



EPF European Polymer Congress

Martini Plaza, Groningen, the Netherlands

(June 22-27)

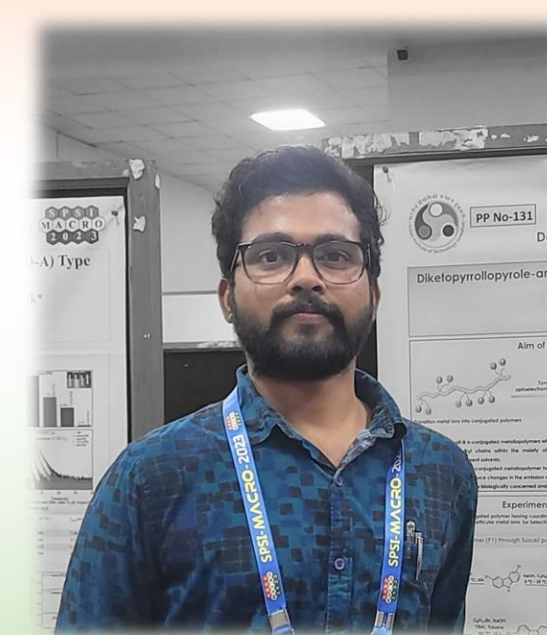


Visible-Light mediated Controlled and Living Radical Polymerization of Functional Vinyl Monomers by N-substituted benzo[ghi]perylene derivatives as organocatalyst

Chinmoy Kumar Behera,^a Premnath Das,^a and Sanjib K. Patra*

Department of chemistry, IIT Kharagpur

email: skpatra@chemiitkgp.ac.in

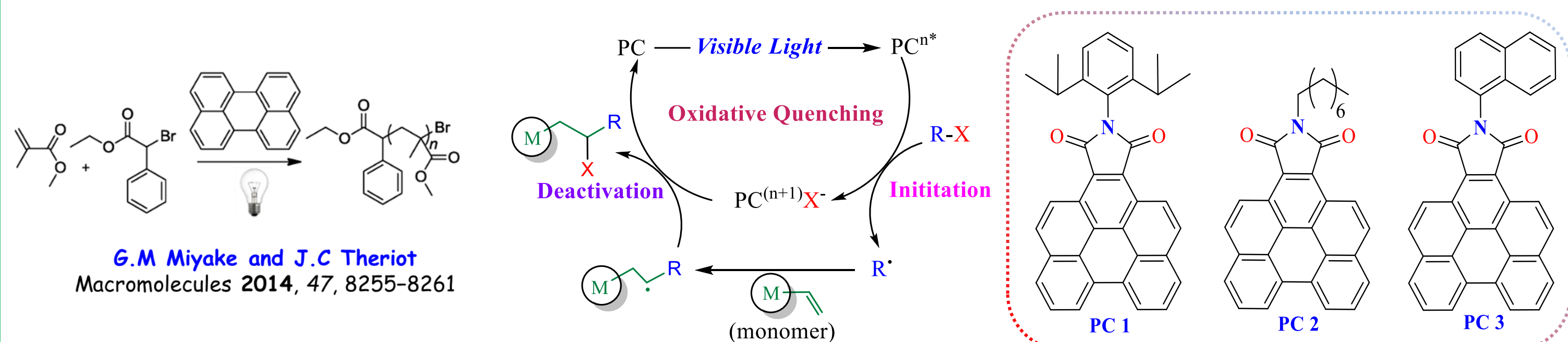


Abstract

Controlled radical polymerization is essential for synthesizing well-defined functional polymers. Recently, organic chromophores have enabled visible light-induced ATRP using alkyl bromide initiators. In this work, we explore N-substituted benzo[ghi]perylene (BPI) as an efficient organic photocatalyst. Under visible light, BPI mediates the controlled polymerization of various vinyl monomers (MMA, BMA, LMA, styrene, and NIPAM), yielding polymers with predictable molecular weights and low dispersity. Notably, the polymerization shows excellent temporal control, as it can be paused and resumed by toggling the light.

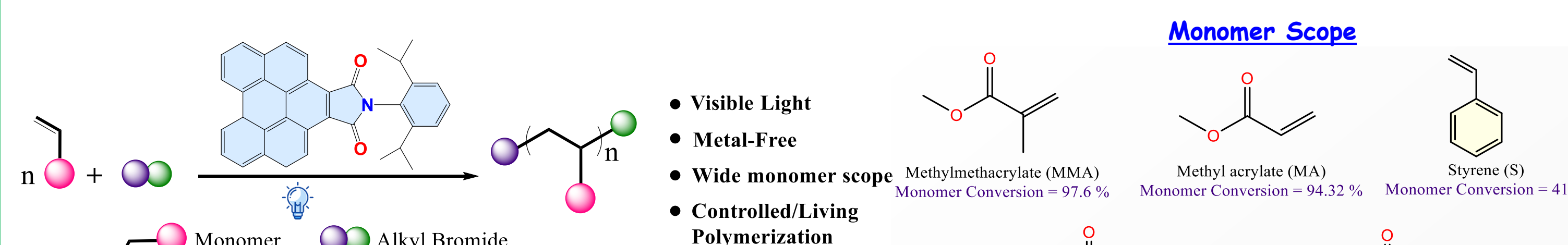
Aim of the study

- To design and develop benzo[ghi]perylene-based chromophores with strong $\pi-\pi^*$ absorption in the visible region for efficient light harvesting in photoredox catalysis.
- To introduce N-substituents on the benzo[ghi]perylene core to enhance solubility and improve processability compared to the parent structures.
- Exploring its compatibility with light-driven polymerization processes.



Experimental section

General Polymerization procedure using PC [1-3] as Photocatalyst:



Scheme 1: General procedure for polymerization by photocatalyst (PC 1-3) with EBPA as the initiator. [V_{DMF} : V_M = 1:1]

Nature of light	Conversion %	Time	M _n (theo)	M _n (GPC)	M _w (GPC)	PDI(M _w /M _n)	I*
Blue LED	97.2	16h	9.73	15.4	16.8	1.09	93.2
Green LED	57.5	24h	5.76	10.9	14.17	1.30	79.5
Orange LED	-	10h-24 h	-	-	-	-	-
white (CFL)	34.9	18h	7.47	8.84	10.1	1.14	84.5
no light	-	24h-36h	-	-	-	-	-

Table 1: Comparison of Photopolymerization under different light source by photocatalyst (PC 1) with EBPA as the initiator. [V_{DMF} : V_{MMA} = 1:1]

- PC 1 not only efficiently photopolymerizes traditional monomers but also vinyl-appended NNC-type ligands, highlighting its broad polymerization capability.
- Moreover, it demonstrates compatibility with acid-sensitive monomers such as MAA and GMA

Visible light mediated Kinetics study of MMA Polymerization using PC [1-3]

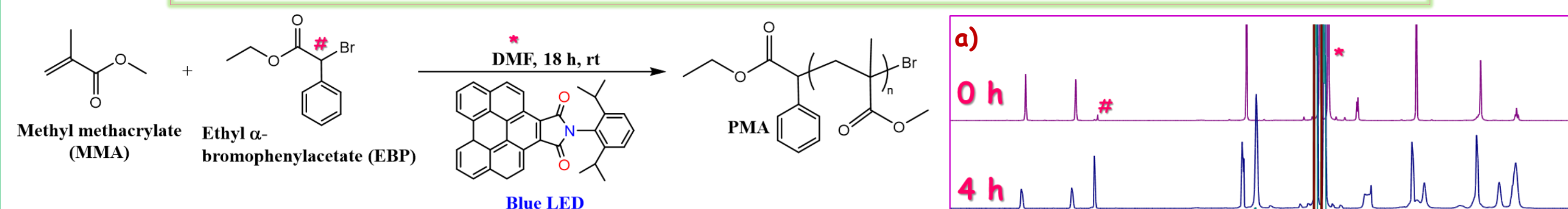


Figure b) First order kinetic plot [ln([M]₀/[M]_t)] vs time demonstrating linearity, confirming a controlled/living radical polymerization process

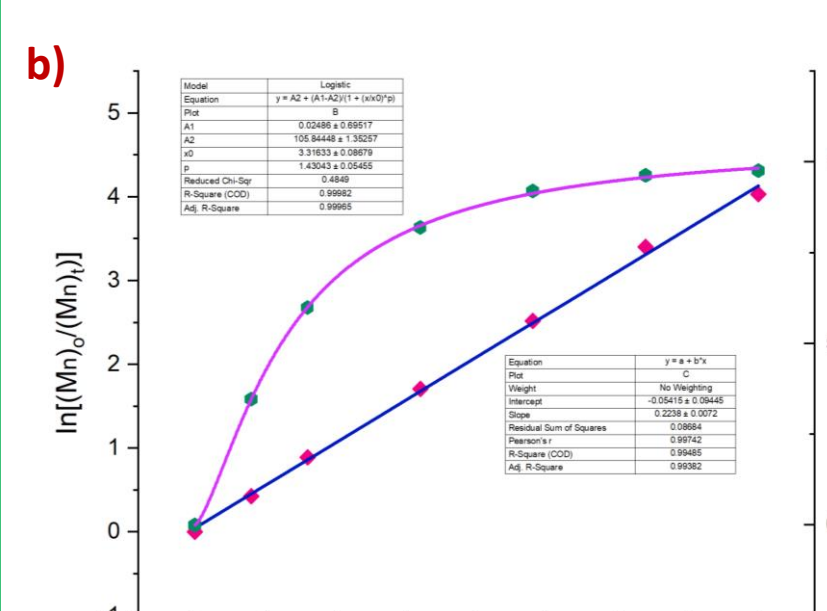
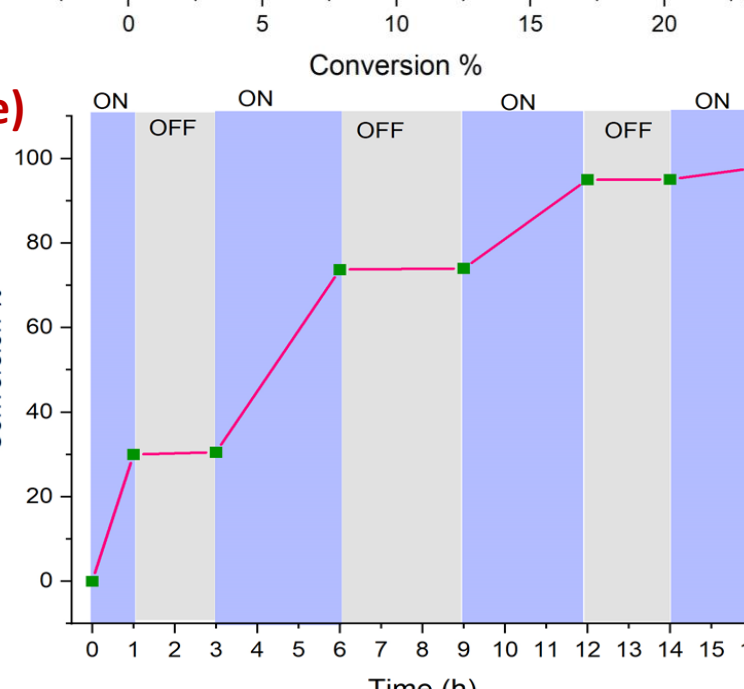
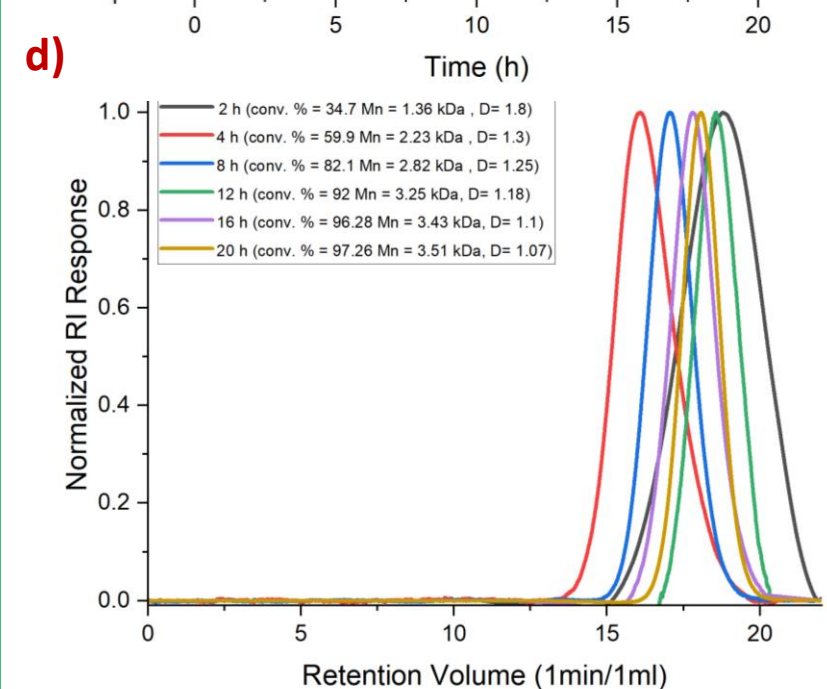
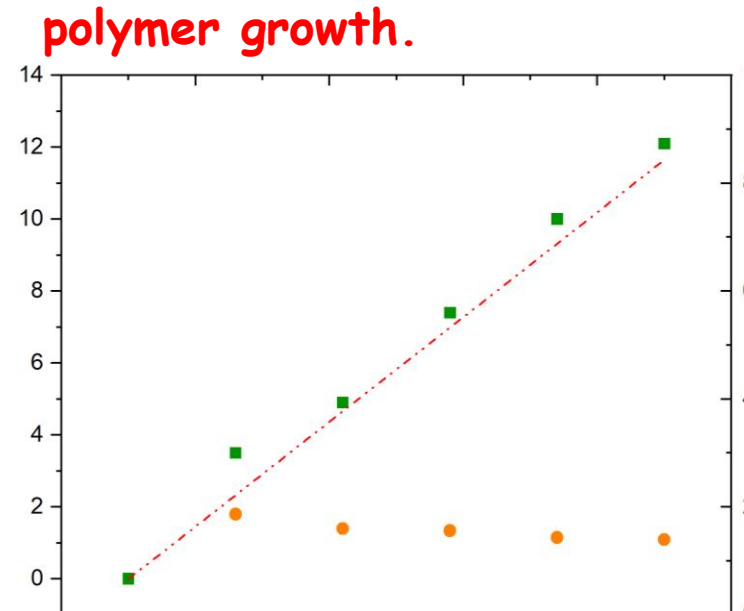
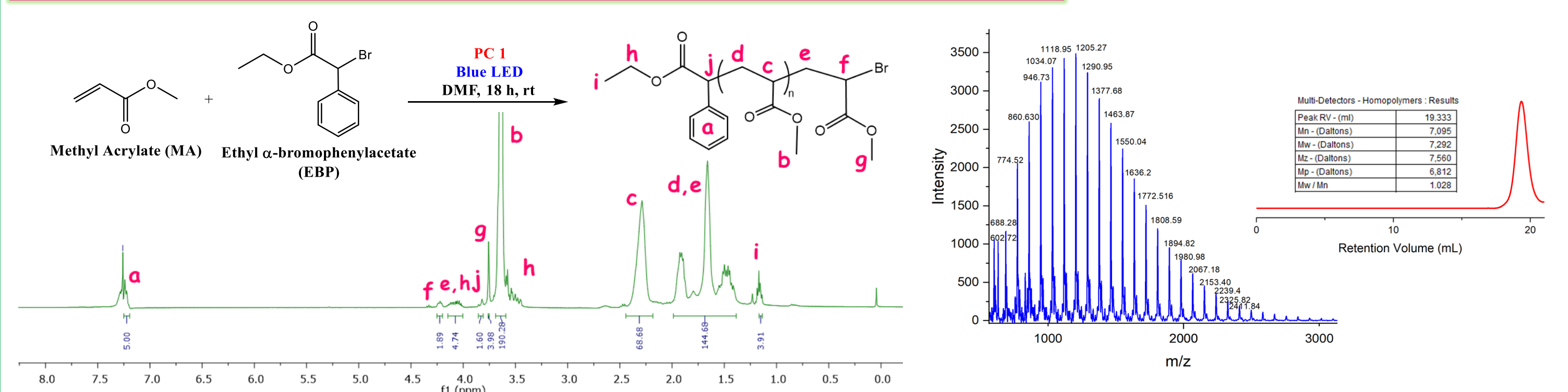


Figure c) Evolution of number-average molecular weight (M_n) and dispersity (M_w/M_n) illustrating good control over polymer growth.

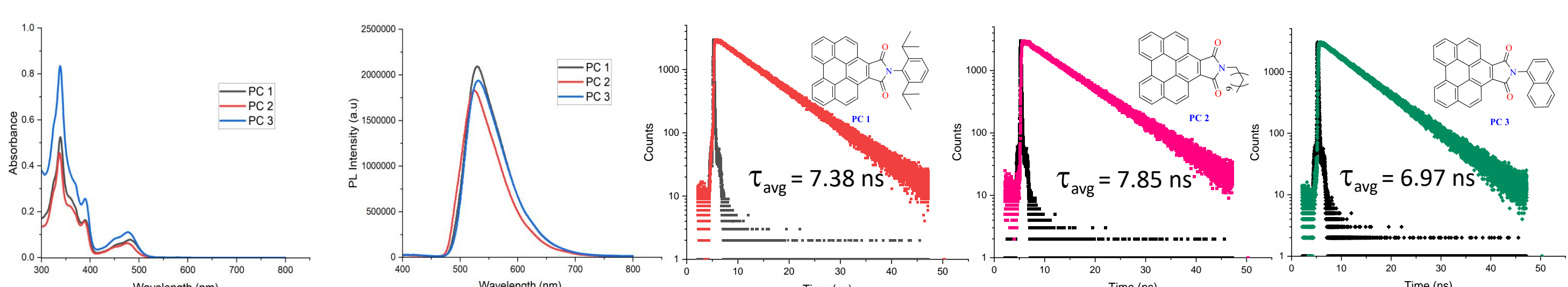


Synthesis of PMA-Br macroinitiator with high chain fidelity:



Results and Discussion

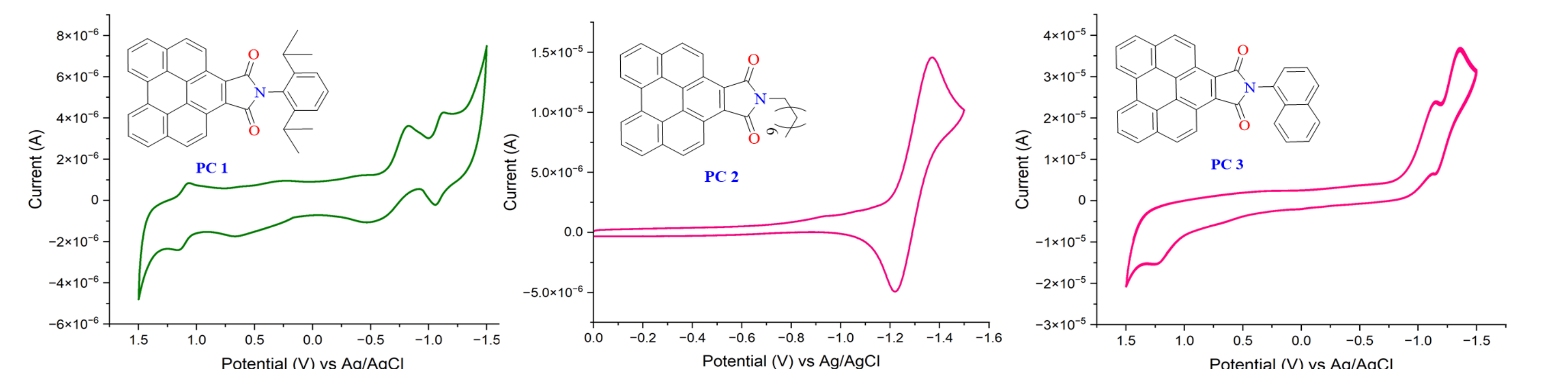
Photophysical & Electrochemical Properties of PC 1-3 :



- PC1 is the most balanced: good light absorption, long-lived excited state, and reasonable radiative decay.
- PC2 is inefficient due to weak absorption and shorter excited-state lifetime.
- PC3 absorbs light best but loses energy too quickly non-radiatively

Photocatalyst	λ_{max} (nm) ^a	ϵ_{max} (10 ⁴ M ⁻¹ cm ⁻¹) ^b	λ_{em} (nm) ^c	Stokes shift (nm)	Φ_{s}	τ (ns) ^e	k_r (s ⁻¹) ^f	k_{nr} (s ⁻¹) ^f
PC1	338, 390, 482	5.2, 1.62, 0.8	529	191	0.11	7.85	1.50×10^7	1.21×10^8
PC2	337, 388, 476	4.56, 1.52, 8.5	525	188	0.17	7.385	2.17×10^7	1.06×10^8
PC3	339, 389, 477	8.2, 2.5, 1.1	531	192	0.076	6.97	1.09×10^7	1.33×10^8

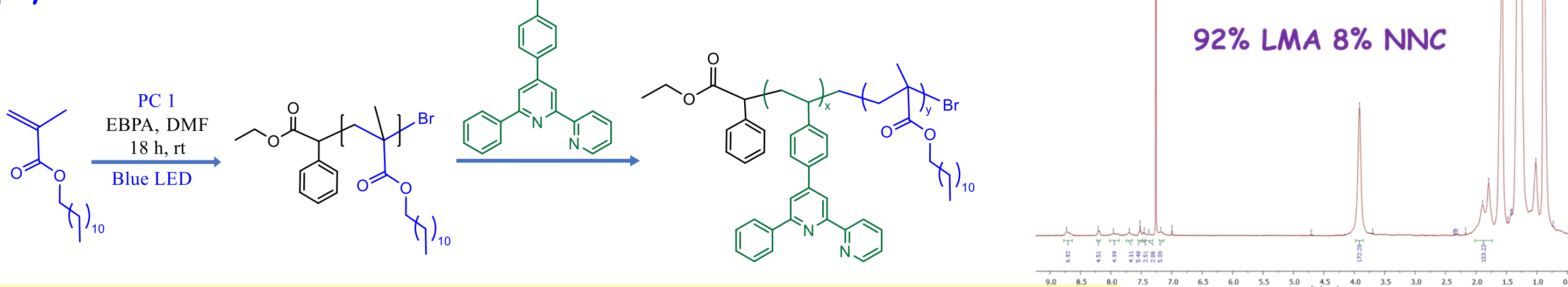
Table 1: a) λ_{max} (maximum absorption wavelength) measured in DMF by UV-vis absorption spectra. b) Molar absorptivity calculated at λ_{max} in DMF. c) Emission wavelength recorded by fluorescence spectroscopy in DMF ($\lambda_{\text{excitation}} = 390$) (d) Relative fluorescence quantum yield determination of PCs 1-3 using quinine sulphate ($\Phi = 0.546$ in 0.1 M H₂SO₄) as the reference standard. e) Lifetime recorded in DMF by TCSPC f) rate constants are calculated using the following equations: Radiative decay rate: $k_r = \Phi_s / \tau$, Non-radiative decay rate: $k_{\text{nr}} = (1 - \Phi_s) / \tau$



Photocatalyst	λ_{onset} (nm)	E ₀₀	E _{HOMO}	E _{LUMO}
PC1	490	2.53ev	-5.93	-3.69
PC2	482	2.57ev	-	-3.56
PC3	492	2.52ev	-5.97	-3.67

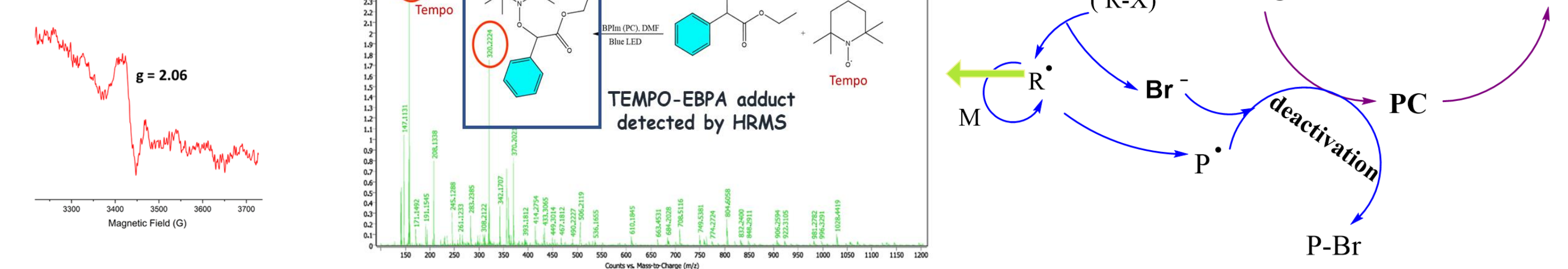
Sequence-controlled polymers study with N-heterocyclic ligands:

- Schematic representation of block copolymer synthesis by sequential addition of LMA and NNC demonstrating temporal control and living nature of polymerization



Proposed Catalytic cycle & Mechanistic Evidence for Visible-Light Induced Polymerization:

- HRMS showing detection of TEMPO-EBPA adduct, confirming the generation of propagating radical intermediate via homolytic cleavage of EBPA (alkyl halide).
- This is also supported by EPR spectroscopy.



Conclusion

- N-substituted benzo[ghi]perylene absorbs strongly in the visible region, particularly around 450 nm, aligning well with blue LED excitation (2.76 eV) due to its E₀₀ of 2.53 eV, enabling efficient photocatalysis.
- Its excellent visible-light compatibility and photostability make it well-suited for spatiotemporally controlled photopolymerization.
- The N-substituted derivative shows a large Stokes shift (~192 nm), possibly due to ICT and excited-state relaxation, which may help suppress self-absorption and enhance PET.
- Among the series, PC 1 delivers the highest polymerization yield and exhibits superior control over polymer growth compared to PC 2 and PC 3.

References

- Shao, H.; Long, R.; Xu, H.; Sun, P.; Wang, G.; Li, Y.; Liao, S. The Development of Visible-Light Organic Photocatalysts for Atom Transfer Radical Polymerization via Conjugation Extension. *Molecules*. 2024, 12, 2763.
- Corbin, D.A.; Miyake, G.M. Photoinduced Organocatalyzed Atom Transfer Radical Polymerization (O-ATRP): Precision Polymer Synthesis Using Organic Photoredox Catalysis. *Chem. Rev.* 2021, 122, 1830–1874.
- Wu, C.; Corrigan, N.; Lim, C.H.; Liu, W.; Miyake, G.; Boyer, C. Rational Design of Photocatalysts for Controlled Polymerization: Effect of Structures on Photocatalytic Activities. *J. Chem. Rev.* 2022, 122, 5476–5518.
- Miyake, G.M.; Theriot, J.C. Perylene as an Organic Photocatalyst for the Radical Polymerization of Functionalized Vinyl Monomers through Oxidative Quenching with Alkyl Bromides and Visible Light. *Macromolecules* 2014, 47, 8255–8261.
- Behera, C.K.; Das, P.; Patra, S.K. Visible-Light mediated Controlled/Living Radical Polymerization of Functional Vinyl Monomers using N-substituted benzo[ghi]perylene derivatives as organocatalyst. (Manuscript submitted)

Acknowledgement



IIT Kharagpur, Department of Chemistry
CRF for instrumental facilities
UGC for doctoral fellowship
SERB for financial support.

