

Kilingaru I. Shivakumar, PhD

(Family name) (Given name)

DOB: 10th July 1986, Indian

✉ Institute for Chemical Reaction Design and Discovery (WPI-ICReDD)

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RESEARCHERID [AAC-5485-2019](https://pubs.acs.org/doi/10.26434/chemrxiv-2019-00000)



PROFILE

- 10 years of research experience in synthetic organic and supramolecular chemistry.
- Experience in milligram to multigram synthesis of macrocycles (pillar[5]arene and pillar[5]quinone), redox-active donor-acceptor (D-A) charge-transfer systems, stable organic radicals, liquid crystals, and porous hydrogen-bonded organic frameworks.
- Expertise in characterization of compounds exhibiting porous network, charge conduction, ferroelectricity, magnetism and liquid crystalline behavior.



PROFESSIONAL EXPERIENCES

May 2019- March 2021:

**Postdoctoral Researcher at Research Institute for Electronic Science,
Hokkaido University, Sapporo, Japan**

Title of the project

Porous hydrogen-bonded organic frameworks (HOFs) based on redox-active building blocks

Areas of Research

• Synthesis of redox-active, π -conjugated tetra-, penta-, hexatopic carboxylic acids • Recrystallization at elevated temperatures to obtain H-bonded Hex-Net • Investigation of the framework stability employing XRD and thermal techniques • Evaluation of permanent porosity by gas adsorption • Photoconductivity, cyclic voltammetry, photophysics and DFT calculation.

Supervisors

Prof. Ichiro Hisaki and Prof. Takayoshi Nakamura

Dec 2017-April 2019:

**Postdoctoral Researcher at Centre of Molecular and Macromolecular
Studies, Polish Academy of Sciences, Poland**

Title of the project

Stable π -delocalized radical based bent-core liquid crystals

Area of Research

• Multi-step organic synthesis of a stable π -delocalized planar radical • Suitable functionalization of the radical to obtain a series of bent-core liquid crystals • Investigation of mesogenic properties using POM, thermal and XRD techniques • Magnetic studies using SQUID and solution/solid-state EPR • Electrooptical studies, photoconductivity, cyclic voltammetry, photophysics and DFT calculation.

Supervisor

Prof. dr hab. inż. Piotr Kaszyński

Aug 2017-Nov 2019:

**SERB- National Postdoctoral Fellow at Indian Institute of Technology
Guwahati, India**

Areas of Research

• Discotic liquid crystals • Semiconducting property of shape-persistent arylene-ethynylene macrocycles • Friedal-Crafts alkenylation using Zeolite Y, hydrogen



EDUCATIONAL QUALIFICATIONS

<u>Jan 2011-Jun 2017:</u>	PhD in Chemistry from CSIR-National Chemical Laboratory, Pune, India
Title of the Thesis	<i>De Novo Designed Organic Donor-Acceptor Systems Featuring Inter- and Intramolecular Charge Transfer Interactions</i>
Areas of Research	<ul style="list-style-type: none"> • Synthesis of macrocycles: Pillar[5]arene and Pillar[5]quinone • Solvent-assisted self-assembly of Pillar[5]quinone • Studies on the intermolecular charge-transfer crystals of Pillar[5]quinone with electron donors • Synthesis of a series of C₃ symmetric intramolecular donor-acceptor system based on tri(dithiolyldiene) cyclohexanetrione • Physical studies: ferroelectricity, conductivity, gelation, photophysics and electrochemistry.
CGPA (10)	8.35, Distinction
Supervisor	<i>Prof. Gangadhar J. Sanjayan</i>
<u>July 2008-May 2010:</u>	Master of Science (M.Sc.) in Chemistry from National Institute of Technology Karnataka, Suratkal, India
Title of the Thesis	<i>Synthesis and Third Order Non-Linear Optical Studies of Copper(I)-phenanthroline based Complexes</i>
CGPA (10)	9.84, Distinction, First Rank, 2 gold medals
Supervisor	<i>Prof. Badekai Ramachandra Bhat</i>
<u>July 2004-May 2008:</u>	Bachelor of Science Education (B.Sc.Ed.) from Regional Institute of Education NCERT, Mysuru, India
	Dual degree with teaching certificate
Percentage marks	71.8%, First-class



RESEARCH INTERNSHIPS

<u>Sept 2010-Dec 2010:</u>	Visiting Student at Raman Research Institute, Bengaluru, India
Area of Research	Synthesis of Polymer-Stabilized Liquid Crystalline Blue Phases
Supervisor	<i>Prof. Sandeep Kumar</i>
<u>May 2009-July 2009:</u>	Summer Research Student at Indian Institute of Technology Bombay, India
Area of Research	Routes to Synthesize Functionalized Phosphines
Supervisor	<i>Prof. Maravanji S. Balakrishna</i>



AWARDS/ACHIEVEMENTS

2017	National Postdoctoral Fellowship with research grant from SERB-DST, Government of India
2013-2015	Senior Research Fellowship from CSIR-UGC, Government of India
2011-2012	Junior Research Fellowship from CSIR-UGC, Government of India
2010	Qualified competitive all-India level exams for research fellowships: GATE and CSIR-UGC
2010	Prof. G H Kulkarni and NITK Gold medals for securing first rank in MSc. Chemistry
2009	Summer Research Fellowship , Indian Institute of Technology (IIT) Bombay, India



RESEARCH PUBLICATIONS

7. **Shivakumar, K. I.**, Noro, S-i., Yamaguchi, Y., Ishigaki, Y., Saeki, A., Takahashi, K., Nakamura, T., Hisaki, I.
“Hydrogen-Bonded Organic Framework Based on Redox-Active Tri(dithiolylidene)cyclohexanetrione”
Chem. Commun. **2021**, 57, 1157. (citations 0)
6. **Shivakumar, K. I.**; Pociecha, D.; Szczytko, J.; Kapuscinski, S.; Monobe, H.; Kaszynski, P.
“Photoconductive Bent-Core Liquid Crystalline Radicals with a Paramagnetic Polar Switchable Phase”
J. Mater. Chem. C, **2020**, 8, 1083. (citations 6)
5. **Shivakumar, K. I.**; Goudappagouda; Gonnade, R.; Babu, S. S.; Sanjayan, G. J.
“Conducting Nanofibres of Solvatofluorochromic Cyclohexanetrione–Dithiolylidene-Based C_3 Symmetric Molecule”
Chem. Commun. **2018**, 54, 212. (citations 2)
4. **Shivakumar, K. I.**; Swathi, K.; Goudappagouda; Das, T.; Kumar, A.; Makde, R.D.; Vanka, K.; Narayan, K. S.; Babu, S. S.; Sanjayan, G. J.
“Mixed-Stack Charge Transfer Crystals of Pillar[5]quinone and Tetrathiafulvalene Exhibiting Ferroelectric Features”
Chem. Eur. J. **2017**, 23, 12630. (**Hot Paper**, citations 6)
3. **Shivakumar, K. I.**; Yan, Y.; Hughes, C. E.; Apperley, D. C.; Harris, K. D. M.; Sanjayan, G. J.
“Exploiting Powder X-ray Diffraction to Establish the Solvent-Assisted Solid-State Supramolecular Assembly of Pillar[5]quinone”
Cryst. Growth Des., **2015**, 15, 1583. (citations 14)
2. **Shivakumar, K. I.** and Sanjayan, G. J.
“An Easy and Multigram-Scale Synthesis of Pillar[5]quinone by the Hypervalent Iodine Oxidation of 1,4-Dimethoxypillar[5]arene”
Synthesis **2013**, 45, 896. (citations 16)
1. Rudresha, B. J.; Bhat, B. R.; Kumar, H. C. S.; **Shivakumar, K. I.**; Safakath, K.; Philip, R.
“Synthesis, Characterization and Third-Order Nonlinear Optical Studies of Copper Complexes Containing 1,10-Phenanthroline-5,6-dione and Triphenylphosphine Ligands”
Synth. Met. **2011**, 161, 535. (citations 11)



PATENTS

1. Process for the Preparation of Pillar[5]quinone
G. J. Sanjayan and **K. I. Shivakumar**
US Patent 9000224, April 7, 2015



SCIENCE JOURNALISM

1. **Shivakumar K. I.** *Scigem* **2018**, 5, 6 ([pdf](#))
“Chemistry is right under our nose all the time”



RESEARCH SUMMARY

My research focuses on studying various material applications arising from the self-organization of electro-active organic molecules due to non-covalent interactions.

❖ Redox-active porous hydrogen-bonded organic frameworks (HOFs)

Hydrogen-bonded Organic Framework (HOF)s are porous materials endowed with reversible intermolecular H-bonds and consequent high crystallinity. Unfortunately, the labile nature of H-bonds frequently causes the collapse of frameworks during activation, making it challenging to obtain HOF with permanent porosity. We have reported the first 3D H-bonded network of redox-active hexakis(4-carboxylphenyl) tridithiolylenecyclohexanetrione, **CPDC-1**, exhibiting permanent porosity, amphoteric redox behavior and photoconductivity. Interestingly, the bite angle made by H-bonding groups crucially effects the H-bonding pattern and resulting network of HOF.



Chem. Commun., 2021, 57, 1157

❖ Stable π -Delocalized Liquid Crystalline (LC) Radicals

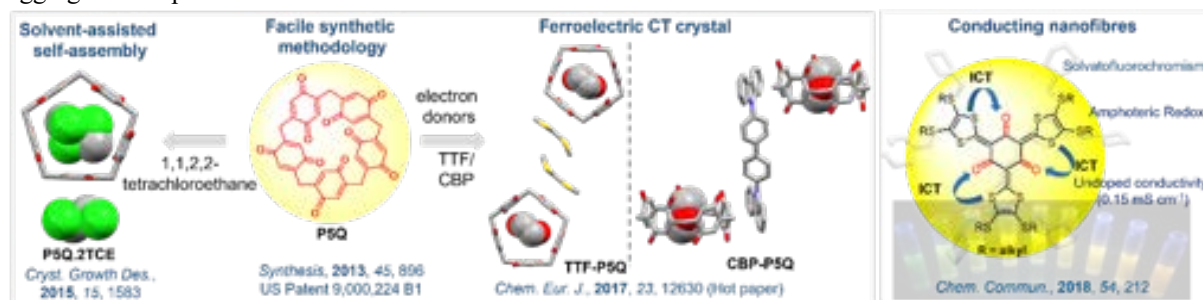
Stable π -delocalized radical-based multifunctional materials with controllable electrochemical, photophysical, semiconductive and magnetic properties, which can be enhanced by self-organization in LC state are in high demand. In this work, we planarized the central paramagnetic unit to enhance the π -stacking, which resulted in strong spin-spin interaction, high-charge mobility, bathochromic shift, and facilitated the formation of an antiferroelectric B2 phase, exhibiting tri-stable electrooptic switching.



❖ Donor-Acceptor Molecules Featuring Charge Transfer Interactions (Doctoral Work)

Pillar[5]quinone (**P5Q**), containing five 1,4-benzoquinone moieties, is an efficient electron acceptor; however, poses difficulty in isolation owing to its poor solubility in most common organic solvents. Hence, we developed an alternate, facile synthetic methodology to obtain **P5Q** using hypervalent iodine oxidation and purified it by recrystallization. We observed that solvent 1,1,2,2-tetrachloroethane (TCE) induces self-organization of **P5Q** through an anion- π type interactions. In addition, **P5Q** forms 1:1 mixed-stack charge transfer crystals with donors such as tetrathiafulvalene (**TTF**) and 4,4'-bis(*N*-carbazolyl)-1,1'-biphenyl (**CBP**). Interestingly, the **TTF-P5Q** crystals exhibit ferroelectric features with ferroelectric to paraelectric phase transition at 329 K.

On the other hand, a set of easily tailorable, C_3 symmetric molecules having a π -extended push-pull core was synthesized. These molecules exhibited intramolecular charge transfer (ICT) interactions, solvatochromism, large Stokes shift, amphoteric redox behavior, gelation and conductivity in the *J*-aggregate undoped nanofibers.



EQUIPMENT EXPERTISE AND SKILLS

Analytical Techniques: NMR (Bruker DPX200 and JEOL ECS400 & 600), UV-vis-NIR, ATR/FT-IR, Fluorescence spectroscopy, mass spectrometry (MALDI-TOF, LC-MS, GC-MS), preparative HPLC, cyclic voltammetry, powder and single crystal XRD, electron paramagnetic resonance (EPR), polarizing optical microscopy (POM), thermal analysis: TGA and DSC, Solvent Purification System (SPS), Kugelrohr vacuum distillation and sample preparation for SEM, TEM, AFM and SQUID.

Reaction Techniques: Air-free technique (Glovebox and Schlenk line), High-pressure reaction in autoclave and sealed tubes, and microwave reactor.

Softwares: ChemDraw, PyMOL, Mercury, Origin, Kaleidagraph, Endnote, Sci-finder, Adobe illustrator and photoshop, NMR softwares, and MS office.

ORAL COMMUNICATIONS

4. "Paramagnetic Antiferroelectrics: Bent-Core Mesogens Derived from the Blatter Radical"
Piotr Kaszyński, * **Shivakumar I. Kilingaru**, Damian Pocięcha, Jacek Szczytko, and Hirosato Monobe
'17th International Conference on Ferroelectric Liquid Crystals', University of Colorado, USA, August 2019
 3. "Self-Organizing Planar Blatter Radicals – Design, Synthesis and Consequences of Planarization on the Key Properties"
Martin Cigl, **Shivakumar I. Kilingaru**, Damian Pocięcha, Jacek Szczytko, Hirosato Monobe and Piotr Kaszyński*
'15th European Conference on Liquid Crystals', Wrocław, Poland, July 2019
 2. "Organic Donor-Acceptor Systems Featuring Inter- and Intramolecular Charge Transfer Interactions"
Kilingaru I. Shivakumar and Gangadhar J. Sanjayan*
'National Conference on Advanced Organic Synthesis - 2017', CSIR-NCL, Pune, India, Feb 2017
 1. "Pillar[5]quinone: Facile Synthesis, Self-assembly, Crystal Structure and their Application in Semiconductors"
Kilingaru I. Shivakumar and Gangadhar J. Sanjayan*
'National Conference on Advanced Organic Synthesis - 2016', CSIR-NCL, Pune, India, April 2016
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POSTER PRESENTATION

5. Planar Blatter Radical-Based Bent-Core Mesogens, 17th **ACHC**, CBMM- PAN, Lodz, Poland, November 2018
 4. Solvent-Assisted Solid-State Self-Assembly of Pillar[5]quinone, **NSC- 2015**, CRSI-CSIR-NCL, Pune, India, February 2015
 3. Solvent-Assisted Solid-State Self-Assembly of Pillar[5]quinone, **NSD celebration**, CSIR-NCL, Pune, India, February 2015
 2. An Easy and Multi-Gram Scale Synthesis of Pillar[5]quinone, its Self-Assembly and Electrochemical Properties, **FAPS-MACRO 2013**, IISc., Bengaluru, India, May 2013
 1. An Easy and Multi-Gram Scale Synthesis of Pillar[5]quinone, **NSD celebration**, CSIR-NCL, Pune, India, February 2013
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CHEMISTRY OUTREACH

2. Demonstrated hands-on chemistry experiments to high school children, with ingredients that are used in daily life, as a part of CSIR Platinum Jubilee Technofest at 36th India International Trade Fair, New Delhi, India, November 2016.
 1. Demonstrated hands-on, home do-able, colorful experiments to students from sixty secondary schools as a part of International Year of Chemistry (IYC) – 2011.
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LANGUAGE SKILLS

English (Fluent), Kannada (Fluent), Tulu (Fluent), Hindi (Fluent), Polish (Basic), Japanese (Basic)
