SRI VENKATESWARA INTERNSHIP PROGRAM
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Student Internship

SRI-VIPRA

Project Report of 2025

SVP-2508

"Synergistic Interactions between MOFs and Thermo-Responsive Polymers: A Study on Stimuli-Driven Phase Transition"

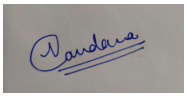
IQAC
Sri Venkateswara College
University of Delhi
Benito Juarez Road, Dhaula Kuan, New Delhi
New Delhi -110021

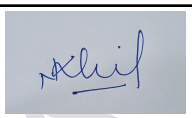
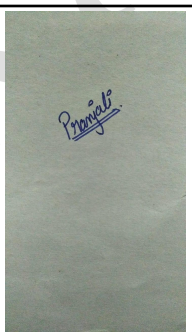
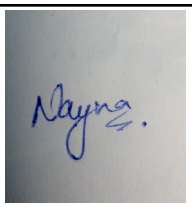
SRIVIPRA PROJECT 2025

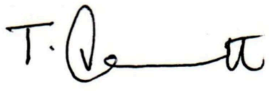
Title : Synergistic Interactions between MOFs and Thermo-Responsive Polymers: A Study on Stimuli-Driven Phase Transition

Name of Mentor: Dr. T. Vasantha **Name of Department:** Chemistry **Designation:** Assistant Professor Sri Venkateswara College University of Delhi	**Photo** 

List of students under the SRIVIPRA Project

S.No	Photo	Name of the student	Roll number	Course	Signature
1		Nandana Santhosh	1223006	Bsc (H) Biochemistry	
2		Sreejesh Nair	1124176	Bsc (P) Life Sciences	

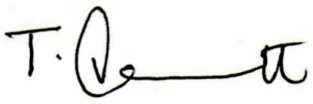
3		Rimjhim Jeena	1123096	Bsc (P) Life Sciences	
4		Nikhil Mathur	1523078	Bsc (H) Chemistry	
5		Pranjali	1523010	Bsc (H) Chemistry	
6		Nayna	1124128	Bsc (P) Life Sciences	



Signature of Mentor

Certificate of Originality

This is to certify that the aforementioned students from Sri Venkateswara College have participated in the summer project SVP-2508 titled "**Synergistic Interactions between MOFs and Thermo-Responsive Polymers: A Study on Stimuli-Driven Phase Transition"**.The participants have carried out the research project work under my guidance and supervision from 1st July, 2025 to 30th September 2025. The work carried out is original and carried out in an hybrid mode (offline and online).



Signature of Mentor

Acknowledgement

We express our deepest gratitude to **Sri Venkateswara College** for offering us this invaluable opportunity. Our sincere thanks extend to the **Department of Chemistry**, **Sri Venkateswara College**, for their unwavering support throughout the project.

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List of Abbreviations

Abbreviation	Full Form
MOF	Metal Organic Framework
nMOF	Nano Metal Organic Framework
PCN	Porous Coordination Network
PCP	Porous Coordination Polymer
ZIF	Zeolitic Imidazolate Framework
UiO	Universitetet i Oslo (Oslo University MOF family, e.g., UiO-66)
MIL	Materials of Institute Lavoisier (MOF family, e.g., MIL-101)
HKUST	Hong Kong University of Science and Technology (MOF family, aka Cu-BTC)
IRMOF	Isoreticular Metal Organic Framework
PNIPAM	Poly(N-isopropylacrylamide)
PVCL	Poly(N-vinylcaprolactam)
OEGMA	Oligo(ethylene glycol) methacrylate
PU	Polyurethane
FA	Folic Acid
CMC	Carboxymethyl Cellulose
PEO	Polyethylene Oxide

PA-g-CS	Polyacrylamide-grafted-Chitosan
LCST	Lower Critical Solution Temperature
DLS	Dynamic Light Scattering
UV-Vis	Ultraviolet Visible Spectroscopy
AuNP	Gold Nanoparticle
Eu^{3+}	Europium (III) ion
Tb^{3+}	Terbium (III) ion
ANS	1-Anilino-8-naphthalenesulfonate

Introduction

A polymer is a macromolecule composed of many repeated small units called monomers that are covalently linked into long chains or networks. Polymers span an enormous range of structures from linear and branched chains to crosslinked networks, and from completely synthetic (for example polyolefins and polyacrylates) to naturally occurring biopolymers (for example polysaccharides and proteins). The defining features of polymers — large molecular weight, chain connectivity, and the possibility of structural heterogeneity — underlie their unique mechanical, thermal, and solution behaviors and make them a distinct class of materials in chemistry and materials science [1]. Polymer properties arise from chemistry at two length scales: the chemical identity of repeat units and the chain-level architecture. Key thermal properties include glass transition temperature, melting temperature and decomposition temperature, all of which reflect chain mobility and intermolecular interactions. Mechanical properties such as tensile strength, modulus and toughness depend on chain entanglement, crystallinity and crosslink density. Solution and surface properties — solubility, hydrophobicity/hydrophilicity, and surface energy — control processing and interactions with solvents, biological media and other materials. In addition, functional polymers can show stimuli-responsiveness (temperature, pH, light, ionic strength) where small environmental changes produce large property changes; these phenomena are now well documented and exploited. These properties allow for their effective tuning and exploitation for various applications [2]. Because polymer properties are highly tunable, applications are extremely broad. Structural polymers are ubiquitous in packaging, textiles and construction. Functional and specialty polymers find use in electronics, membranes, catalysts and coatings. In the biomedical arena, polymers provide controlled drug release matrices, tissue scaffolds, surgical adhesives and medical devices; their biocompatibility and biodegradability are central design criteria for many applications. Thermo- and stimuli-responsive polymers enable smart drug delivery, actuators and adaptive surfaces where the polymer responds to body temperature or other cues [3], [4]. Polymers that show a lower critical solution temperature (LCST) behavior in an aqueous solution are soluble below LCST due to extensive hydrogen bonding interactions between the polymer and surrounding water molecules. Above LCST, hydrogen bonding with water molecules is disturbed and the intra- and intermolecular hydrophobic and hydrogen bonding interactions become more dominant, as a result, the polymer becomes insoluble in an aqueous solution upon heating. When water molecules are repelled from the polymer chain at elevated temperatures, hydrogen bonds (between water and polymer

chain) are broken and new hydrogen bonds are formed resulting in a change in enthalpy. In addition, entropy increases as water molecules are no longer constrained. Hence, based on Gibbs free energy equation ($\Delta G = \Delta H - T\Delta S$), phase transition from soluble to insoluble polymer chains becomes spontaneous as the temperature gets above the threshold value (LCST) due to so-called "hydrophobic effect" [5]**.** Thus, polymers exhibiting a lower critical solution temperature (LCST) are soluble below the LCST (due to polymer-water hydrogen bonding) but collapse and phase-separate above LCST as hydrophobic interactions dominate [6], [7]. Among these, poly(N-isopropylacrylamide) (PNIPAM) is the most extensively studied. PNIPAM has LCST of ~32 °C, that is close to body temperature which makes it highly relevant for biomedical applications such as drug delivery, diagnostics, and tissue engineering [8], [9]. PNIPAM contains hydrophilic amide groups (-CO-NH-) and hydrophobic isopropyl groups (-CH(CH3)2). When the temperature is below LCST, amide groups form hydrogen bonds with water molecules, causing polymer expansion and dissolution in water for uniform phases. Upon exceeding the LCST, the hydrophobic group's action surpasses the hydrogen bond between the amide group and the water molecule, resulting in polymer contraction, aggregation, and phase separation [10]. However, PNIPAM faces concerns regarding cytotoxicity and hysteresis effects, limiting its in vivo utility [11], [12], [13]. By contrast, poly(N-vinylcaprolactam) (PVCL) is considered more biocompatible and tunable. Unlike PNIPAM, PVCL displays a classical Flory-Huggins (Type I) thermoresponsive behavior, where LCST decreases with increasing molecular weight and concentration. This allows easier adjustment of the transition temperature without complex copolymerization strategies [13], [14].Reported LCST values for PVCL in pure water commonly lie in roughly 32–37 °C, though some reports give a broader range (25–50 °C) depending on conditions and polymer details [15]. Importantly, PVCL hydrolysis does not yield toxic small molecules, enhancing its suitability for biomedical use. Other examples include oligo(ethylene glycol) methacrylate (OEGMA) based polymers and poly(ethylene oxide)/poly(propylene oxide) block copolymers (Pluronics or poloxamers), whose cloud points depend on block composition and concentration [16], [17].

For tuning the LCST, the polymer can be attached to a Metal Organic Framework(s) (MOFs). Metal–organic frameworks (MOFs), also called porous coordination networks (PCNs) or porous coordination polymers (PCPs), are a class of porous materials constructed by metal nodes/clusters and organic linkers, forming numerous architectures. The metal ions can create compounds with unique coordination modes, having tetrahedral, trigonal bipyramidal, square planar, and octahedral geometries.

Meanwhile, the most used organic linkers are polytopic carboxylates and other aromatic heterocyclic molecules, facilitating coordination chemistry with the metal ions [18], [19].

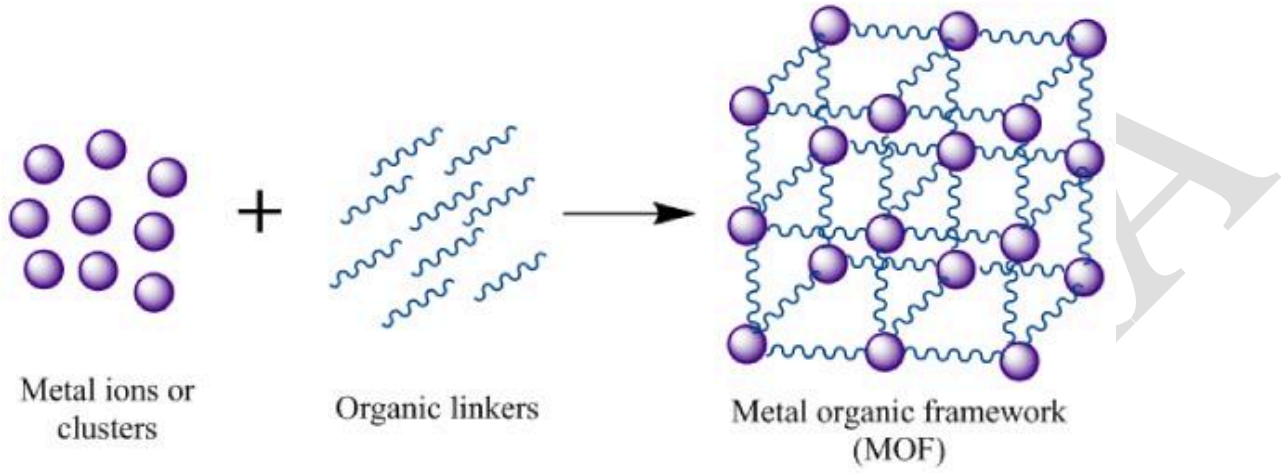


Fig.1. General structure of an MOF

This design of MOFs allows precise control over pore size, shape, and chemistry, providing exceptionally high surface areas and tunable adsorption properties. Since the founding work of Hoskins and Robson in 1989, MOFs have been explored for a wide range of applications including gas storage, purification, separation, catalysis, and chemical sensing [20], [21]. At nanoscale, nano-MOFs (nMOFs) offer additional advantages relevant for biological applications, including enhanced cellular uptake, controlled degradation, and low cytotoxicity when synthesized with biocompatible metals and linkers [22], [23]. Variety of combinations including, ZIF-8 and UiO-based nMOFs have been extensively studied as drug delivery carriers, offering controlled release under acidic conditions and superior protection of biomolecules compared to mesoporous silica and dendrimers [24], [25]. But the drawback regarding them is that these MOFs often exhibit limited thermal stability, susceptibility to degradation, and sensitivity to acidic and basic conditions. To address these limitations, the integration of MOFs with polymers has shown promising potential. Conventional MOFs face two major limitations: 1. Aggregation during synthesis or post-processing, which reduces surface area and pore accessibility. 2. Poor stability in aqueous or physiological environments, where hydrolysis can release toxic organic linkers [26]. To

overcome these issues, bio-MOFs which are constructed with biomolecules such as amino acids, peptides, and polysaccharides have emerged as sustainable alternatives. These bio-MOFs offer biocompatibility, structural diversity, and improved stability, while reducing environmental and biological toxicity [27]. The integration of biomass-derived templates further enhances dispersity and promotes sustainable synthesis routes.

When a thermoresponsive polymer is tethered to a MOF surface, grown inside pores, or embedded as a network around MOF particles, the MOF can (1) change effective solvent quality by sequestering water or salts, (2) impose confinement that alters chain conformation and transition cooperativity, and (3) provide additional responsive inputs (for example adsorption/desorption of guests that change local humidity or ionic strength). These effects have been exploited to make switchable adsorbents for temperature-mediated water capture and to create MOF–hydrogel composites with temperature-controlled porosity and release [28], [29]. Such MOF-polymer hybrids have already shown promise in drug delivery systems, where polymer swelling/collapse controls drug release kinetics, and in biosensing, where polymer conformational changes modulate analyte access to MOF-embedded sensing sites [30], [31]. Building upon these insights, the present work focuses on designing Cu-based MOFs (Cu-VA type) integrated with LCST thermoresponsive polymers (PNIPAM, PVCL, and their derivatives). When combined with thermoresponsive polymers, these hybrids are expected to yield smart systems with temperature-triggered functional control.

Such hybrid materials could be applied to:

- Drug delivery, where temperature-controlled release is desirable in localized therapy.
- Catalysis and sensing, where polymer conformational changes regulate substrate access.
- Sustainable materials, where bio-inspired MOFs and polymers enable safe, environmentally friendly designs.

Thus, the aim of this study is to explore the synergistic properties of MOF-polymer hybrids, with a focus on Cu-based MOFs and LCST polymers, highlighting their structural, functional, and application-driven potential.

Literature Survey

MOF	Polymer / Additive	Combination type	Key Insight	Application	References
UiO-66	PNIPAM	Surface-functionalized MOF	Regulated release of guest molecules (resorufin, caffeine, procainamide); stability at 37 °C	Temperature-controlled drug delivery	[32], [33]
ZJU-64 / ZJU-64-CH_3	None (biomolecular linker: adenine + carboxylate)	Zn-based porous MOF	3D frameworks with 1D channels; low toxicity	Anticancer drug delivery	[34]
ZIF-8	AuNP + Eu^{3+}/Tb^{3+}	Core-shell MOF + nanoparticles	Light-triggered thermoresponsive drug release; dual function: heater + thermometer	Smart drug release, responsive nanomaterials	[35]
nMOFs	PNIPAM	Core-shell microgel hybrid	Reversible swelling/collapse of polymer; in vitro thermal-responsive drug release; biocompatible	Lubrication & thermoresponsive drug delivery	[36]
IRMOF-3	PNIPAM (gel)	Surface-coated MOF	Nanocarrier for norcantharidin; sustained release; cell	Anticancer therapy	[37]

			cycle arrest & apoptosis induction		
UiO-66 / HKUST-1	PU / FA / CMC / PEO	MOF-polymer composite / nanofiber	High drug loading, controlled release, catalytic sites	Cancer therapy, catalytic drug release	[38]
MIL-53 / MIL-101 / MOF cores	PA-g-CS / PU	Core-shell nanofibers	Combined chemo-thermal therapy; hydrophilic MOF + hydrophobic polymer synergy	Glioblastoma therapy; responsive drug release	[39]
MIL-101(Cr)	PNIPAM	Polymer-filled MOF cavities	Thermoresponsive water adsorption; phase-change triggered hydrophilicity; high water uptake (≈440 wt.%)	Smart water sorption, adsorption heat pumps	[40]

Research Methodology

Materials Required; PNIPAM crystals, PVCL crystals, Cu-Va MOF crystals, ANS solution, Distilled Water, UV-Vis Spectrophotometer, Fluorimeter, DLS instrument.

Procedure:

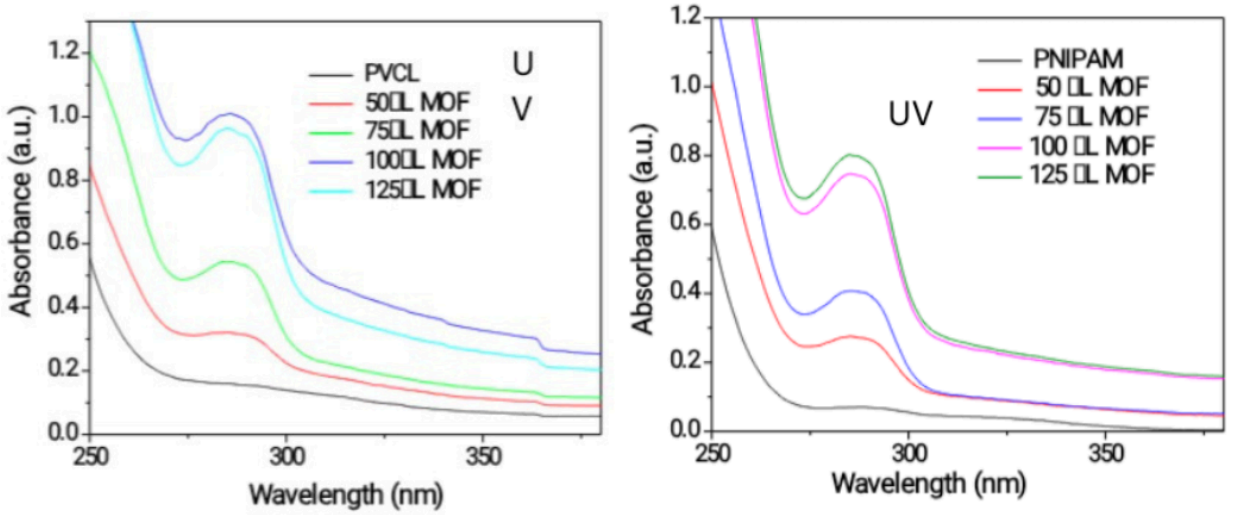
1. 20mg/ml stock solutions of polymer were prepared by addition of 40g polymer crystals in 2 ml of distilled water (For both PNIPAM, PNVCL).
2. 1mg/ml stock solution of CD-CuVa MOF was prepared by addition of 4 mg of MOF in 4 ml of distilled water.
3. The following samples were prepared with the final volume of 1 ml. Two batches of the polymer solutions were prepared; one with ANS as the solvent and the other with distilled water.

	Polymer (µL)	**CuVa MOF (µL)**	**ANS/Distilled water (µL)**
A	250	0	750
B	250	50	700
C	250	75	675
D	250	100	650
E	250	125	625

ANS was used for UV, Fluori samples whereas distilled water was used for DLS. However, the volumes were kept the same as shown.

4. The samples were subjected to the UV-Vis, Fluorimetry, Thermal Fluorimetry and DLS (The blank was set with ANS for UV-Vis and Fluorimetry whereas distilled water was used for DLS). Data was collected and analysed.

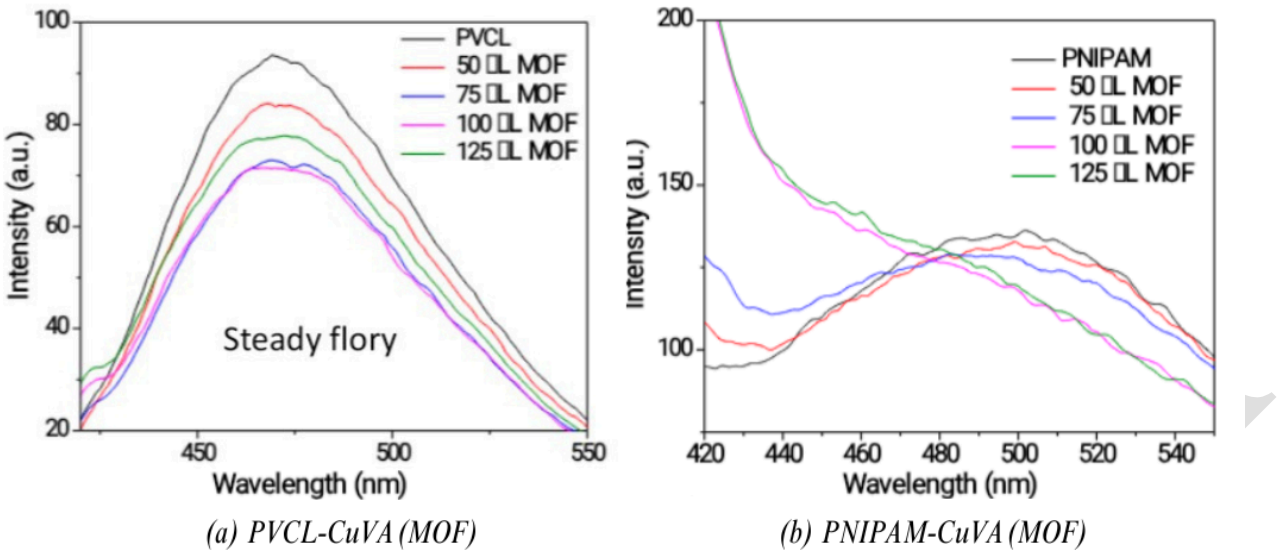
Results and Discussion



(a) PVCL-CuVA (MOF) *(b) PNIPAM-CuVA (MOF)*

Fig.2. UV-Vis spectra of (a) PVCL-CuVA(MOF) and (b) PNIPAM-CuVA(MOF) at varying MOF concentrations.

Fig. 2. (a) represents UV-Vis spectra of PVCL on addition of CuVa MOF at varying concentrations ranging from 50-125 µL. Fig. 2. (b) represents UV-Vis spectra of PNIPAM on addition of CuVa MOF at varying concentrations ranging from 50-125 µL. For both PNIPAM and PVCL, the UV-Vis spectra show a sharp increase in absorbance with increasing amounts of CuVa, indicating enhanced interactions between the polymer and the MOF. In both systems, the spectra begin to overlap at 100–125 µL of CuVa, suggesting minimal additional changes in absorbance beyond this range.



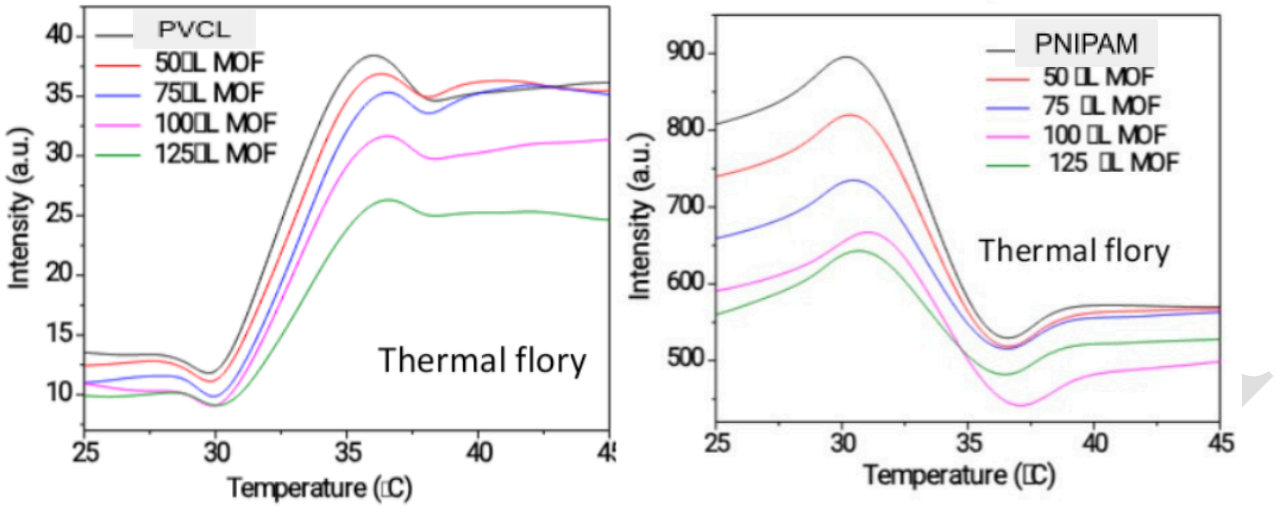
(a) PVCL-CuVA (MOF) *(b) PNIPAM-CuVA (MOF)*

Fig.3. Steady-state fluorescence spectra of (a) PVCL-CuVA(MOF) and (b) PNIPAM-CuVA(MOF) at varying MOF concentrations.

Fig.3(a) represents steady state fluorescence spectra of PVCL on addition of CuVa MOF at varying concentrations ranging from 50-125 µL. For the PVCL-CuVa system, the pure polymer exhibits the highest fluorescence intensity. Subsequent addition of CuVa leads to a gradual decrease in intensity, suggesting quenching of PVCL fluorescence by CuVa. The spectra converge around 100–125 µL, consistent with a saturation point where most polymer binding sites are occupied.

Fig.3(b) represents steady state fluorescence spectra of PNIPAM on addition of CuVa MOF at varying concentrations ranging from 50-125 µL. In contrast, the PNIPAM-CuVa system shows less uniform fluorescence quenching. This irregularity may result from aggregation or scattering effects, leading to noisier spectra rather than smooth quenching.

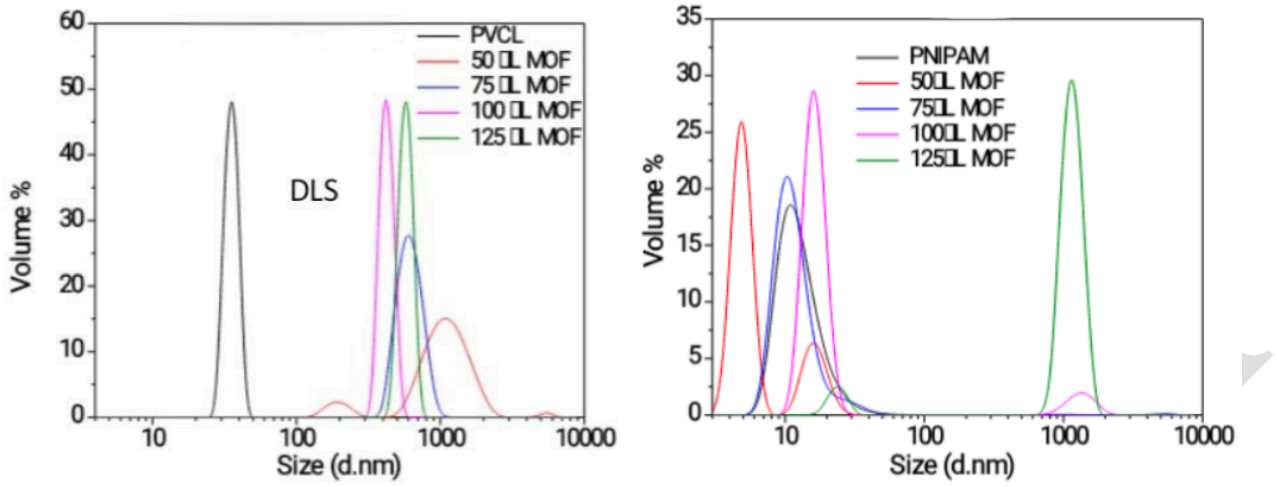
Overall, these observations suggest that increasing amounts of MOF induce conformational changes in both polymers.



(a) PVCL-CuVA (MOF) *(b) PNIPAM-CuVA (MOF)*

Fig. 4. Temperature-dependent fluorescence (thermal fluorescence) profiles of (a) PVCL-CuVA(MOF) and (b) PNIPAM-CuVA(MOF) at varying MOF concentrations.

Fig.4(a) represents temperature dependent fluorescence for PVCL-CuVa on addition of Cu-Va MOF at varying concentrations ranging from 50-125µL. For pure PVCL, the fluorescence intensity sharply increased at around 30 °C, indicating exposure of hydrophobic patches. On addition of different concentrations of Cu-Va ranging from 50 to 125 µL, a slight increase in LCST was observed. Fig.4(b) represents temperature dependent fluorescence for PNIPAM-CuVa. For PNIPAM, the observed LCST is at 36°C. This corresponds to a conformational change in PNIPAM that exposes hydrophobic regions. This temperature falls within the known LCST range of PNIPAM. Different concentrations of Cu-Va were added to PNIPAM ranging from 50 to 125 µL. A similar effect was observed in this as well. With increased concentration of Cu-Va, an increase in LCST was observed.



(a) PVCL-CuVA (MOF) *(b) PNIPAM-CuVA (MOF)*

Fig. 5. DLS size distribution curves of (a) PVCL-CuVA(MOF) and (b) PNIPAM-CuVA(MOF) at varying MOF concentrations.

Fig. 5 (a) represents DLS size distribution curves of PVCL on addition of Cu-Va MOF *at varying* concentrations ranging from 50-120µL. In the PVCL-CuVa system, both particle size and distribution are increasing more prominently as CuVa is added, indicating complex formation. Fig. 5 (b) represents DLS size distribution curves of PNIPAM on addition of Cu-Va MOF at varying concentrations ranging from 50-120µL. On addition of Cu-Va, the particle size and size distribution were lesser as compared to PVCL system. Although at 125µL, a distinct peak around 1000 d.nm appears, possibly due to aggregation, conformational changes, or the presence of a few large complexes.

Conclusion

Thus, the incorporation of CuVA (MOF) into thermo-responsive polymers PVCL and PNIPAM showed successful modification properties. Both UV-Vis and fluorescence confirmed interaction between the polymers and MOF. Meanwhile thermal fluorescence showed that MOF presence influenced the LCST-driven phase transition. DLS measurements revealed an increase in particle size and aggregation upon MOF addition. Addition of Cu-Va increased the LCST slightly in both polymer systems. These results suggest that combining MOFs with thermo-responsive polymers can create hybrid systems with useful properties for responsive and functional applications.

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