

Indian Science Technology and Engineering facilities Map (I-STEM)

Invites application for

1. Partial financial support for using R&D facilities in other institutions through the I-STEM web portal to Users from Academic Institutions and Start-ups (Format-1)

Format for requesting support for accessing and using facilities through the I-STEM web portal.

(i) Details of the Personal Information

- a. Name of the Researcher : **SEHRA SHUROOQUE KANNETH**
- b. Name of the Institution : **National Institute of Technology, Calicut**
- c. Name of the Department : **Chemistry**
- d. Degree registered : **PhD**
- e. Mob. No. **9744407948**
- f. Email ID: sehrashurooque@gmail.com

(ii) Project/Research topic Details:

- a. Project Title/Research Title: Design, synthesis and photophysical evaluation of solid emissive 1, 4-dihydropyridine derivatives
- b. Sub area: Organic chemistry
- c. Area Description: Design and synthesis of solid emissive organic fluorescent molecules for the application in the field of optoelectronics, sensing and imaging
- d. Aims & Objective (in Bullets):
 - Design and synthesis of solid emissive 1,4-dihydropyridine derivatives by incorporating different electron-withdrawing groups at C-4.
 - Modulation of their mode of aggregation via incorporation of different substituents on ring nitrogen.
 - Evaluation of photophysical properties of these molecules in solution / aggregated state and their application in fluorescent sensing.
- e. Duration (MM/YYYY): **6 months (11/2022-04/2023)**
- f. Project Summary:

Organic luminescent materials have attracted the attention of both academia and industry due to their potential applications in the diverse areas ranging from biomedical to information technology. Several research groups are actively involved

in the design and development of solid-state emissive organic chromophores due to the prospects of using them in optoelectronic devices such as organic/ polymeric light-emitting diodes (OLEDs/PLEDs), organic solid-state lasers, ultrasensitive sensors and in imaging. In these devices, emissive materials are practically used in the aggregated state such as liquid crystals, crystals and thin films. For instance, emissive solid thin films and crystals are used in optoelectronics such as organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). However, getting solid-state emission from organic chromophores is not easy owing to molecular aggregation in the solid state. As a result of this, fluorophores generally show reduced emission in the solid state compared to their solutions. The phenomenon of partial or complete emission quenching in the aggregated state is known as aggregation-caused quenching (ACQ). In the aggregated state, strong intermolecular π - π stacking interactions occur between the aromatic rings of neighbouring fluorophores. As a result of this interaction, the excited states of such aggregates often relax back or decay to the ground state via non-radiative channels, which results in emission quenching. Thus, in order to achieve efficient emission in the aggregated/solid state, numerous efforts including both covalent (chemical modification of fluorophore core such as attachment of a bulky substituent/alkyl group, electron donating / withdrawing group to the core) and non-covalent methods (excited state intramolecular proton-transfer, cocrystal formation, etc.,) have been attempted by many researchers with the aid of modern synthetic chemistry. The common structural features of solid-state emitters are the presence of multiple aromatic rings and/or polycyclic aromatic hydrocarbons as molecular building blocks which have either partially or fully twisted structures. In addition, the introduction of bulky groups is also useful in preventing the π - π stacking interactions in the solid. The various strategies adopted for the preparation of solid-emissive fluorophores are detailed below.

Twisted molecular building blocks: Partially or fully twisted structures are advantageous for preventing intermolecular interaction in the solid state by suppressing π - π stacking interactions. Tetraphenylethene (TPE) is a classic example of a twisted molecular system, which in dilute solution (in good solvent) emits almost no light because of the dynamic rotations of the phenyl rings against the

olefinic center resulting in the non-radiative dissipation of the exciton energy. In the solid or aggregated state, it becomes highly emissive due to the synergistic effects of the restricted intramolecular rotation (RIR) and the highly twisted molecular conformation that hampers the intermolecular π - π stacking interaction. This phenomenon is widely called aggregation-induced emission (AIE).

Introduction of bulky groups: Bulky substituents/groups are introduced in the molecular framework to prevent the molecules from close packing in the solid-state. Which will prevent the pi-pi stacking interaction leading to a high quantum yield in the condensed state.

Donor-acceptor molecular framework: One of the strategies adopted for the design of organic fluorophores having emission at longer wavelength is the extension of the conjugation. Molecular framework consisting of suitable arrangement of appropriate electron donor (D) and acceptor (A) units is also effective in obtaining longer wavelength emissions with tunability. Achieving red emission requires a narrow HOMO-LUMO gap, which is usually seen in π -extended polycyclic aromatic hydrocarbons, or π -conjugated systems with electron-donating and accepting groups at the terminal of the π -conjugated system. However, these kinds of molecules generally have a strong tendency for aggregation in the solid state that results in quenched fluorescence emission. Apart from the π - π stacking of planar polycyclic skeletons, the dipole-dipole interaction of the strong D-A framework also leads to emission quenching. For instance, simple fluorophores based on 2,5-bis(alkylamino)terephthalates which consist of a small π -system (only one benzene ring) exhibited emission maxima in the longer wavelength region (608 nm) in the crystalline state. This unique emission of the crystal originated from the combined effect of intramolecular hydrogen bonds and negligible π - π interactions.

The aim of this proposal is to synthesize and evaluate a series of solid-emissive fluorophores with tunable photophysical properties based on 1,4-dihydropyridine (DHP). We anticipate that the incorporation of different acceptor groups at C-4 would tune their photophysical behavior through electronic effects. N-alkylation of the dihydropyridine ring with structurally diverse alkyl units is expected to prevent their proximity in the solid state, and thus control their molecular packing in the

solid state. It's been reported that the solid state emission in solids depends upon the organization pattern of the individual molecules.

The various steps involved in the implementation of the project are:

- i) Synthesis and characterization of N-alkylated 1,4-DHP derivatives having different electron withdrawing groups at C-4 of DHP.
- ii) Evaluation of their photophysical properties and application potentials.

If the proposed objectives are achieved, we anticipate that this work would result in a series of molecules with high quantum yield in the solid state with possible applications in the field of optoelectronics. We also expect that the fluorophores obtained through this study could find application in bio-imaging and in fluorescent sensing.

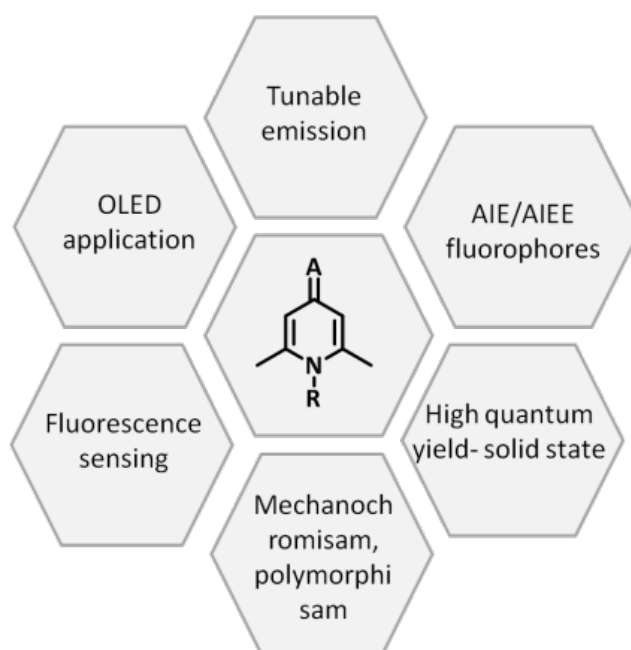


Figure 1. General structure of DHP fluorophores and possible outcomes

- [1] J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* **2015**, *115*, 11718–11940.
- [2] H. Li, Y. Guo, G. Li, H. Xiao, Y. Lei, X. Huang, J. Chen, H. Wu, J. Ding, Y. Cheng, *J. Phys. Chem. C* **2015**, *119*, 6737–6748.
- [3] Y. Liu, Y. Lei, M. Liu, F. Li, H. Xiao, J. Chen, X. Huang, W. Gao, H. Wu, Y. Cheng, *J. Mater. Chem. C* **2016**, *4*, 5970–5980.

Technical Details

a. TRL

TRL 1	:	Scientific review of knowledge base and identification of research gap
TRL 2	:	<i>Designing of novel fluorophore based on 1,4-Dihydropyridine derivatives</i>
TRL 3	:	<i>Designing of synthetic methodology</i>
TRL 4	:	Procurement of equipment, chemicals and glassware
TRL 5	:	Synthesis and characterization of the fluorophores
TRL 6	:	Preliminary evaluation of their physical properties in the solid and aggregated state
TRL 7	:	Detailed evaluation of solid emissive properties
TRL 8	:	Application of molecules in the field of OLED, fluorescence imaging and sensing
TRL 9	:	Publish in peer- reviewed journals

b. Methodology

The project aims the design, synthesis and evaluation of solid emissive fluorophores with high quantum yield in the condensed state. The 1,4-dihydropyridine (DHP) based fluorophores have been shown to be effective building blocks for the development of donor-acceptor solid emissive fluorescent materials among the numerous classes of fluorophores that have been reported. The DHP core is amenable to modification at three positions, which can lead to alteration in its photophysical properties (**Figure 2**).

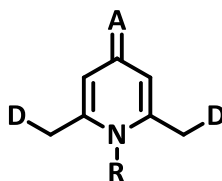
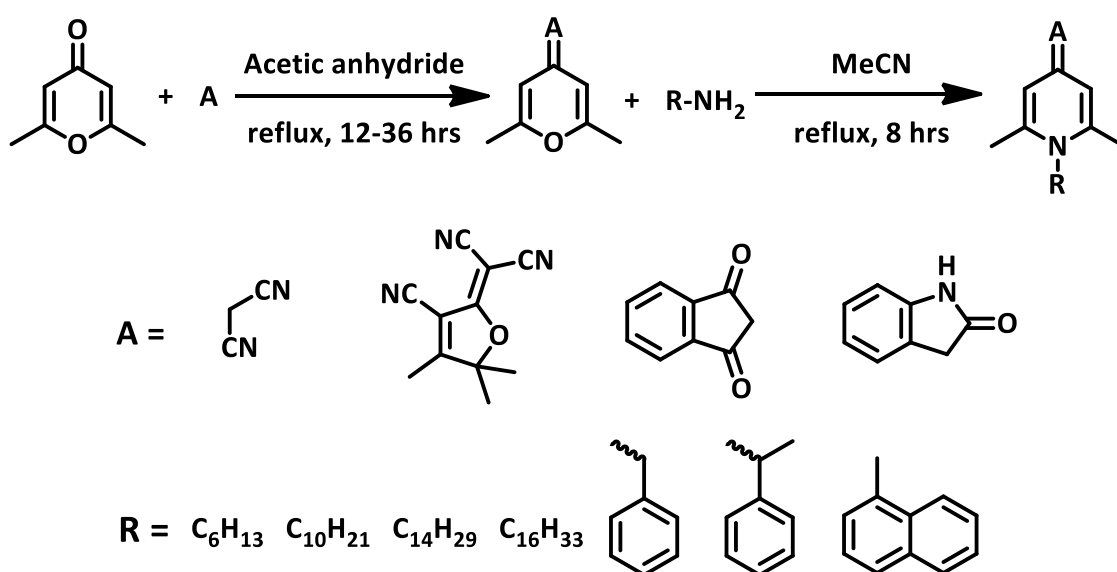


Figure 2. General structure of DHP-based fluorophores.

Although modification at C-4 and extension of conjugation at 2- and 6-positions have been reported, the effect of substituents on ring nitrogen on their solid

emission behavior has not been investigated. Herein, malononitrile, 2-dicyanomethylene-3-cyano-2,5-dihydrofuran (DCDHF), 1H-indene-1,3-(2H)-dione, and oxindole will be used as the electron-withdrawing groups at C-4 to construct a variety of DHP derivatives with various alkyl-aryl substituents on the nitrogen atom. The general synthetic strategy adopted for the designed compounds is given in **Scheme 1**. The 2,6-dimethyl- γ -pyrone and the corresponding active methylene compounds were condensed under refluxing conditions in acetic anhydride to obtain the pyran-based precursor. The end compounds can be generated by reacting this precursor with the appropriate primary amines.



Scheme 1. Synthetic route for the DHP derivatives

- [1] Y. Lei, D. Yang, H. Hua, C. Dai, L. Wang, M. Liu, X. Huang, Y. Guo, Y. Cheng, H. Wu, *Dye. Pigment.* **2016**, *133*, 261–272.
- [2] H. Li, Y. Guo, G. Li, H. Xiao, Y. Lei, X. Huang, J. Chen, H. Wu, J. Ding, Y. Cheng, *J. Phys. Chem. C* **2015**, *119*, 6737–6748.

c. Design & development

In recent years, 1,4-dihydropyridine-based fluorescent molecules have received increasing attention because of their simple structures, easy synthesis, and excellent photophysical properties. Importantly, some 1,4-dihydropyridine derivatives are reported to exhibit outstanding AIE properties and solid-state fluorescence. We anticipated that attaching appropriate substituents on the nitrogen atom of the 1,4-dihydropyridine ring would prevent the close packing of

these fluorophores leading to enhanced emission in the solid state. Recently Yunxiang Lei et.al., reported N-alkylated (ethyl, n-butyl, and n-octyl) 1,4-dihydropyridine (DHP) derivatives incorporating different electron-withdrawing group at C-4 and they exhibited polymorphism and mechanochromic properties.¹ According to their results, the electron-withdrawing groups were responsible for the polymorphic and mechanochromic properties. Additionally, the number of polymorphs of these DHP derivatives showed a decreasing trend as the length of the alkyl chain was increased. Considering the fact that different electron-withdrawing groups at C-4 and N-alkyl chain lengths played a role in modulating solid-state photophysical properties, we plan to synthesize a series of DHP derivatives having different alkyl-aryl units (hexyl, n-decyl, n-tetradecyl and n-hexadecyl, and benzyl, naphthyl, etc.) on the ring nitrogen using malononitrile, DCDHF, 1H-indene-1,3-(2H)-dione and oxindole as electron-withdrawing substituents at C-4 of the ring.

- [1] Y. Lei, Y. Zhou, L. Qian, Y. Wang, M. Liu, X. Huang, G. Wu, H. Wu, J. Ding, Y. Cheng, *J. Mater. Chem. C* **2017**, 5, 5183–5192.
- [2] Y. Lei, Y. Liu, Y. Guo, J. Chen, X. Huang, W. Gao, L. Qian, H. Wu, M. Liu, Y. Cheng, *J. Phys. Chem. C* **2015**, 119, 23138–23148.

d. Facilities and Instrumentation required

- **NMR spectrometer**
- **FT-IR**
- **HR-MS**
- **UV-Vis spectrophotometer**
- **Fluorimeter with integrating sphere**
- **Time-resolved fluorescence spectrometer**
- **Single crystal XRD**
- **SEM, TEM, AFM**

e. Consumables (Scientific materials)

- **Glass wares**
- **Chemicals**

(iii) Expected output and outcome

The research work would result in a series of solid emissive fluorophores with possible applications in optoelectronics, imaging, and sensing. Additionally, a fundamental understanding of the effect of various steric/electronic parameters in crystal packing that contribute to their photophysical properties is also anticipated.

(iv) Industry/Institute Collaboration If, yes: Not applicable

(v) Funding required from I-STEM (with justification):

	Item	Vendor/institute	cost	No. of samples/ items	Total cost
CHARACTERISATION & ANALYSIS	Single crystal XRD	SAIF-IIT Madras	4,580	10	45,800
	Time-resolved fluorescence spectrometer	MG University	300	50	15,000
	Solid state quantum yield measurements	MG University	300	36	10,800
	FE-SEM	SAIF-IIT Madras	900	5	4,500
	HR-MS	SAIF-IIT Madras	1,000	15	15,000
	Travel Cost				10,000
TOTAL					1,01,100/-

(vi) Details of Requirements & Mode of the Engagement:

(i) Short term Engagement:

a. Usage of testing/characterization facilities across the country (Characterization Mode)

i. Testing Charges : **91,100/-**

ii. Consumable charges : **0/-**

iii. Travel Cost : **10,000/-**

b. Usage of fabrication and testing facilities across the country (Fabrication Mode)

i. Fabrication and testing Charges

ii. Consumable charges (if any)

iii. Travel Cost (Boarding and Lodging, if any)

(ii) Medium term Engagement:

- a. Execution of project in any one of the Host Institution (Project Mode)
 - a. Fabrication and or testing Charges
 - b. Consumable charges (if any)
 - c. Travel Cost (Boarding and Lodging, if any)
- b. Execution of project in Multi Host Institutions (Project Mode)
 - a. Fabrication and or testing Charges
 - b. Consumable charges (if any)
 - c. Travel Cost (Boarding and Lodging, if any)

(Round-trip to the Host Institution by 2nd class (Non-AC) railway via the nearest route)

Details of User's Bank Account:

Beneficiary Name: **Sehra Shurooque Kanneth**

PAN: **JTRPS4617A**

Bank Account No. **67078079440**

Name of the Branch: **SBI Tirurangadi**

IFSC Code: **SBIN0070344**

Note: Proposed proposal must be executed within stipulated duration (max. 6 month) to avoid fund availability issues. Travel form will be provided by the I-STEM office. The users will submit the technical report, original invoice (duly signed by the Head of the Institution) raised by the Host Institution through I-STEM portal only along with a copy of the travel forms and original tickets through post to the Nodal Officer, I-STEM, Indian Institute of Science, Bangalore. A scan copy of all the documents may be sent in advance.