SYNOPSIS

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Degree for which the thesis is submitted:	Ph.D.
Department:	Chemistry
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Thesis title:	Conjugated porous organic polymers: fluorescence-based sensing, photocatalysis and energy storage
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Porous materials have become an active field of research over the past few decades due to their immense potential applications ranging from gas storage, gas and liquid separation, catalysis to sensing and energy storage. Porous materials are of different kinds such as activated carbons, zeolites, metal-organic framework (MOF), covalent organic framework (COF) and porous organic polymers (POP). Zeolites, activated carbons and MOFs have been investigated quite extensively in the last few decades. However, in recent times conjugated porous organic polymers (CPOPs) have emerged as a new class of functional materials. The CPOPs have drawn much attention to the scientific community because of the high thermal and physicochemical stability in addition to the permanent porous nature. CPOPs contain extended π-electron conjugation and thus become more advantageous compared to the other porous materials in the field of light harvesting and optoelectronic applications. Even though several studies appeared in recent years, the solution processability of these network polymers remains a challenge.

In this dissertation, we have attempted to address the solubility issue of conjugated porous organic polymers and explore in detail the structure-property relationship of these novel class of materials in fluorescence-based sensing, photocatalysis and energy storage. We provide a brief outline of the specific themes developed in each chapter.

Chapter 1: **Introduction**

A brief introduction is presented to various kinds of porous materials highlighting their emergence and relevance. This is followed by a discussion on the origin of porosity in porous organic polymers and their advantages. An overview of the historical perspectives and the various

classes of porous organic polymers are discussed. A special emphasis is paid to their application in gas storage and separation, catalysis, energy storage and sensing. Finally, the salient features of the subsequent chapters in the thesis are outlined.

Chapter 2: **Fabrication of porous organic polymers in the form of powder, solution in organic solvents and nanoparticles: exploration of nitroaromatics sensing**

In this chapter, we have discussed the design principle and fabrication of porous organic polymers in the form of powder, solution in common organic solvents and nanoparticles by using a novel core of tetraphenyl-5,5-dioctylcyclopentadiene (TPDC). The fine tuning of reaction conditions involving tetrakis(4-bromophenyl)-5,5-dioctylcyclopentadiene and diethynylbenzene (DB) led to the formation of TPDC based polymers in three different forms (Fig. 1). The POPs were thermally stable and the porosity of these materials was investigated by nitrogen sorption measurements at 77K. The detailed photophysical properties of the solution-processable POP and the aqueous dispersion of nanoparticles were explored by absorption and steady-state and time-resolved fluorescence spectroscopy. The nitroaromatics sensing was carried out using a set of 30 closely related analytes such as nitrophenols, nitrotoluenes, nitroanilines, nitobenzenes, and quinones. Nitroanilines were found to be the most efficient quenchers in contrast to the extensively studied picric acid, which is unprecedented among POPs. The rigorous spectroscopic investigations coupled with computational studies provided new insights into the underlying photophysical phenomenon of fluorescence quenching. We observed that the electron-deficient nature of the nitroaromatics is not the sole governing factor responsible for fluorescence quenching.

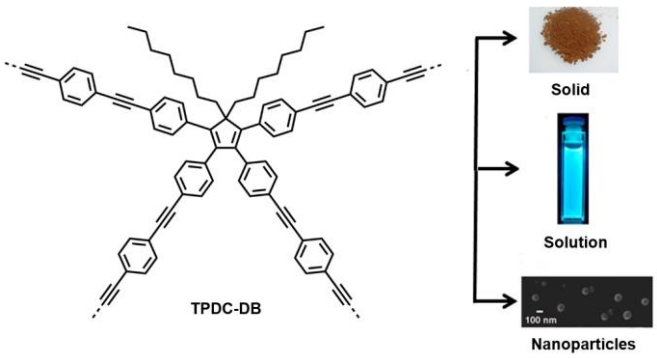

Fig. 1. TPDC-DB based conjugated porous organic polymers in three different forms.

Chapter 3: **Multifunctional porous organic polymers: tuning of porosity, visible light-driven photocatalysis and supercapacitive energy storage**

This chapter deals with the fabrication and properties of a series of CPOPs based on boron dipyrromethene (BODIPY) core. The variation of the substituents in the meso position of BODIPY core and the fine-tuning the Songashira polycondensation reaction with 1,3,5-triethynylbenzene led to the development of CPOPs with a wide range of surface area and

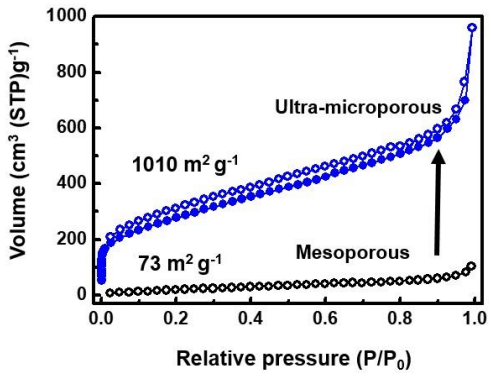

Fig. 2. Nitrogen sorption isotherms of BODIPY based POPs depicting tunable surface area.

porosity. A ten-fold increase in BET surface area from 73 $m^2 g^{-1}$ to 1010 $m^2 g^{-1}$ was obtained (Fig 2). Simultaneously, the porosity was changed from mesoporous to ultra-microporous. The gas adsorption studies of the polymers revealed a high uptake of CO_2 and H_2. Electron paramagnetic resonance (EPR) studies revealed the generation of singlet oxygen upon photoexcitation of these polymers. We explored the CPOPs developed in this study as heterogeneous photocatalyst for oxidation of thioanisole. The energy storage capacity of the porous polymers was found to be very low. However, the calcination of one of the CPOPs resulted in porous carbon which was found to exhibit an appreciable specific capacitance.

***Chapter 4*: Red emitting solution-processable conjugated porous organic polymer: generation of reactive oxygen species and photo-oxidation of benzylamine**

This chapter describes the fabrication and characterizations of a solution-processable CPOP based on a combination of BODIPY and carbazole core linked through a long alkyl chain. The polymer was obtained by palladium(0)-catalyzed (A_4 + B_2) type Suzuki-Miyaura polycondensation reaction between the boronic ester of bicarbazole octane and diiodo derivative of BODIPY. The resultant polymer Cz-BDP is soluble in common organic solvents having a moderate BET surface area. Cz-BDP is red fluorescent and generates the reactive oxygen species (ROS) upon exposure to visible light. It was explored for a visible light-driven photocatalysis in the oxidative coupling of primary amine. This work highlights the development of solution-processable CPOPs promising for metal-free visible light-driven organic transformation.

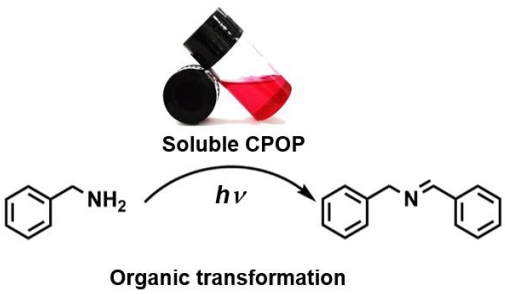

Fig. 3. Soluble conjugated porous organic polymer Cz-BDP in visible light-driven organic transformation.

***Chapter 5*: New directions, overview of the present work and future prospects**

In this chapter, we propose new directions towards (i) the fabrication of soluble POPs having tunable emission and (ii) CPOPs for high supercapacitive energy storage. The cyan fluorescent POPs with TPDC core presented in the second chapter was fabricated using diethynylbenzene (DB) as comonomer. Employing tetraphenylethylene (TPE) and

benzothiadiazole (Bz) as comonomers, we obtained TPDC-TPE and TPDC-Bz respectively as green and orange fluorescent soluble polymers (Fig. 4a).

Pyrene based CPOPs were fabricated by palladium-catalyzed Buchwald-Hartwig cross-coupling reaction. The resultant polymers were found to exhibit high specific capacitance in its pristine form. The highest specific capacitance by pyrene based CPOP was found to be ~ 456 F g^{-1} in 2 M H_2SO_4 (Fig. 4b). These polymers also exhibited high cyclic stability promising for device application.

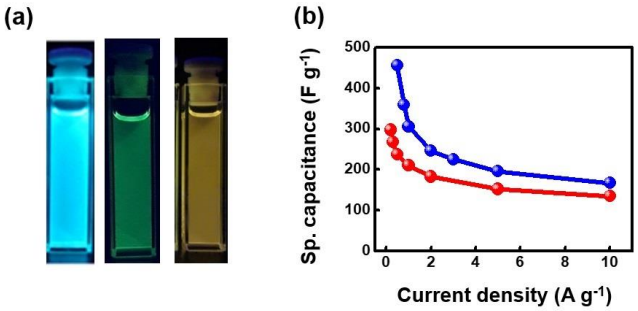

Fig. 4. (a) Solution-processable CPOPs with tunable emission based on TPDC core. (b) The specific capacitance of pyrene based CPOPs at different current densities.

In the following section, we summarize the various work presented in the thesis towards the development of multifunctional porous organic polymers. The highlights of the work include (i) fabrication of TPDC based fluorescent soluble POPs and the detailed exploration of nitroaromatics sensing, (ii) BODIPY based POPs with tunable surface area and porosity for photocatalysis and energy storage, (ii) BODIPY-carbazole based solution-processable porous organic polymer as a visible light-driven photocatalyst for organic transformation.

In the concluding section, I delineate some of the important avenues for the exploration in future. An approach for developing surfactant-free water soluble fluorescent CPOPs is described. Application of the strongly fluorescent POPs developed in the present study in organic photovoltaic devices and fabrication of novel metal-organic hybrid materials with improved optical attributes are some of the interesting avenues to be explored further.

Publications referred

1. Bandyopadhyay, S.; Pallavi, P.; Anil, A. G.; Patra, A. Fabrication of porous organic polymers in the form of powder, soluble in organic solvents and nanoparticles: a unique platform for gas adsorption and efficient chemosensing. *Polym. Chem.* **2015**, *6* (20), 3775−3780.

2. Deshmukh, A.; Bandyopadhyay, S.; James, A.; Patra, A., Trace level detection of nitroanilines using a solution processable fluorescent porous organic polymer. *J. Mater. Chem. C* **2016**, *4* (20), 4427-4433.

3. Bandyopadhyay, S.; Anil, A. G.; James, A.; Patra, A., Multifunctional porous organic polymers: tuning of porosity, CO_2, and H_2 storage and visible-light-driven photocatalysis. *ACS Appl. Mater. Interfaces.* **2016**, *8* (41), 27669-27678.

4. Pallavi, P.;[#] Bandyopadhyay, S.;[#] Louis, J.; Deshmukh, A.; Patra, A. A soluble conjugated porous organic polymer: efficient white light emission in solution, nanoparticles, gel and transparent thin film. *Chem. Commun.* **2017**, *53*,(7), 1257-1260.

   [#] *Equal contribution*

5. Bandyopadhyay, S.; Kundu, S.; Patra, A. Red emitting solution-processable conjugated porous organic polymer: generation of reactive oxygen species and photooxidation of benzylamine *(manuscript under preparation).*

6. Bandyopadhyay, S.; Patra, A. *et al.* Redox-active conjugated porous organic polymers for supercapacitive energy storage *(manuscript under preparation).*

Presentations

1. Bandyopadhyay, S.
   Attended National Organic Symposium Trust (**J-NOST**) conference at IISER Bhopal, India, December 4–6, 2013.

2. Bandyopadhyay, S.
   Oral presentation at the In-House Symposium **InTeRaCTiONS-2014** at IISER Bhopal, India on August 30, 2014.
   Fabrication of porous organic polymers in the form of powder, soluble in organic solvents and nanoparticles: a unique platform for gas adsorption and efficient chemosensing

3. Bandyopadhyay, S.; Pallavi, P.; Anil, A. G.; Patra, A.
   Poster presented at the international symposium on polymer science and technology (**MACRO 2015**) at Kolkata, India January 23-26, 2015.
   Fabrication of porous organic polymers in the form of powder, soluble in organic solvents and nanoparticles: a unique platform for gas adsorption and efficient chemosensing

4. Bandyopadhyay, S.; Anil, A. G.; James, A.; Patra, A.,
   Oral presentation at the international symposium on polymer science and technology (**MACRO 2017**) at Thiruvananthapuram, India, January 8-11, 2017.
   Multifunctional porous organic polymers POPs