthesized using chemicals such as 2-amino-4,5-dimethyl thiazole hydrochloride (>98%) and 4-hexylresorcinol (98%) purchased from Sigma Aldrich. The host matrix, mesoporous hexagonal silica framework (MHSF), was fabricated by using tetraethyl orthosilicate (TEOS, $\geq 99\%$), 1,3,5-triisopropyl benzene (TIPB, 95%), and Pluronic P123 (P123, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, average $M_n \sim 5800$). The pH adjustments were done by utilizing various combinations of buffers, such as 0.2 M $\text{ClCH}_2\text{COOH-HCl}$ (pH 1.0-3.0), $\text{CH}_3\text{COONa-CH}_3\text{COOH}$ (pH 4.0-6.0), MOPS-NaOH (pH 7.0-8.0), and CHES-NaOH (pH 9.0-10.0). The standard metal ion solutions (1000 mg/L), metal salts, and the solvents used for the experimental procedure were purchased from Sigma Aldrich and TCI chemicals with high purity grade.

The photomicrographs of the continuous mesoporous hexagonal network and sponge-like surface pattern of the host silica matrix were recorded on a transmission electron microscopy (TEM-SAED, G2 20 S-Twin, FEI-Tecnai model, 200kV) and field emission scanning electronic microscopy (FE-SEM-EDX, Quanta FEG-250, Thermo Fisher, 20kV), respectively. The elemental analysis was obtained by energy-dispersive X-ray spectrometer (EDS) using an Ultim Max EDS silicon detector coupled with the FE-SEM instrument. The well-packed mesoporous hexagonal nature (low-angle diffractogram) and amorphous nature (wide-angle diffractogram) of the parent silica monolith and corresponding chromogenic sensor material were examined using p-XRD instrument (D8 advance Bruker model, $\text{Cu(K}\alpha\text{)}$ radiation source (2.2 kW)). The BET surface areas of the synthesized products were analyzed by nitrogen adsorption-desorption isotherm measurements at 77 K on a nitrogen adsorption apparatus using a surface area analyzer (Quanta Chrome, autosorb iQ TRx). Pore size distributions were calculated from the desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. The authentication of the probe impregnation process and functionalities of receptor molecules were scrutinized using an FT-IR spectrophotometer (Thermo Scientific Inst. LLC, USA). The FT-IR spectra were recorded using the pressed pellet disc technique (KBr pellets) in the wavenumber range from 4000 to 400 cm^{-1} . The thermal stability and water retention capacity of the host matrix and DMTHBD@MHSF were analyzed using a thermogravimetric and differential thermal analyzer (TG-DTA, Seiko, SII 7200). The surface elemental composition and oxidation state of the analyte complexed sensor material and chromogenic sensory system were investigated using X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe III model, ULVAC-PHI. Inc., X-ray source of $\text{Al(K}\alpha\text{)}$ radiation (1486.6 eV). The colorimetric/spectral responses of the azo receptor in liquid and solid states were analyzed in the 200-800 nm range using a UV-Vis-DRS spectrophotometer (JASCO, V670). The composition of various existing metal ions in the collected environmental/industrial/non-industrial water samples was estimated using an inductively coupled plasma-mass spectrometer (ICP-MS, Agilent 7900). The structural elucidation of DMTHBD receptor molecules was analyzed using NMR spectra (Bruker Avance-II series 400 MHz) and CHNOS elemental analysis (PerkinElmer 2400 Series II elemental analyzer).

S2. Characterization of Azo receptor (DMTHBD):

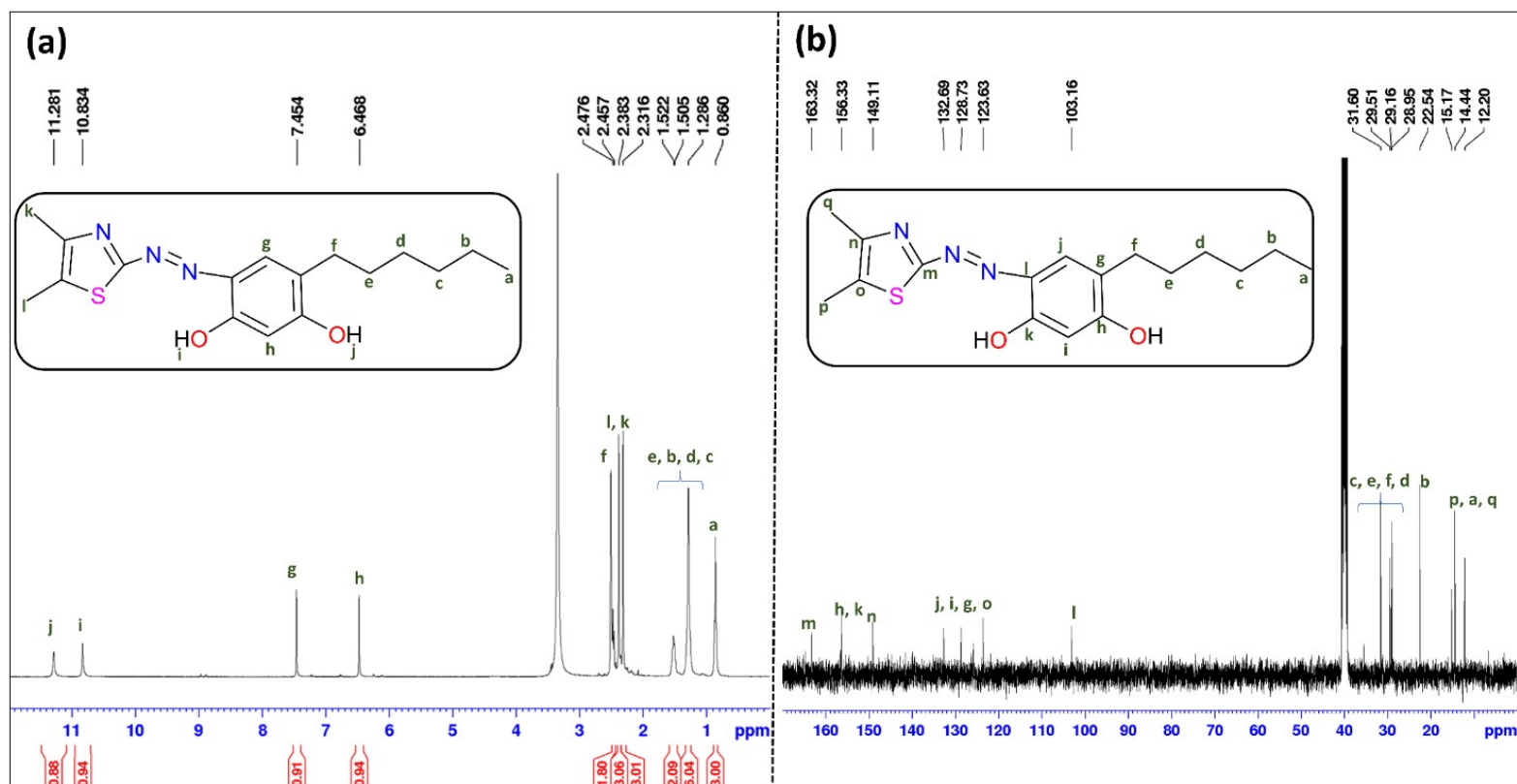


Fig. S1(a). ^1H NMR and (b) ^{13}C NMR spectra for the DMTHBD azo receptor in d_6 -DMSO.

DMTHBD Receptor: Yield: 83 % (Scarlet red solid). ^1H NMR (400 MHz) δ : 11.28 (s, 1H), 10.83 (s, 1H), 7.45 (s, 1H), 6.47 (s, 1H), 8.46 (d, $J = 7.6$ Hz, 2H), 2.38 (s, 3H), 2.31 (s, 3H), 1.51 (d, $J = 6.8$ Hz, 2H), 1.28 (s, 6H), 0.86 (s, 3H). ^{13}C NMR (d_6 -DMSO, 100.6 MHz) δ : 12.20, 14.44, 15.17, 22.54, 28.95, 29.16, 29.51, 31.60, 103.16, 123.63, 128.73, 132.69, 149.11, 156.33, and 163.32. FT-IR Spectra: O-H: 1328 and 3213 cm^{-1} , C=N^{Ar}: 1531 cm^{-1} , N=N: 1500 cm^{-1} , C-N: 1290 cm^{-1} , C-S: 1238 cm^{-1} CHNSO Analysis: %C 61.33 (61.23), %H 6.83 (6.95), %N 12.68 (12.60), %O 9.59 (9.60), and %S 9.57 (9.61); the theoretical data are implicated in parentheses.

S3. XPS Analysis for DMTHBD@MHSF Sensor Material

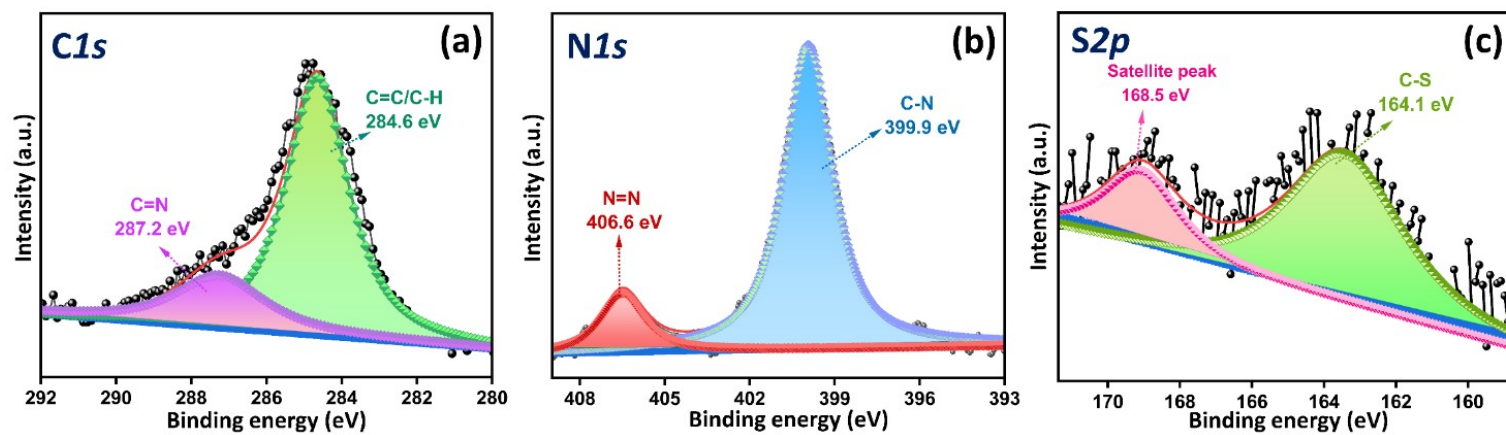


Fig. S2(a-c). Deconvoluted high-resolution spectra for $\text{C}1s$, $\text{N}1s$, and $\text{S}2p$ orbital states of DMTHBD@MHSF sensor.

S4. Binding Mechanism for DMTHBD- Cd^{2+} Complexation

S4.1. Benesi-Hildebrand Plot

The binding constant studies for the DMTHBD-Cd²⁺ complex were carried out by the Benesi-Hildebrand method, and the resultant data are depicted in **Fig. S3(a&b)**. The binding constant values computed for DMTHBD-Cd²⁺ complex in solid and liquid states were 8.08×10² and 3.29×10² M⁻¹, respectively. The DMTHBD-Cd²⁺ complex exhibits more excellent stability in the solid-state mode, affirming the superior ion-selectivity and stability of the probe-anchored silica monolithic sensor compared to the liquid-state sensor. The aliphatic nature of the hexyl group enhances the stability of complexes formed between the azo-receptor and target analyte, thereby maintaining the integrity of the sensing system over time. The binding constant values for the azo receptor with Cd²⁺ in both liquid and solid methods have been calculated using the equation,

$$\frac{1}{(A - A_0)} = \frac{1}{(A_{max} - A_0)} + \frac{1}{(A_{max} - A_0)K_{BH}[M^{n+}]}$$

Where A and A_0 are the absorbance values at λ_{max} in the presence and absence of Cd²⁺, A_{max} is the maximum absorbance recorded for the [DMTHBD-Cd²⁺] complex, K_{BH} is the binding constant and $[M^{n+}]$ is the concentration of the Cd²⁺.

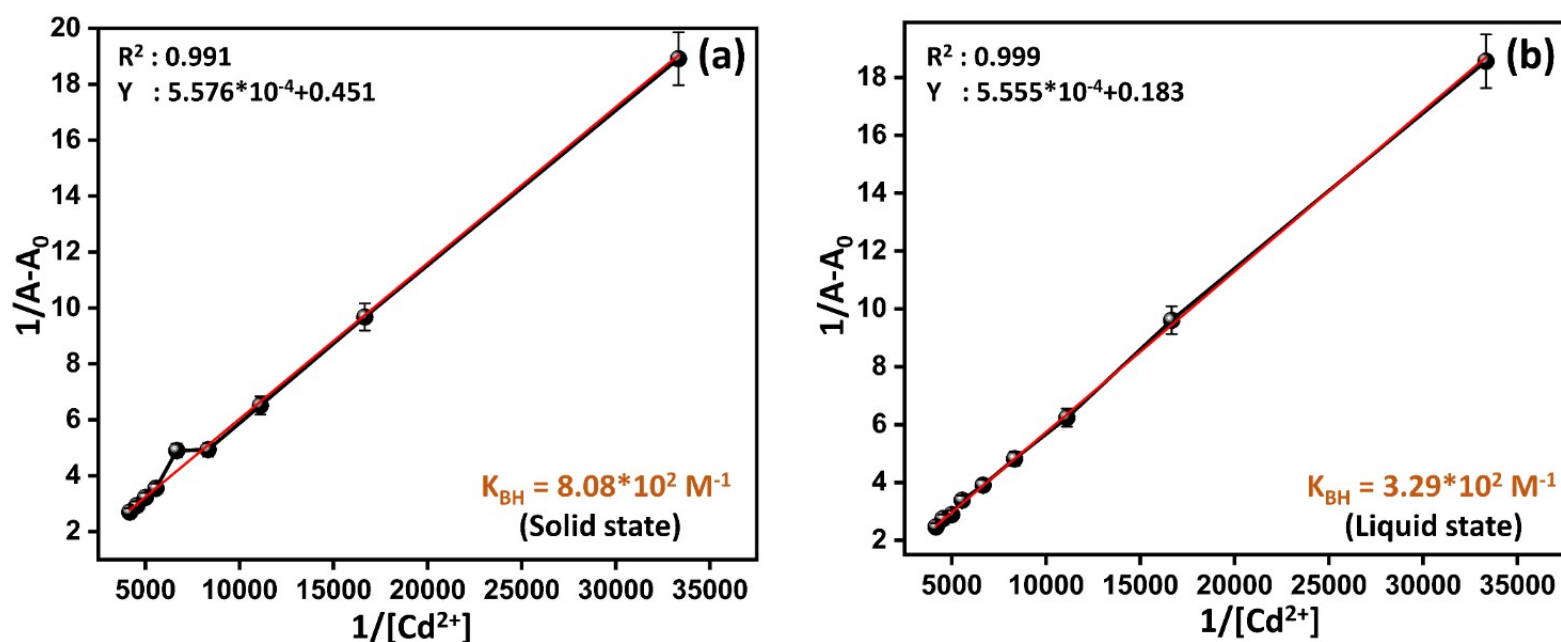


Fig. S3. Binding constant studies for DMTHBD-Cd²⁺ complex, (a) solid-state studies in aqueous medium and (b) liquid-state studies in ethanol medium.

S4.2. Job's Plot

The stoichiometric binding ratio between Cd²⁺ and azo receptor molecular probe (DMTHBD) was examined by continuous variation method (Job's method). These were carried out by adding various volumes (ranging from 0 to 2.0 mL) of 1.0×10⁻⁴ M of target analyte with different volumes of 2.0, 1.8, 1.6, 1.4, 1.2, 1.0, 0.8, 0.6, 0.4, 0.2, and 0.0 mL of the azo receptor probe (1.0×10⁻⁴ M). Here, the total volume of the solution was maintained at 2.5 mL by adding 0.5 mL of optimized buffer system (pH 8). The colorimetric and spectral change on incremental mole fraction values are depicted in **Fig. S4 (a & b)**. The absorbance was recorded at λ_{max} =560 nm and plotted against the mole fraction (**Fig. S4 (c)**). The maximum absorbance was recorded at a mole fraction of 0.5, which confirms that Cd²⁺ reacts with the receptor molecular probes in a 1:1 (metal: ligand) ratio.

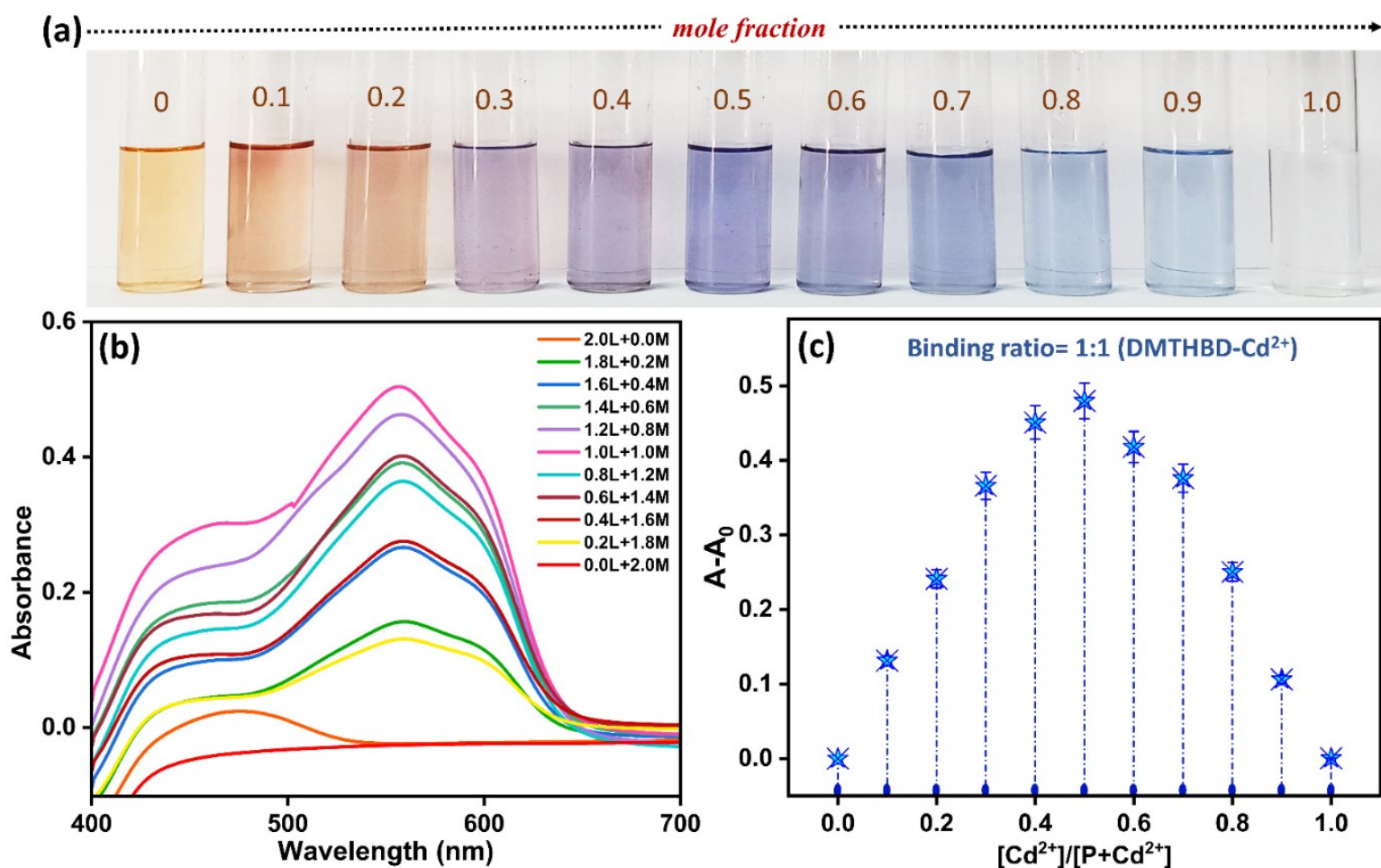


Fig. S4(a-c). Colorimetric response, UV-visible absorption spectra and Job's plot for DMTHBD-Cd²⁺ complex in ethanol medium.

S4.3. ¹H NMR Titrations

The stoichiometric binding interaction of the azo receptor (DMTHBD) with Cd²⁺ was further confirmed by a ¹H NMR titration experiment using DMSO-d₆ as the solvent medium. The ¹H NMR spectra of the ligand molecules revealed two -OH protons at the downfield region of 11.28 & 10.83 ppm, respectively. The titration plot, as depicted in Fig. S5, demonstrates a noticeable disappearance of the hydroxyl protons and a mild shift in the aromatic proton region upon the incremental addition of the target analyte. These observations align with the progressive nature of the complexation process, which reaches its maximum effectiveness at a stoichiometric receptor-analyte (DMTHBD-Cd²⁺) ratio of 1:1. This finding is consistent with the results obtained from the Job's plot, further corroborating the 1:1 binding ratio between the target analyte and the azo receptor.

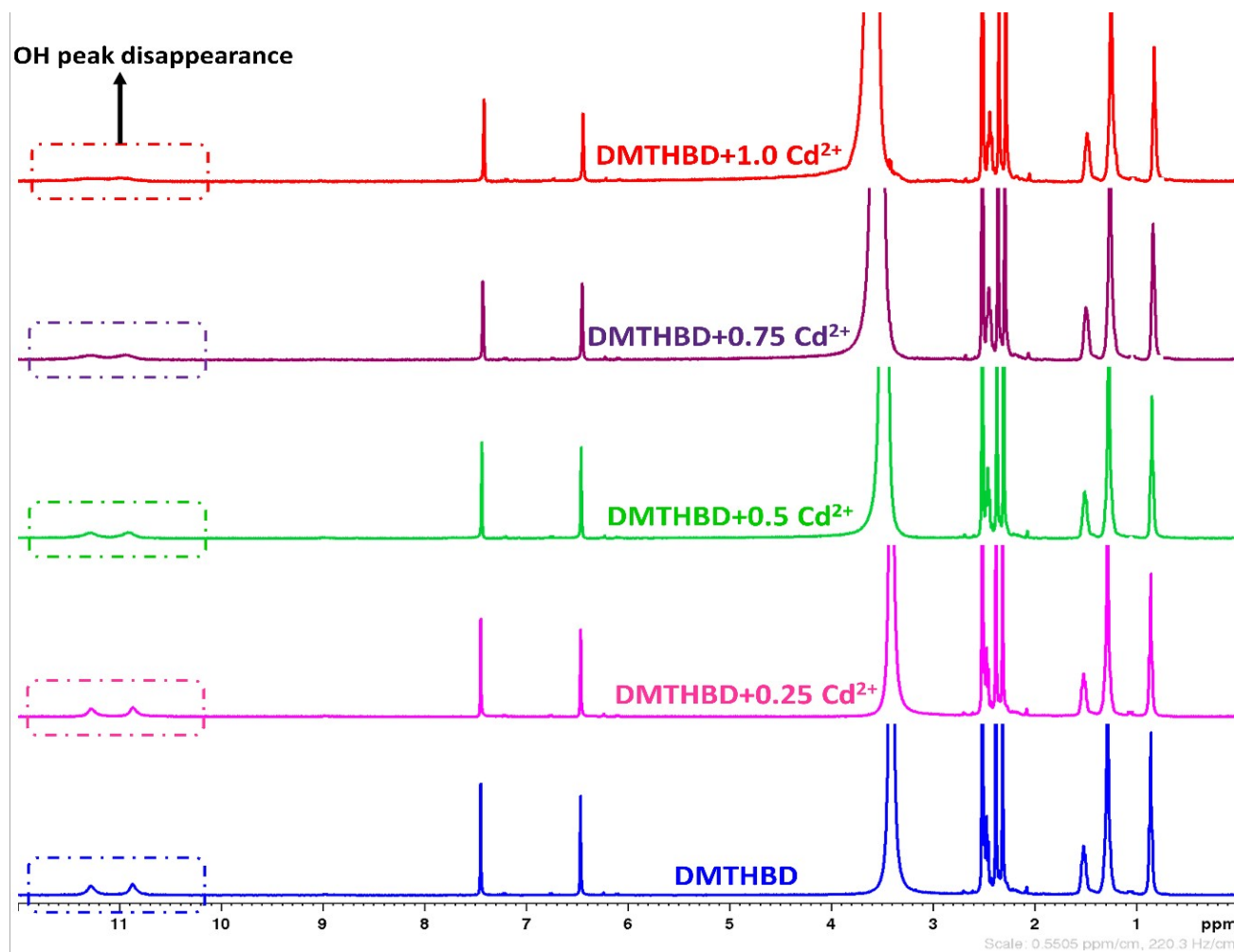
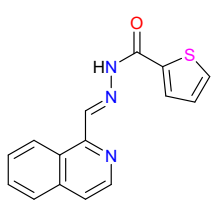
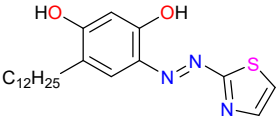
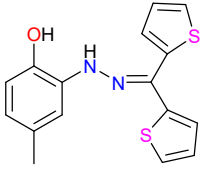

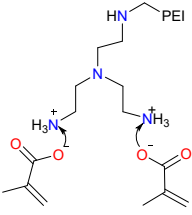
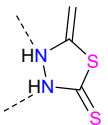
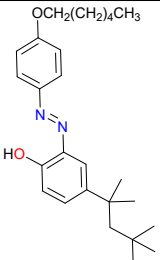


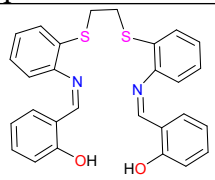
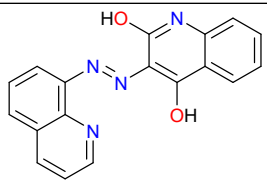
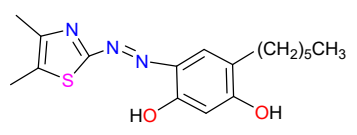
Fig. S5. ^1H NMR titration studies for DMTHBD azo receptor with incremental addition of Cd^{2+} in d_6 -DMSO.

S5. Performance Comparison Studies with Literature Reports

Table S1. Comparative literature survey portraying superior analytical features of the proposed DMTHBD@MHSF sensor.

S. No.	Probe Structure & Detection method	Sensor performance metrics ($\mu\text{g/L}$)	pH	Medium	λ_{max} (nm)	Application Studies (Yes/No)
1	 <p>Thiophene-2-carboxylic acid hydrazide-based colorimetric sensor for detection of cadmium ions.</p>	<p>Linear range: 562.07-3372.42</p> <p>R^2 : 0.995</p> <p>LOD: 22.48</p>	‡	Aqueous	425	Yes

2	 <p>Solid-state colorimetric detection of Cd²⁺ using L-B (Langmuir-Blodgett) thin-film methodology.²</p>	Linear range: 2.81-501.36	R ² : 0.996	7.5	Aqueous	607	Yes
			LOD: 4.38				
3	 <p>Wheat straw agricultural waste nanocomposite material for selective removal of Cd²⁺.³</p>	Linear range: 0-7.1	R ² : 0.993	5.5	Aqueous	450	Yes
			LOD: 4.17				
4	 <p>Gold nanoparticle-based colorimetric sensor for sensitive detection of Cd²⁺.⁴</p>	Linear range: 6.74-53.95	R ² : 0.996	6.5	Aqueous	520	Yes
			LOD: 3.37				
5	 <p>Ion imprinted polymer paper composite for detection of Cd²⁺.⁵</p>	Linear range: 1-100	R ² : 0.978	13	H ₂ O/HCl	560	Yes
			LOD: 0.4				
6	 <p>Functional ligand grafted mesoporous silica material as a sensor material for optical monitoring of Cd²⁺.⁶</p>	Linear range: 1-100	R ² : 0.979	5.5	†	362	No
			LOD: 0.36				
7	 <p>Innovative nanocomposite</p>	Linear range: 2-100	R ² : 0.999	6.0	†	515	No
			LOD: 0.33				

materials for detection and adsorption of Cd ²⁺ . ⁷						
8	 <p>Selective and effective detection of Cd²⁺ using ligand-modified composite material.⁸</p>	<p>Linear range: 2-100</p> <p>R² : 0.998</p> <p>LOD: 0.32</p>	3.5	Aqueous	412	No
9	 <p>Probe impregnated polymer material as a sensor for visual detection of Cd²⁺.⁹</p>	<p>Linear range: 2-150</p> <p>R² : 0.999</p> <p>LOD: 0.31</p>	8.0	Aqueous	475	Yes
10	 <p>Azo receptor conjoined mesoporous hexagonal silica framework as a solid-state colorimetric sensor for Cd²⁺. (This work)</p>	<p>Linear range: 1-150</p> <p>R² : 0.998</p> <p>LOD: 0.15</p>	8.0	Aqueous	560	Yes

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