

*Synthesis and Studies of Solution Processable Pyromellitic
Diimide Based Phosphorescent Polymers*

Research Project-3 (JNC 212)

Master of Science (M.Sc.) in Chemistry

Submitted By

Chahat

Serial No: 2020/53/S0896



Research Supervisor

Prof. Subi J. George

New Chemistry Unit (NCU)
Jawaharlal Nehru Centre for Advanced Scientific Research

(A Deemed University)
Bengaluru- 560064 (India)

09.05.2022

Chahat.

Signature of student

Subi

Signature of supervisor

Table of Contents

Chapter 1: (Introduction) Ambient Room Temperature Phosphorescence

1. Introduction.....	3
1.2 Photoluminescence pathways	3-5
1.3 Room temperature phosphorescence	5
1.3.1 Organic room temperature phosphorescent materials	5
1.3.2 Current challenges in the field	5
1.4 Requirements to obtain efficient RTP	6
1.5 Strategies for ambient RTP.....	7
1.6 Conclusions.....	7
1.7 References.....	9-10

Chapter 2: Monomeric Room Temperature Phosphorescence from N-substituted *Pyromellitic Diimide* Based Polymers

2.1 Abstract.....	11
2.2 Introduction.....	11-13
2.3 Molecular Design.....	13
2.4 Results and Discussion.....	15-18
2.5 Conclusions.....	18
2.6 Future Outlook.....	18
2.7 References.....	18-20

Chapter 3: Ring Opening Metathesis Polymers with Pendant pyromellitic diimides for Charge-Transfer Phosphorescence

3.1 Abstract.....	21
3.2 Introduction.....	21
3.3 Molecular Design.....	22
3.4 Results and Discussion.....	22-24
3.5 Conclusions.....	24
3.6 Future Outlook.....	25
3.7 References.....	25

Chapter 1 (Introduction)

Ambient Room Temperature Phosphorescence

1.1 Introduction

To understand the origin of phosphorescence in a π -conjugated molecule, the detailed photophysical processes need to be understood. Before a π -conjugated organic molecule emits a photon, a series of photophysical processes occur described as follows. First, a molecule from the ground state (S_0) is excited to a higher electronic state (S_1 or higher) after irradiated by light through a process called absorption which has a timescale of 10^{-15} s.^[1-4] In this transition, one of the two electrons in the highest occupied molecular orbital (HOMO) of the molecule is transferred to the lowest unoccupied molecular orbital (LUMO).^[1] The two electrons in the HOMO must have opposite spins and therefore, the total spin number is '0'. This primary state is called the singlet state (S_n).^[1-2] Then, the excited molecule returns to the ground state via radiative or non-radiative pathways. If the molecule comes back to the ground state radiatively, then the molecule shows luminescence.^[1] Luminescence is mainly divided into two main categories: fluorescence and phosphorescence.^[1] The emission of a photon from the S_1 state is called fluorescence, having a time scale of 10^{-9} s. When a molecule is in the S_1 state, the mutual orientation of the spins of the two electrons can change from antiparallel to parallel.^[1-2] The process where the excited singlet state can convert to the triplet state (a state where the total spin number is '1' i.e., T_1) is called intersystem crossing (ISC).^[1] After ISC, if photons come from the triplet state to the ground state radiatively, the process is called phosphorescence. The time scale of the phosphorescence can vary from ms to s depending upon the inter-system crossing rate.^[1]

1.2 Photoluminescence Pathways

The difference between fluorescence and phosphorescence in organic molecules can be understood from the Jablonski diagram including vibration levels that illustrate the electronic states of molecules and the possible transitions between them.^[5] (Figure 1.1). The vertical coordination is arranged by energy, and the electron spin configuration arranges the grouped horizontal state.

In the process of absorption, an electron of the molecule is excited from the ground state (S_0) to a higher-energy state, corresponding to the energy of the absorbed photon. Only specific wavelengths of light can be absorbed because, for efficient absorption, the energy of a photon

should correspond to the energy difference between the two energy levels. Absorption transition solely occurs from S_0 to S_n in an organic molecule, and not from S_0 to T_n because of the selection rule ($\Delta S=0$).

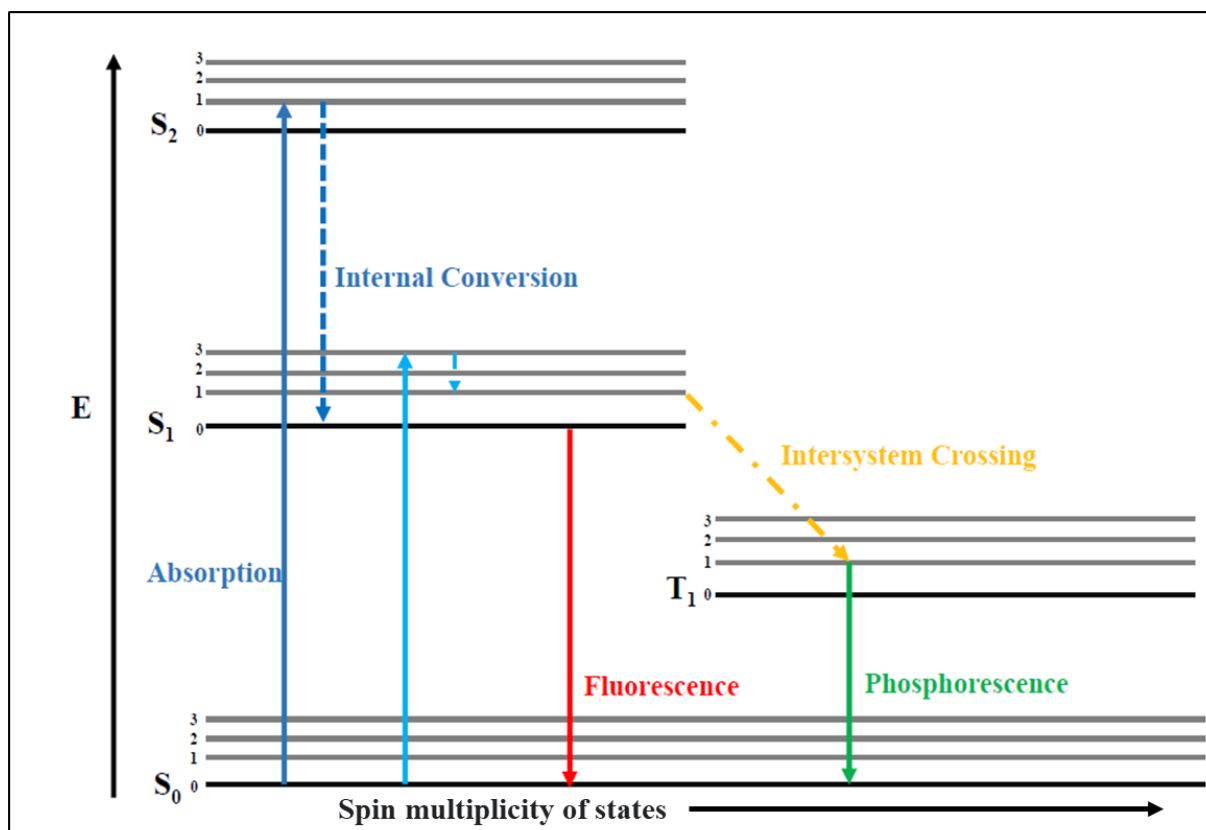


Fig. 1.1.: A typical Jablonski diagram showing the possible radiative and non-radiative transitions that can occur in the excited state of a molecule.

The total momentum of molecules must be conserved after the absorption of light. Absorption always takes place through vertical transition without changing the molecular geometry due to the swift transition. After the excitation and following vibrational energy relaxation, the molecular geometry changes to a more thermodynamically stable one in the excited state. This process is called internal conversion (IC). IC is also a speedy process that happens immediately after absorption within the time scale of 10^{-14} to 10^{-11} s. Although a molecule can be excited to various higher electronic states by the absorption of light, the higher-order energy state quickly relaxes to the S_1 state according to Kasha's rule.

The only exception to Kasha's rule is that vibration levels of S_2 and S_1 are not likely to overlap because of the significant energy difference between them. Therefore, S_1 is considered as the excited state from which the emission occurs. [2-3]

When the excited electron relaxes to S_1 three probable successive processes namely fluorescence, internal conversion, and intersystem crossing compete with each other. The fluorescence of an organic molecule is a radiative decay transition between an excited singlet to a ground state of the singlet. In general, due to the similar orbital configuration in the ground state and excited state, the rate of fluorescence (k_F) is high (high oscillator strength). The wavelength of fluorescence is different from that of the absorption due to the energy loss from the vibrational relaxation preceding fluorescence. This difference in wavelength is what is called the Stokes shift. Another standard route to singlet relaxation is intersystem crossing (ISC), a non-radiative decay process involving a transition between two electronic states with different state spin multiplicity. The singlet excited state of a molecule can be converted to the triplet state by changing the electron spin. However, spin flipping violates the law of conservation of angular momentum and is therefore forbidden by the selection rule. Hence, the intersystem crossing from singlet S_n to T_n is very slow and generally not competitive with fluorescence and internal conversion without the application of an external energy. Consequently, in many cases the triplet state cannot be accessed by photo-excitation. [2-3]

1.3 Room Temperature Phosphorescence

Room temperature phosphorescence (RTP) is the outcome of radiative transitions between two states of different spin multiplicities i.e., $T_1 \rightarrow S_0$. As this is a spin forbidden transition, its rate constant is much lower than the fluorescence.[2] To date, most of the room temperature phosphorescent materials are either inorganic or noble metal-containing organo-metallic complexes, which are expensive, highly toxic, and brittle to process.[6] Therefore, organic RTP materials could be a perfect choice as a promising alternative to the organometallic/inorganic phosphors.[7] However, it is a formidable task to realize phosphorescence under ambient conditions as it is accompanied by various hindering factors which will be discussed in the forthcoming sections

1.3.1 Current Challenges in the Field

Our objective to achieve efficient room temperature phosphorescence from purely organic chromophores is met with the challenge of harvesting triplet excitons under ambient conditions.

Oxygen and vibration mediated quenching of the triplet emitters in the organic molecules are the major causes of this roadblock. Hence phosphorescence from organic molecules is observed at cryogenic temperature and under an inert atmosphere.^[14-15] Therefore to access the triplets of the organic phosphor at room temperature, the molecules need to satisfy the requirements discussed in the following section.

1.4 Requirements to obtain efficient RTP

To attain highly coherent RTP, the designed molecule should have a high intersystem crossing (ISC) rate from the singlet (S_1) to triplet (T_n) state in addition to an efficient spin-orbit coupling matrix element between the singlet (S_1) and triplet (T_n) state. Incorporating various functional groups in the molecular design helps in effectively achieving a high ISC rate and good spin orbital coupling (SOC) value.^[2] According to the El-Sayed's rule, incorporating heteroatoms, carbonyl, or sulfonyl groups can significantly increase the ISC rate through the adequate mixing of singlet and triplet states from different molecular orbitals.^[16] On the other hand, heavy atom substitution like halogen atom in the molecular design constructively increases the SOC, which can enhance ISC and thereby populate triplet state.

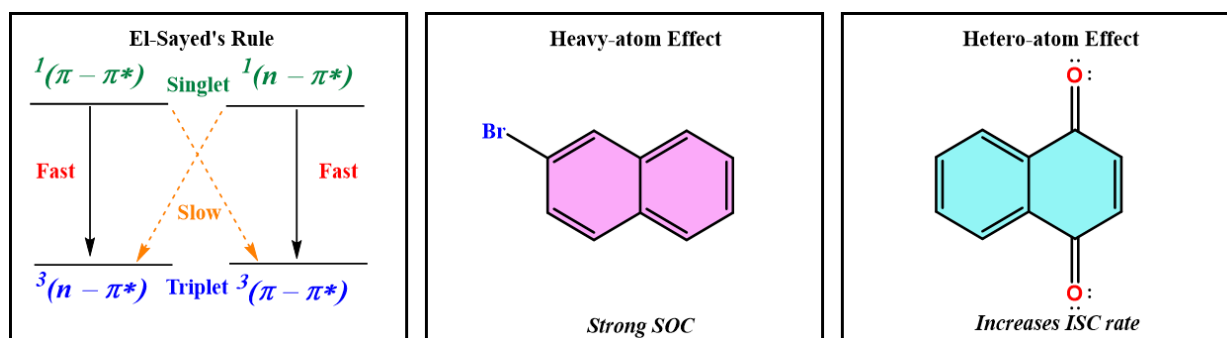


Fig. 1.2.: Factors contributing towards the enhancement of room temperature phosphorescence of organic molecules.

1.5 Strategies for ambient RTP

The strategies, as mentioned earlier for increasing the ISC rate and SOC can help access the triplets. The next challenge is to achieve phosphorescence at room temperature under ambient conditions. In order to accomplish the RTP we have to minimize the vibrational dissipation. This has been achieved by minimizing the vibrational motion of the molecules. For this, various strategies have been developed and implemented to enhance the efficiency of RTP in organic materials under ambient conditions.

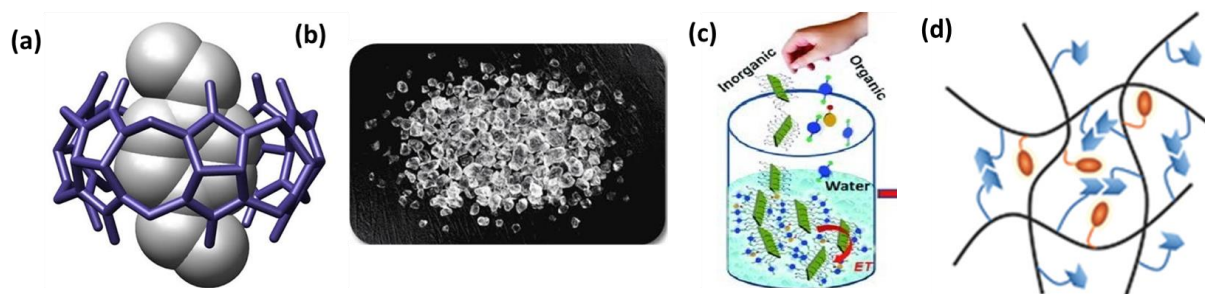


Fig. 1.3.: Strategies for ambient RTP are (a) Host-guest strategy, (b) Crystallization and (c) Inorganic-Organic hybrid scaffolding (d) Polymerization.

Some of the recently developed methods to achieve efficient RTP under air are crystallization, host-guest strategy, hydrogen bonding in polymeric host and inorganic-organic hybrid scaffolding, Polymerization etc.

1.5.1 Importance of solution-processable RTP materials

As we discussed above, efficient phosphorescence emission can be achieved in the crystalline state by minimizing the vibrational dissipation of the triplet states. However, lack of solution processability is the major disadvantage of this method for its further application in various fields such as in display technology. Thus, dispersing the phosphors into a rigid matrix could be an effective way to achieve RTP under ambient conditions. The rigid matrix can be a glassy polymer like polyvinyl alcohol (PVA), polymethylmethacrylate (PMMA) or small organic host material like a steroid (β -estradiol). The host PVA is the most used efficient host matrix due to the multiple hydrogen bonding units from the hydroxyl group efficiently rigidifying the organic phosphors. [22-31]

Another efficient approach to achieve the phosphorescence in the solution phase and amorphous state is via formation of non-doped luminescent polymers without using additional matrices which generates phosphorescence. The ring opening polymerization, covalent crosslinking reaction are the most useful strategies to achieve room temperature phosphorescence. The stiff molecular environment through polymerization can efficiently inhibit non-radiative relaxation for RTP enhancement.

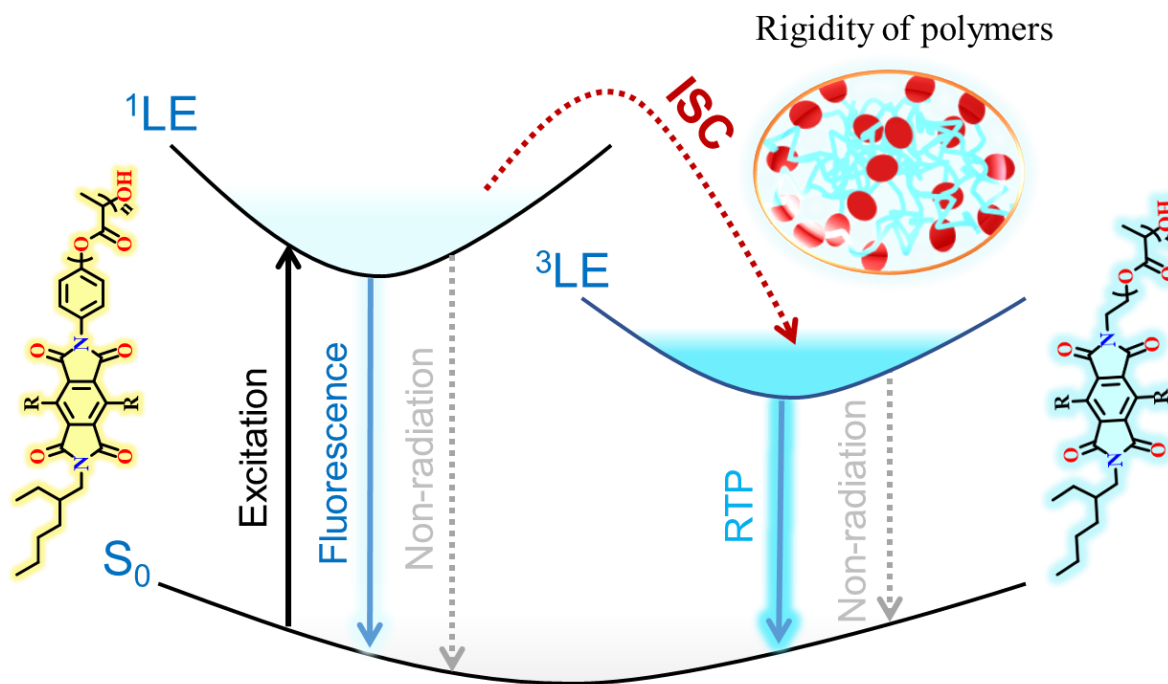


Fig. 1.4.: Our Strategies for ambient RTP is Polymerization using poly (lactic acid) and initiator *N*-substituted Pyromellitic diimide derivative.

So, herein we have synthesized the non-doped polymers including poly (lactic acid) and ring opening metathesis polymers and studied their luminescent properties in the solution state. We envisage that this methodology will help in directly accessing the triplet state without the use of any external polymeric matrix system and thus lowering the cost of production with enhanced efficiency.

1.6 Conclusion and Outlook

In this chapter, we looked at the basics of photoluminescence, especially phosphorescence. We also discussed the need for organic polymeric phosphors as promising alternatives from the traditional organometallic phosphorescent materials. We also discussed the challenges for the scientific community to develop organic room temperature phosphorescent materials and the various requirements that need to be met to achieve the goal. We also reviewed different strategies adopted to attain room temperature phosphorescence from organic molecules. Our ultimate objective is to achieve RTP by designing various organic molecules, keeping in mind all the possible ways to achieve maximum efficiency while using different ring opening covalent polymers to decrease the effects of quenching by providing the required stability to the organic phosphor molecules. Going a step further, we also aim at achieving excellent quantum yields via this strategy.

1.7 References:

1. Data, P.; Takeda, Y. Recent Advancements in and the Future of Organic Emitters: TADF- and RTP-Active Multifunctional Organic Materials. *Chem Asian J*, **2019**, *14*, 1613–1636.
2. Hirata, S. Recent Advances in Materials with Room-Temperature Phosphorescence: Photo physics for Triplet Exciton Stabilization. *Adv. Opt. Mater.*, **2017**, *5*, 1700116.
3. Lakowicz, J. R., Ed. *Principles of Fluorescence Spectroscopy*, (2nd ed).; Kluwer Academic/Plenum Publishers: New York, **1996**.
4. Turro, N. J. *Modern Molecular Photochemistry*: University Science Books: Sausalito, CA, **1991**.
5. Frackowiak, D. The Jablonski Diagram. *J. Photochem. Photobiol. B: Biol.*, **1988**, *2*, 399.
6. W. J. Zhao, Z. K. He, J. W. Y. Lam, Q. Peng, H. L. Ma, Z. G. Shuai, G. X. Bai, J. H. Hao, B. Z. Tang, *Chem-Us*, **2016**, *1*, 592-602.
7. Han, S.; Lian, G.; Zeng, X.; Cao, Z.; Wang, Q.; Cui, D.; Wong, C.-P. Water-Soluble Boron Carbon Oxynitride Dots with Excellent Solid-State Fluorescence and Ultralong Room-Temperature Phosphorescence. *Nano Res.*, **2020**, *13*, 3261–3267.
8. Kenry; Chen, C.; Liu, B. Enhancing the Performance of Pure Organic Room-Temperature Phosphorescent Luminophores. *Nat. Commun.*, **2019**, *10*, 2111.
9. Xu, S.; Chen, R.; Zheng, C.; Huang, W. Excited State Modulation for Organic Afterglow: Materials and Applications. *Adv. Mater.*, **2016**, *28*, 9920–9940.
10. Zhi, J.; Zhou, Q.; Shi, H.; An, Z.; Huang, W. Organic Room Temperature Phosphorescence Materials for Biomedical Applications. *Chem Asian J*, **2020**, *15*, 947–957.
11. B. Song, W. H. Shao, J. Jung, S. J. Yoon, J. Kim, *ACS Appl. Mater. Interfaces*, **2020**, *12*, 6137-6143.
12. Zhang, X.; Cheng, Y.; You, J.; Zhang, J.; Yin, C.; Zhang, J. Ultralong Phosphorescence Cellulose with Excellent Anti-Bacterial, Water-Resistant and Ease-to-Process Performance. *Nat. Commun.*, **2022**, *13*, 1117.
13. Lewis, G. N.; Lipkin, D.; Magel, T. T. Reversible Photochemical Processes in Rigid Media. A Study of the Phosphorescent State. *J. Am. Chem. Soc.*, **1941**, *63*, 3005–3018.
14. Azumi, T.; O'Donnell, C. M.; McGlynn, S. P. On the Multiplicity of the Phosphorescent State of Organic Molecules. *J. Chem. Phys.*, **1966**, *45*, 2735–2742.
15. Lower, S. K.; El-Sayed, M. A. The Triplet State and Molecular Electronic Processes in Organic Molecules. *Chem. Rev.*, **1966**, *66*, 199–241.

- 16.** Bolton, O.; Lee, K.; Kim, H.-J.; Lin, K. Y.; Kim, J. Activating Efficient Phosphorescence from Purely Organic Materials by Crystal Design. *Nat. Chem.*, **2011**, 3, 415.

Chapter-2

Monomeric Room Temperature Phosphorescence from N-substituted Pyromellitic Diimide Based Polymers

2.1 Abstract

Polymer-based materials have gained attention in the research field of solution processable room-temperature phosphorescence (RTP) because they cannot only possess fantastic properties such as good stretchability, easy processing, low cost, high thermal stability and so forth, but also serve as rigid matrices to suppress the nonradiative decay process and thus contribute to phosphorescence emission at room temperature. Our group has gained expertise in showing RTP from arylene diimide based compounds, and pyromellitic diimides. Herein, my thesis outlines the development of the RTP in organic polymer materials using derivatives of pyromellitic diimides as initiators. To achieve solution processable polymers showing RTP, we synthesized the polymers having PmDI derivatives as an initiator for the polymerization of D and L lactide monomers. The photophysical studies predict that out of all synthesized polymers, polymer PmDIBr-P₂ is showing the cyan colour from solution-processable state at room temperature which is the biggest challenge to achieve. Remarkably, the air-stable solution processable phosphorescence presented here own one of the highest quantum yields (11%) among various neat polymer reported till date.

2.2 Introduction

Metal-free purely organic phosphors, with significant Stokes shift and longer lifetimes, have garnered much attention recently as a promising substitute to expensive and toxic metal-based inorganic phosphors materials.^[1] Pure organic RTP luminogens are advantageous over the well-developed inorganic counterparts by their low toxicity, value, environmental load, and considerable stability, allowing a wide range of optoelectronic and biological applications.^[2-5] Although this alternative seems very plausible, it has its own challenges; as an example, the quantum yield of purely organic phosphors is affected by its poor intersystem crossing yield and high susceptibility towards oxygen and vibration mediated triplet state quenching.^[6] This is why most bright organic phosphors are obtained only in a highly crystalline state because its rigid network of molecules minimizes the non-radiative quenching of the triplet excitons and reduces oxygen diffusion.^[6-11] In general, metal-free RTP materials can be divided into small molecules

and polymers. Organic phosphor molecules find their applications as integral parts in various display devices, sensors, in the field of bioimaging, etc. [12-17] Now since these crystalline phosphors lack solution-processability, their application is restricted in the fields mentioned earlier. Therefore, the challenge is to design and develop solution-processable, amorphous state or solution state organic materials to realize RTP under ambient conditions. Thus, some strategies had been adopted to “stabilize” the vulnerable triplet excitons, such as synthesis of non-doped solution processable luminescent polymers,⁹⁻¹¹ introducing various intermolecular interactions,^{4,12-14} and doping guests into rigid host matrices.

Herein, in this Chapter, we have synthesized **non doped luminescence polymer** which shows solution processable room temperature phosphorescence based on N-substituted pyromellitic diimide as an initiator and D and L- lactide as a monomer for the polymerization. The structural rigidity and oxygen tolerance of these polymeric systems further minimize the molecular vibrations and triplet quenching of organic phosphors, which in turn stabilizes the phosphorescence in solution phase and films under ambient conditions. Recently, our group has reported pyromellitic diimide as one the most efficient ambient phosphors, in the crystalline state.⁹ So, introducing the concept of non-doped luminescent polymerization in these kinds of derivatives of pyromellitic diimides can in-built populate the intersystem crossing of the system which can give solution processable cyan emission room temperature phosphorescence without the use of external polymer matrix.

To confirm, the emission is originating from the monomeric state of PmDI, we have performed the photophysical studies for our initiator molecule i.e., (**C7**) using polymethyl methacrylate (PMMA) an amorphous polymeric host to stabilize RTP, at very low concentration (1wt% with respect to PMMA). Remarkably, cyan emission was observed for PMMA film also confirming the monomeric emission under ambient conditions. Further, studies at 77 K suggest the phosphorescence coming from monomeric states.

2.3 Molecular Design

Based on all the strategies and challenges described above, our motive is to design a molecule that eliminates the factors affecting RTP and increases the efficiency of triplet harvesting in solution state. Due to the presence of four carbonyl groups and heavy atoms, pyromellitic diimide (PmDI) has a good SOC and high intersystem crossing rate (k_{isc}). Recently our group has observed RTP with PmDI derivatives with good quantum yield.

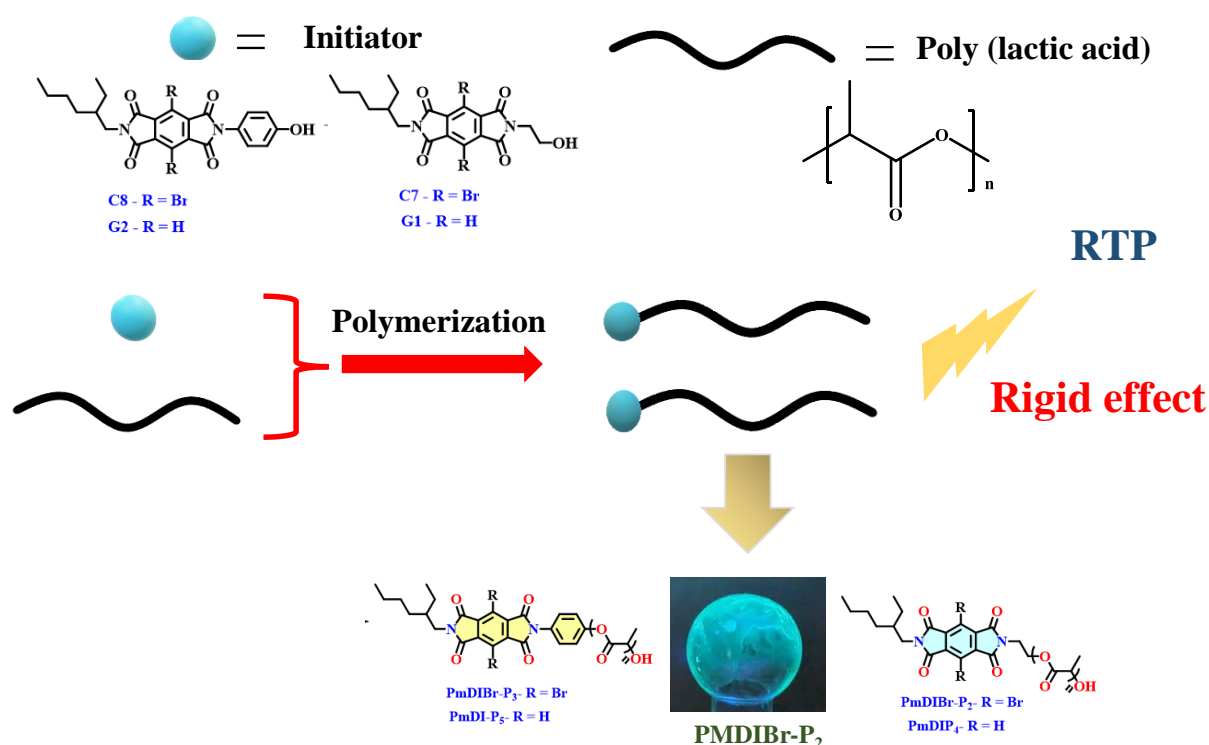


Fig. 2.1.: Strategy for ambient RTP used here i.e., polymerization using poly (lactic acid) and initiator N-substituted Pyromellitic diimide derivative.

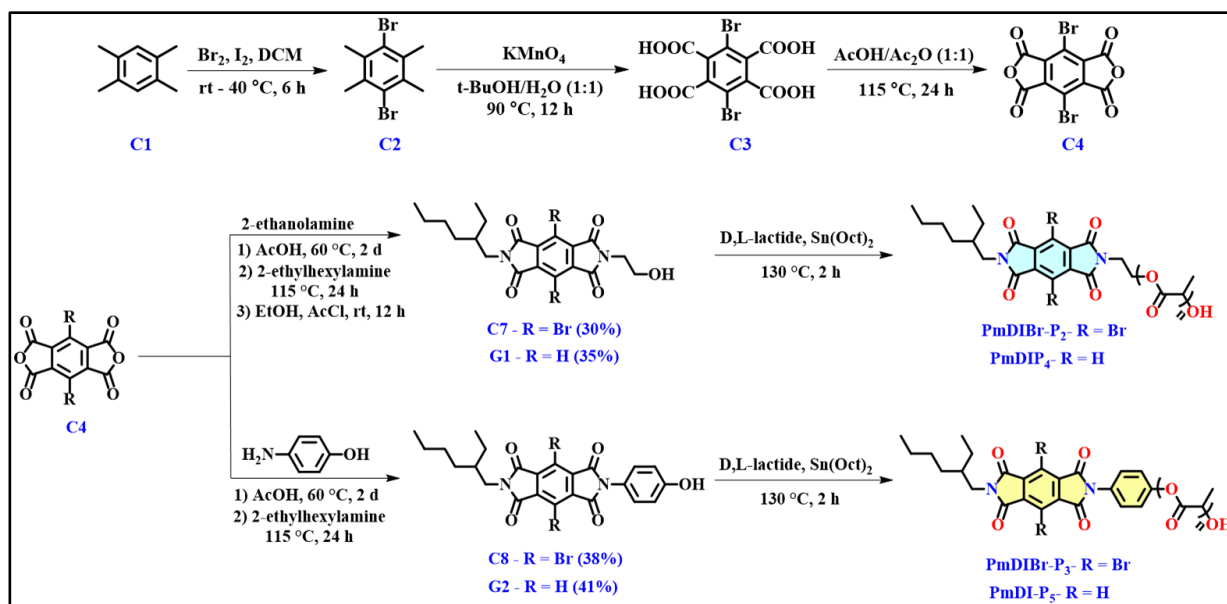
Herein, we have used the polymeric strategy where a simple N-substituted PmDI core is used as an initiator and long polymer chain is attached to it. The presence of long polymer chain can rigidify the system and impart stability to the triplet state and enhance the intramolecular CT states. The long chains also ensure that the aggregation of PmDI molecules can be hindered to the larger extent. The polymer synthesized is using the polymerization of D and L- lactide monomer i.e., coupling our initiator N-substituted pyromellitic diimide with poly (lactic acid) (PLA), which is biodegradable and biocompatible in nature, and is commercially available. With this polymer, the fluorescence quantum yield is enhanced, and unexpected optical properties emerge, oxygen-sensitive solution processable room-temperature phosphorescence (RTP).

Using this concept, we introduced the method of covalent dye conjugation with a polymer by ring-opening polymerization (ROP), which was developed by Fraser and co-workers¹⁷. Hence, designed N-substituted Pyromellitic diimide (PmDI) non-doped luminescent solution processable polymers are showing the monomeric cyan colour emission at room temperature with high quantum yield (11 %).

2.3.1 Design Strategy and Synthesis

The preparation strategy for **PmDIBr-P₂**, **PmDIBr-P₃**, **PmDI-P₄** and **PmDI-P₅** via multistep synthetic pathway by using simple reagents. The first synthetic pathway of dibromo pyromellitic dianhydride (**C4**) is shown below (Scheme 1).

The dibromo pyromellitic (**C4**) was prepared according to the reported method⁹ initially from our group, we prepared dibromo durene (**C2**) from durene (**C1**) with the presence of molecular bromine as a bromine source. Further **C3** formation with the help of KMnO₄, t-BuOH:H₂O at 80 °C for 12 h was achieved with 46.85 % yield. Later ring-closing step in acidic medium, the obtained compound of (**C4**) with quantitative yield.



Scheme 1: (A) Synthetic scheme of lactide based polymers.

A mixture of (**C4**) was dissolved in AcOH and stirred for 10 mins under inert atmosphere. Then, PmDIBr and PmDI derivatives i.e., alcohol or 4-aminophenol derivative was added with respect to its corresponding reactions, and the reaction mixture was stirred for another 48 h at 60 °C. To this mixture, 2-ethylhexylamine was added dropwise according to the reaction requirement and allowed to reflux for 24 h at 80 °C and reaction was monitored using TLC. The precipitate was collected through filtration and the crude compound was dried under vacuum. The crude residue was purified using silica gel column chromatography by eluting with the solvent system of hexane and DCM to afford the solid as our final compound (C7, C8, G1, G2) with yield 30-45 %.

Further, we have synthesized the four PmDI lactide based polymers **PmDIBr-P₂**, **PmDIBr-P₃**, **PmDI-P₄** and **PmDI-P₅** having ratio (initiator: monomer: catalyst = 1:100:0.08). A Schlenk tube was charged with L-lactide and the corresponding initiator. The tube was filled

with nitrogen, sealed, and placed in an oil bath set at 130 °C to produce a homogeneous melt. Then Sn(oct)₂ solution in methylcyclohexane was added to the reaction mixture under a nitrogen atmosphere, and the flask was resealed and heated at 130 °C to form a viscous solid. The crude mixture was cooled to room temperature and precipitated from CH₂Cl₂/MeOH (3×) and CH₂Cl₂/hexanes (1×) to remove unreacted lactide compound to yield the viscous solid as final polymer.

The structure of polymer has been characterized by the ¹H NMR, ¹³C NMR and Polydispersity index and molecular weight of the polymers by Gel Permeation chromatography (GPC). All the four polymers are highly soluble in organic solvents like chloroform, THF. The thermal stability of all the polymers has been checked by the differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA).

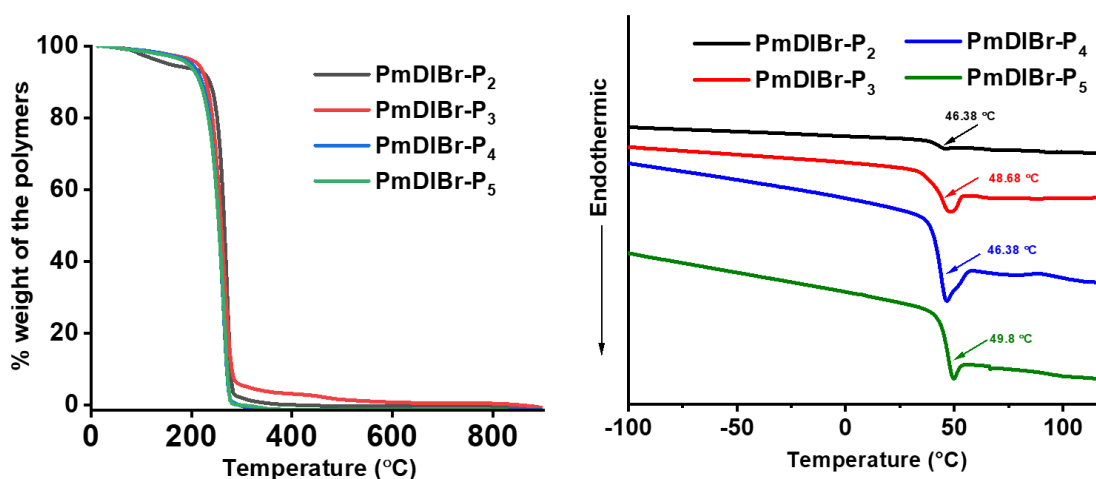


Figure 2.2. (a) TGA traces of *PmDIBr-P₂*, *PmDIBr-P₃*, *PmDI-P₄* and *PmDI-P₅* recorded at a heating rate of 5 °C min⁻¹. (b) DSC traces of *PmDIBr-P₂*, *PmDIBr-P₃*, *PmDI-P₄* and *PmDI-P₅* recorded at a heating rate of 10 °C min⁻¹.

Furthermore, the polymers are showing superior thermal stability with decomposition temperatures T_d, at 187 °C for PmDIBr-P₂, T_d, starts at 203 °C for PmDIBr-P₃, T_d, starts at 204 °C for PmDIBr-P₄, T_d, starts at 205 °C for PmDIBr-P₅, shown in Figure 2.2. (a), which benefited from their molecular weights of polymers M_n = 5111 Da for PmDIBr-P₂, M_n = 6311 Da for PmDIBr-P₃, M_n = 7911 Da for PmDIBr-P₄, M_n = 11845 Da for PmDIBr-P₅. In differential scanning calorimetry (DSC), the glass transition temperatures (T_g) of polymers observed as 46.38 °C for PmDIBr-P₂, 48.68 °C for PmDIBr-P₃, 46.38 °C for PmDIBr-P₄, 49.8 °C for PmDIBr-P₅, shown in Figure 2.2. (b).

2.4 Results and Discussion

To begin with, we have performed a preliminary photophysical study for the neat **PmDI-Br-P₂** polymer. The **PmDI-Br-P₂** polymer shows a band in the excitation spectra when monitored at 550 nm with maximum around 365 nm as shown in figure 2.3(a) which corresponds to the locally excited band of PmDI similar to what we have reported earlier⁹. A weak band with maximum around 450 nm was observed in the excitation spectra which can be mostly from the aggregated state. Emission spectra showed emission peak with a maximum at 483 nm when excited at 340 nm and showed emission around with a maximum at 518 nm when excited at 430 nm as shown in figure 2.3(b).

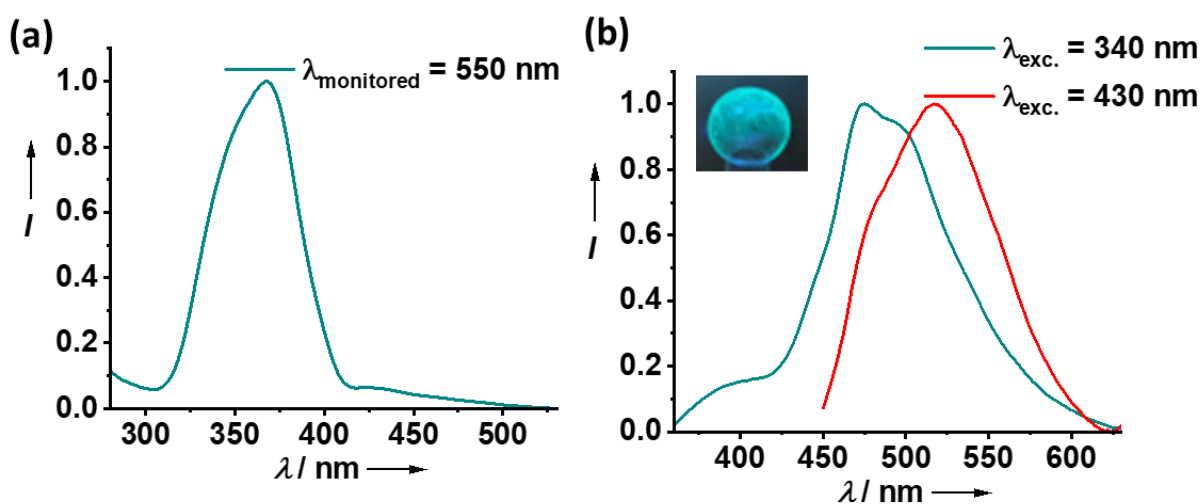


Figure 2.3. Normalized a) excitation spectra monitored at 550 nm, b) emission spectra for the **PmDI-Br-P₂** polymer ((Inset: photographs of **PmDI-Br-P₂** in air under 365 nm UV-lamp excitation))

Next, we dispersed **C7** (our initiator) used for synthesizing **PmDI-Br-P₂** polymer in polymethyl methyl acrylate (PMMA) matrices in very low concentration (1 wt. % with respect to PMMA), to fully disperse the molecules and confirmed the emission arising from the monomeric state. PMMA is known for protecting the phosphors from vibrational dissipation and oxygen mediated quenching to stabilize the triplet state. Remarkably, a strong cyan emission was observed PMMA film with maximum similar to neat polymer confirming the emission originates from monomeric state. Further, we have collected the emission of neat polymer **PmDI-Br-P₂** at 77K glassy matrix to understand the origin of the emission. We found that the emission of PmDI-Br-P₂ polymer at room-temperature, initiator in 1 wt% PMMA overlay perfectly with the emission at 77 K (figure 2.4(a)) implying towards the phosphorescence nature of the emission.

Previous reports from our group suggest that the locally excited triplet state (^3LE) of PmDI is positioned at 490 nm suggesting the emission to be monomeric phosphorescence from PmDI.

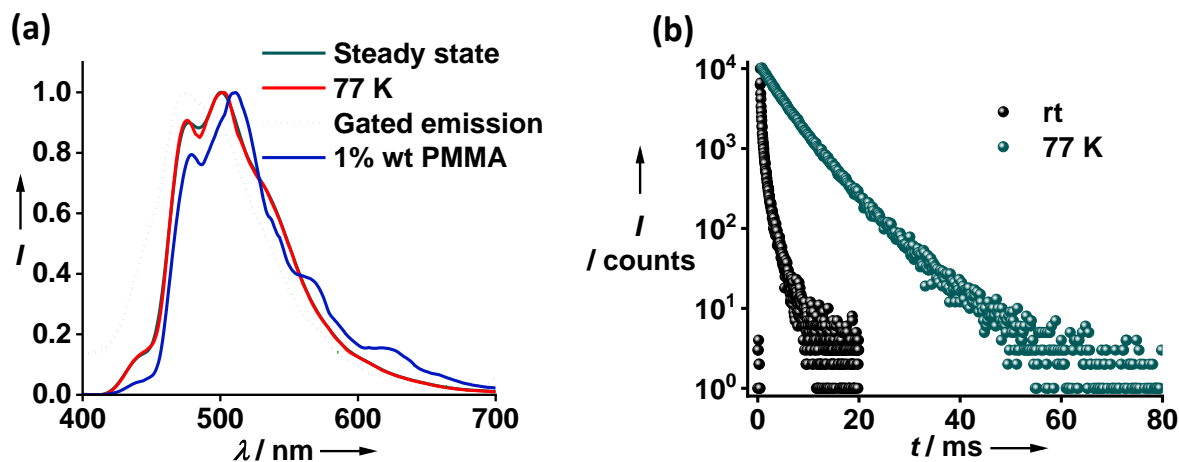


Figure 2.4. Normalised steady-state spectra at room temperature and 77K followed by gated emission spectra of **PmDIBr-P₂**, (delay time = 0.5 ms) and normalised spectra of initiator **C7** in 1 wt% of PMMA matrix at 77K ($\lambda_{\text{exc.}} = 340$ nm, $\lambda_{\text{collected}} = 550$ nm) (b) Phosphorescence lifetime decay plot of **PmDIBr-P₂** ($\lambda_{\text{exc.}} = 340$, $\lambda_{\text{collected}} = 550$ nm).

Lifetime measurements done showed an average lifetime of 5.6 ms when monitored at 550 nm ($\lambda_{\text{exc.}} = 340$ nm) suggesting the phosphorescence origin of the emission. Gated emission spectrum measured with a delay time of 0.5 ms is also similar to the steady-state emission, which further confirms the nature of emission to be phosphorescence (figure 2.4(b)).

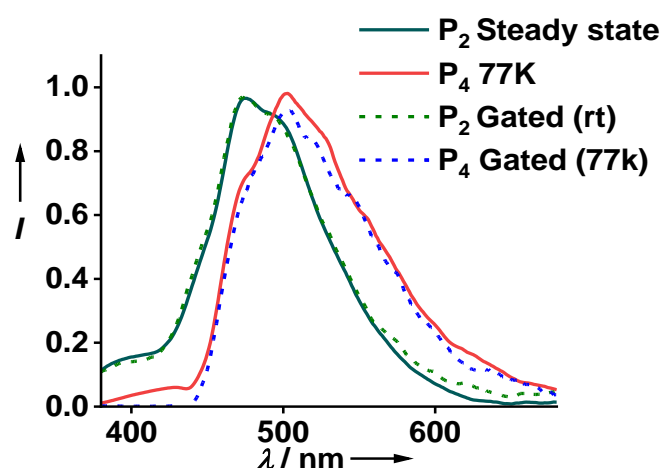


Figure 2.5. Normalised steady-state and gated emission spectra of **PmDIBr-P₂** along with normalised emission spectra at 77K and steady state and gated emission spectra of **PmDI-P₄** at 77K ($\lambda_{\text{exc.}} = 350$ nm, $\lambda_{\text{collected}} = 550$ nm, delay time = 0.5 ms).

The control polymer (**PmDI-P₄**) synthesized without bromine core-substitution showed almost null or feeble emission at ambient conditions. While at 77 K excellent emission (both steady-state and gated) was obtained similar to the bromo-substituted polymer **PmDI-Br-P₂** (figure 2.5). The presence of bromine heavy atoms in **PmDI-Br-P₂** has enhanced the SOC to boost ISC rate and thereby augmented the phosphorescence efficiency to several folds. The absolute phosphorescence quantum efficiencies of **PmDI-Br-P₂** and **PmDI-P₄** in neat film were 11 % and 1 % respectively.

Therefore, it is evident that these non-doped synthesized polymers are operative in these derivatives to facilitate substantial ISC by increasing the rigidity of the system and subsequently to achieve efficient RTP in neat polymer and amorphous matrix which is very interesting result to observe. This is the first-time observation of polymeric phosphorescence from pyromellitic diimides. We envisage that this observation can open up momentous scope in terms of solution processable phosphorescent polymers for various applications.

2.5 Conclusion

In conclusion, we have introduced the new class of organic polymers with smallest family of arylene diimides derivative as initiator and harvested the triplet excitons of the N-substituted PmDI-Br and PmDI through a non-doped luminescent polylactide polymer synthesis in solution state. The hetero and heavy atom substituted molecular design is unique which not only reduces the vibrational dissipations of the triplets but also prevents oxygen-mediated quenching, results efficient cyan emission RTP in the solution state and the thin-film state. Although many organic room temperature phosphors are reported recently, the present system is unique with respect to its new molecular design and properties, with high quantum yield (11%).

2.6 Future Outlook

Synthetic procedures have to be optimized further for getting polymers with enhanced molecular weight and poly dispersity index. Detailed photophysical studies of the synthesized polymers needs to be investigated to understand the system.

2.7 References

1. Xu, S.; Chen, R.; Zheng, C.; Huang, W. Excited State Modulation for Organic Afterglow: Materials and Applications. *Adv. Mater.* **2016**, 28, 9920–994.
2. Hirata, S. Recent Advances in Materials with Room-Temperature Phosphorescence: Photo physics for Triplet Exciton Stabilization. *Adv. Opt. Mater.* **2017**, 5, 1700116.

3. Zhao, W.; He, Z.; Lam, J. W. Y.; Peng, Q.; Ma, H.; Shuai, Z.; Bai, G.; Hao, J.; Tang, B. Z. Rational Molecular Design for Achieving Persistent and Efficient Pure Organic Room-Temperature Phosphorescence. *Chem* **2016**, *1*, 592–602.
4. Yang, Z.; Mao, Z.; Zhang, X.; Ou, D.; Mu, Y.; Zhang, Y.; Zhao, C.; Liu, S.; Chi, Z.; Xu, J.; Wu, Y. C.; Lu, P. Y.; Lien, A.; Bryce, M. R. Intermolecular Electronic Coupling of Organic Units for Efficient Persistent Room-Temperature Phosphorescence. *Angew. Chem., Int. Ed.* **2016**, *55*, 2181–2185.
5. Qiu, W.; Cai, X.; Li, M.; Wang, L.; He, Y.; Xie, W.; Chen, Z.; Liu, M.; Su, S.-J. Dynamic Adjustment of Emission from Both Singlets and Triplets: The Role of Excited State Conformation Relaxation and Charge Transfer in Phenothiazine Derivates. *J. Mater. Chem. C* **2021**, *9* (9), 1378–1386.
6. Narushima, K.; Kiyota, Y.; Mori, T.; Hirata, S.; Vacha, M. Suppressed Triplet Exciton Diffusion Due to Small Orbital Overlap as a Key Design Factor for Ultralong-Lived Room-Temperature Phosphorescence in Molecular Crystals. *Adv. Mater.* **2019**, *31*, 1807268.
7. Hirata, S. Roles of Localized Electronic Structures Caused by pi Degeneracy Due to Highly Symmetric Heavy Atom-Free Conjugated Molecular Crystals Leading to Efficient Persistent Room-Temperature Phosphorescence. *Adv. Sci.* **2019**, *6*, 1900410.
8. Ma, H.; Peng, Q.; An, Z.; Huang, W.; Shuai, Z. Efficient and Long-Lived Room-Temperature Organic Phosphorescence: Theoretical Descriptors for Molecular Designs. *J. Am. Chem. Soc.* **2019**, *141*, 1010–1015.
9. Garain, S.; Kuila, S.; Garain, B. C.; M. Kataria, M.; Borah, A.; Pati, S. K.; George, S. J.; Arylene Diimide Phosphors: Aggregation Modulated Twin Room Temperature Phosphorescence from Pyromellitic Diimides. *Angew. Chem. Int. Ed.* **2021**, *60*, 12323.
10. Chen, X.; Xu, C.; Wang, T.; Zhou, C.; Du, J.; Wang, Z.; Xu, H.; Xie, T.; Bi, G.; Jiang, J.; Zhang, X.; Demas, J. N.; Trindle, C. O.; Luo, Y.; Zhang, G; Versatile Room-Temperature-Phosphorescent Materials Prepared from N-Substituted Naphthalimides: Emission Enhancement and Chemical Conjugation. *Angew. Chem. Int. Ed.* **2016**, *55*, 9872.
11. Garain, S.; Kuila, S.; Garain, B. C.; Kataria, M.; Borah, A.; Pati, S. K.; George, S. J; Arylene Diimide Phosphors: Aggregation Modulated Twin Room Temperature Phosphorescence from Pyromellitic Diimides. *Angew. Chem. Int. Ed.* **2021**, *60*, 12323.
12. Yang, J.; Zhen, X.; Wang, B.; Gao, X.; Ren, Z.; Wang, J.; Xie, Y.; Li, J.; Peng, Q.; Pu, K.; Li, Z. The Influence of the Molecular Packing on the Room Temperature Phosphorescence of Purely Organic Luminogens. *Nat. Commun.* **2018**, *9*, 840.

13. Chen, C.; Chi, Z.; Chong, K. C.; Batsanov, A. S.; Yang, Z.; Mao, Z.; Yang, Z.; Liu, B. Carbazole Isomers Induce Ultralong Organic Phosphorescence. *Nat. Mater.* **2021**, *20*, 175–180.
14. Gu, L.; Shi, H. F.; Bian, L. F.; Gu, M. X.; Ling, K.; Wang, X.; Ma, H. L.; Cai, S. Z.; Ning, W. H.; Fu, L. S.; Wang, H.; Wang, S.; Gao, Y. R.; Yao, W.; Huo, F. W.; Tao, Y. T.; An, Z. F.; Liu, X. G.; Huang, W. Colour-Tunable Ultra-Long Organic Phosphorescence of a Single Component Molecular Crystal. *Nat. Photonics* **2019**, *13*, 406–411.
15. Li, M.; Cai, X.; Qiao, Z.; Liu, K.; Xie, W.; Wang, L.; Zheng, N.; Su, S. J. Achieving High-Efficiency Purely Organic Room-Temperature Phosphorescence Materials by Boronic Ester Substitution of Phenoxathiine. *Chem. Commun.* **2019**, *55*, 7215–7218.
16. Shoji, Y.; Ikabata, Y.; Wang, Q.; Nemoto, D.; Sakamoto, A.; Tanaka, N.; Seino, J.; Nakai, H.; Fukushima, T. Unveiling a New Aspect of Simple Arylboronic Esters: Long-Lived Room-Temperature Phosphorescence from Heavy-Atom-Free Molecules. *J. Am. Chem. Soc.* **2017**, *139*, 2728–2733.
17. Zhang, G.; Chen, J.; Payne, S. J.; Kooi, S. E.; Demas, J. N.; Fraser, C. L. Multi-Emissive Difluoroboron Dibenzoylmethane Polylactide Exhibiting Intense Fluorescence and Oxygen-Sensitive Room-Temperature Phosphorescence. *J. Am. Chem. Soc.*, **2007**, *129*, 8942–8943.

Chapter-3

Ring Opening Metathesis Polymers with Pendant pyromellitic diimides for Charge-Transfer Phosphorescence

3.1 Abstract

Charge-transfer (CT) complexes, formed by electron transfer from a donor to an acceptor, play a crucial role in organic semiconductors. Herein, we are using N-substituted pyromellitic diimides ring opening metathesis polymers which are forming charge transfer (CT) complexes with electron rich solvents like mesitylene. CT based donor-acceptor materials are well-investigated in the field of supramolecular foldamers, ferroelectrics and so on, but the reports based on luminescence-based CT systems are rare. As, charge-transfer (CT) donor-acceptor complexes have been extensively explored in case of supramolecular materials, but their reports in field of phosphorescence are still known very less. Thus, in the present project, we are trying to modulate the excited state emission characteristics of a N-substituted pyromellitic diimide polymers on complexation with appropriate donor molecules.

3.2 Introduction

Luminescent polymers have drawn much attention for the development of low-cost, large-area solution processed organic light-emitting diodes (OLEDs) because of their promising tunable emission colours in the entire visible region¹. However, realization of RTP with an aggregate induced phosphorescence (AIP) feature via harvesting supersensitive excited charge transfer triplet is emerging field of interests²⁻⁴. CT process can help in enhancing the triplet harvesting rate by acting as an intermediate state to channel excitons to triplet state or to enhance the rate of reverse intersystem crossing in thermally activated delayed fluorescence (TADF)^{5,6}. Charge-transfer (CT) interactions between the donor and acceptor are based on the functions of π -conjugated molecules and polymers.

Construction of a donor-acceptor binary system is very attractive for understanding RTP seeing the versatility of the donor and acceptor combinations to obtain RTP with varied emission colours. But the challenge is to design and develop solution-processable, amorphous state or solution state organic materials to realize RTP under ambient conditions. However, solution and amorphous phase RTP are being explored slowly, employing various strategies²⁻⁴.

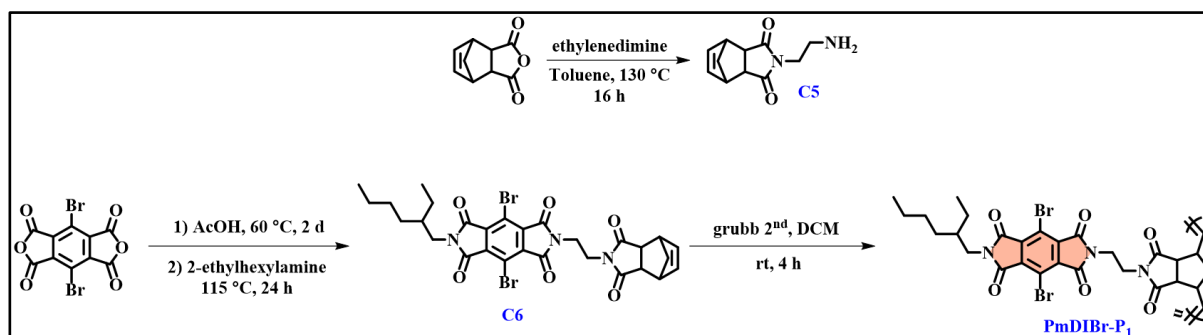
Herein, in our system we introduce a modular donor-acceptor approach to realize the unprecedented ambient CT room temperature phosphorescence with electron-deficient N-substituted PmDI based polymers and electron-rich solvent system like mesitylene. We have used PmDI core which are the well-studied smallest class of the organic phosphors in the class of arylene diimides. After that, ring-opening metathesis polymerization (ROMP) performed by utilizing ruthenium-based Grubbs' second-generation catalyst $\text{Ru}((\text{Cl}_2(\text{CH}_2\text{Ph}))(\text{P}(\text{Cy})_3)_2))$ shows the characterization of living polymerization. The characterization of the synthesized polymer done with the help of the ^1H NMR and thermal stability of the polymer has been checked by the DSC, TGA. This synthesized polymer is non-emissive. After realizing the importance of charge transfer in luminescent materials, we have investigated further to study the spectroscopic properties of our synthesized polymers with electron rich solvent system.

3.3 Molecular design

Based on all the strategies and challenges described above, our motive is to design a molecule that eliminates the factors affecting RTP and increases the efficiency of triplet harvesting. Due to the presence of four carbonyl groups and heavy atoms, pyromellitic diimide (PmDI) has a good SOC and high intersystem crossing rate (K_{isc}). Recently our group has observed RTP with PmDI derivatives with good quantum yield. In our case, we have designed the N-substituted Pyromellitic diimide (PmDI) based on ring opening metathesis luminescent solution processable polymer.

3.3.1 Design Strategy and Synthesis

The preparation strategy for **PmDI-Br-P₁** via multistep synthetic pathway by using simple reagents. The first synthetic pathway of dibromo pyromellitic dianhydride (**C4**) is shown below (Scheme 1).



Scheme 2: Synthetic scheme of ring opening metathesis polymer **PmDI-Br-P₁**.

Herein, we have synthesized the ring opening metathesis PmDI based polymers with the help of 2nd generation ruthenium-based Grubbs catalyst with the feed monomer ratio (100:1). The synthesis of polymers PmDIBr-P₁ has been done at room temperature for 4 hours. After the completion of reaction, the polymerization has been quenched with the help of ethylvinylether. The structure of polymer has been characterized by the ¹H NMR, ¹³C NMR, Gel permeation chromatography. This polymer is highly soluble in organic solvents like chloroform, THF.

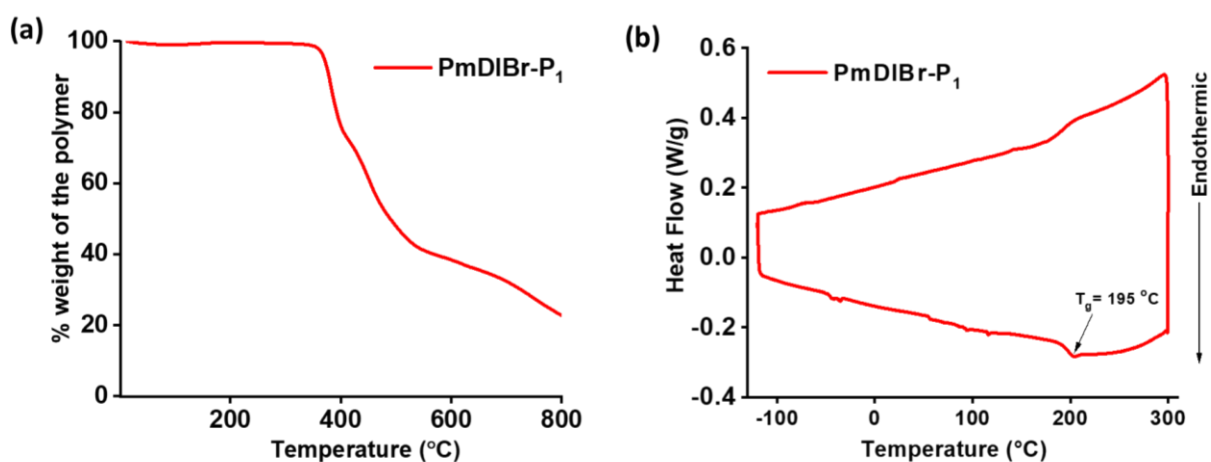


Figure 3.1. (a) TGA traces of **PmDIBr-P₁** recorded at a heating rate of 5 °C min⁻¹. (b) DSC traces of **PmDIBr-P₁** recorded at a heating rate of 10 °C min⁻¹.

Furthermore, the polymer is showing superior thermal stability with decomposition temperatures T_d at 331 °C as shown in figure 3.1.(a). which benefited from their high molecular weights of polymers (M_n =16618). In differential scanning calorimetry (DSC), the glass transition temperatures (T_g) of polymers are in the range of 195 °C as shown in figure 3.1.(b).

3.4 Results and Discussion

This polymer was non-emissive under ambient conditions. However, with an intention to induce emission into this system, we have invoked charge-transfer interactions of the electron-deficient PmDI in the polymeric sidechain with electron-rich aromatic solvents like toluene, mesitylene. Initial results from our group where naphthalene diimides could form CT complex with electron-rich aromatic solvents motivated us to continue this study forward. In addition, we anticipated similar results from PmDI based polymer, smallest congener from the family of arylene diimides. To understand the charge transfer, we choose N-substituted Pyromellitic diimide (PmDI) ring opening metathesis polymers was chosen as the acceptor component for the present study where we have chosen the toluene and mesitylene as the donor moiety in the system. As the **PmDIBr-P₁** is not showing any emission under UV light. Further investigation was carried out to unravel the differences in the spectroscopic properties of **PmDIBr-P₁** in the presence of various aromatic

solvents which is crucial to understand the concept of charge transfer between polymer and aromatic solvent. In toluene, no changes were observed on doping with the polymer.

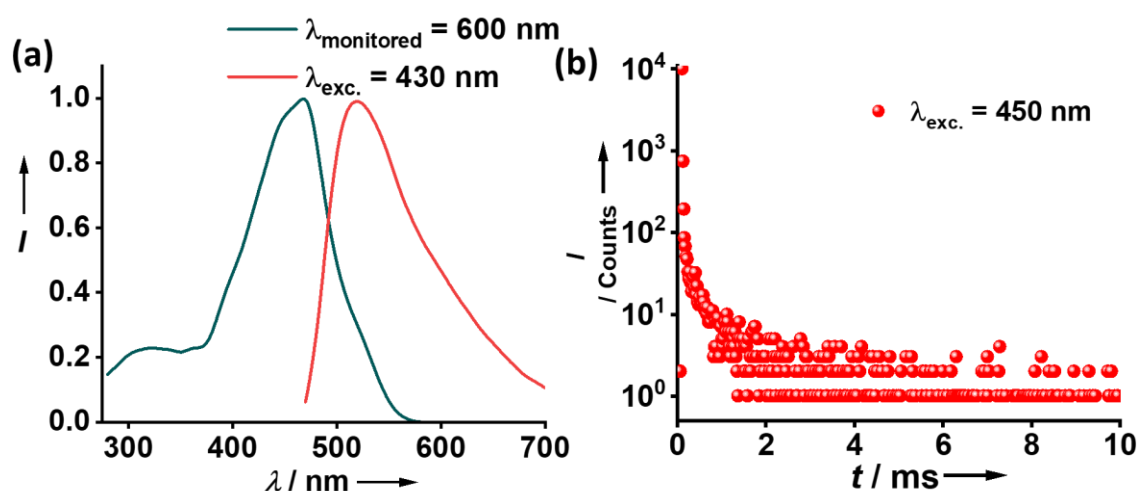


Figure 3.2. Normalized a) excitation (green line) and emission spectra (red line) for the **PmDIBr-P₁** polymer solution in mesitylene (b) Phosphorescence lifetime decay plot of **PmDIBr-P₁** solution in mesitylene ($\lambda_{\text{exc.}} = 450$, $\lambda_{\text{collected}} = 600$ nm).

While a deep-yellow coloration was observed when polymer was mixed with mesitylene. To gain further insights, spectroscopic studies were carried out to specifically probe the origin of the colour change. Excitation spectra monitored at 600 nm exhibited an additional band spanning from 390 nm to 500 nm which can be of charge-transfer in origin. The emission spectra collected by selectively exciting at the CT band showed CT emission. ($\lambda_{\text{exc.}} = 430$ nm). The lifetime decay profiles of emission in mesitylene showed an average lifetime of 0.26 ms in mesitylene ($\lambda_{\text{exc.}} = 450$ nm, $\lambda_{\text{collected}} = 600$ nm) hinting towards the phosphorescence nature of the emission from CT state. However, the recent result we obtained have to investigated further to get deeper insights on the CT induced changes in the system. Although, it is noteworthy to point out that the CT based interaction can play a major role in stabilizing triplet harvesting in the present system. In a broader perspective, it can be inferred that CT based systems can have tremendous potential to give way for flexible systems with excellent solution processability.

3.5 Conclusion

In summary, we have reported room-temperature CT phosphorescence from organic donor-acceptor systems by using N-substituted pyromellitic diimide metathesis polymers as the

acceptor and aromatic solvents as donors. The preliminary studies shows that non-covalent complexation is found majorly in this system. However, we have not done detailed investigation yet.

3.6 Future Outlook

Detailed photophysical studies of the synthesized polymers and their charge transfer characteristics needs to be investigated to understand the system thoroughly.

3.7 References

1. Hu, J.; Chang, Y.; Chen, F.; Yang, Q.; Shao, S.; Wang, L. Design, Synthesis, and Properties of polystyrene-based Through-space Charge Transfer Polymers: Effect of Triplet Energy Level of Electron Donor Moiety on Delayed Fluorescence and Electroluminescence Performance. *J. Polym. Sci.*, **2022**,1-9.
2. Kulkarni, C.; Periyasamy, G.; Balasubramanian, S.; George, S. J. Charge-Transfer Complexation between Naphthalene Diimides and Aromatic Solvents. *Phys. Chem. Chem. Phys.*, **2014**, *16*, 14661.
3. Zeng, X.; Luo, J.; Zhou, T.; Chen, T.; Zhou, X.; Wu, K.; Zou, Y.; Xie, G.; Gong, S.; Yang, C. Using Ring-Opening Metathesis Polymerization of Norbornene to Construct Thermally Activated Delayed Fluorescence Polymers: High-Efficiency Blue Polymer Light-Emitting Diodes. *Macromolecules*, **2018**, *51*, 1598.
4. Karmakar, S.; Dey, S.; Upadhyay, M.; Ray, D. Phenoxazine–Quinoline Conjugates: Impact of Halogenation on Charge Transfer Triplet Energy Harvesting via Aggregate Induced Phosphorescence. *ACS Omega*, **2022**.
5. Tsujimoto, H.; Ha, D.-G.; Markopoulos, G.; Chae, H. S.; Baldo, M. A.; Swager, T. M. Thermally Activated Delayed Fluorescence and Aggregation Induced Emission with Through-Space Charge Transfer. *J. Am. Chem. Soc.* **2017**, *139*, 4894.
6. Li, Q.; Hu, J.; Lv, J.; Wang, X.; Shao, S.; Wang, L.; Jing, X.; Wang, F. Through-Space Charge-Transfer Polynorbornenes with Fixed and Controllable Spatial Alignment of Donor and Acceptor for High-Efficiency Blue Thermally Activated Delayed Fluorescence. *Angew. Chem., Int. Ed.*, **2020**, *59*, 20174.