# SYNTHESIS, CHARACTERIZATION AND VISIBLE-LIGHT-DRIVEN PHOTOELECTROCHEMICAL HYDROGEN EVOLUTION REACTION OF CARBAZOLE-CONTAINING CONJUGATED POLYMERS


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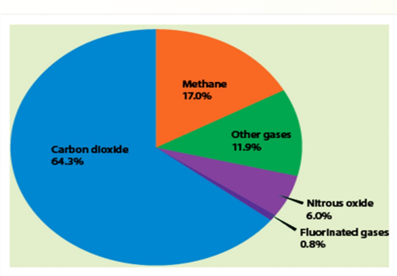
## Introduction

**Burning of excessive fossil fuels:**


Greenhouse Gases


Depletion of Resources

**Alternative Energy Source - Hydrogen**

**Advantages of Hydrogen Gas**

- Clean – No greenhouse gas emission
- Environmental friendly
- Can be Obtained from water
- It has high energy yield
- Portable-high storage capability

### Hydrogen Generation Methods

- Electrolysis
- steam reforming of methane
- Photo-electrochemically (PEC)
- Radiolysis
- Photo-biologically by some Algae

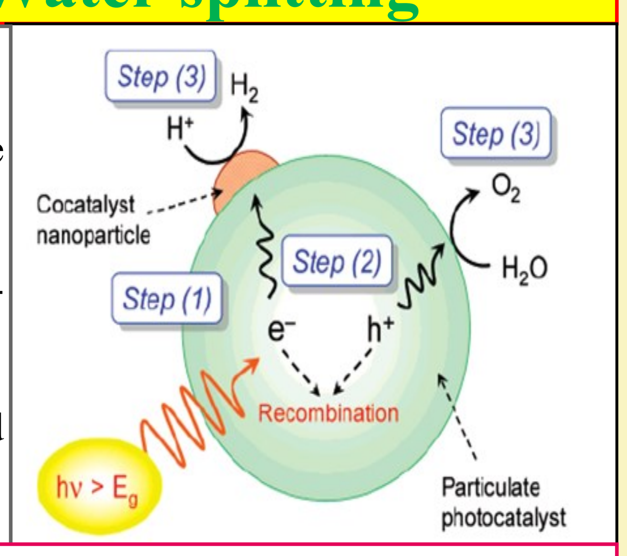
### Mechanism of Water splitting

$2H_2O \rightarrow 2H_2 + O_2$  $\Delta G = 237$ kJ/mol

**Step 1:**
Photon with minimum energy above band gap is absorbed.

**Step 2:**
Photoexcited electrons and holes separate and migrate to surface.

**Step 3:**
Adsorbed species (water) is reduced and oxidized by the electrons and holes.




### Materials used for water splitting applications

1) $d^0$ and $d^{10}$ metal oxides, (oxy) sulfides, (oxy) nitrides

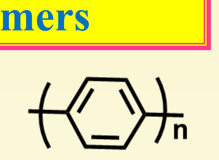
| Noble metals co-catalysts | Defects as recombinant centres |
|---|---|
| Photocorrosion | Intermittent Solar light and 4% UV of light |

**Conjugate Polymers as Alternatives of Inorganic Materials...How?**

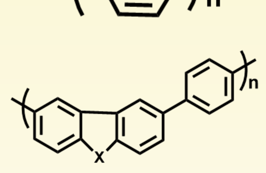
| Extensive delocalized π electron system | Ease of deposition |
|---|---|
| Lower and tunable bandgap | High absorption coefficient |

**Precedents of Water Splitting Conjugate Polymers**

Poly(p-phenylenes) - conjugated polymer used as a photocatalysts for $H_2$ evolution in 1985.



Co-polymers of Poly(p-phenylenes) and carbazole, dibenzo [b,d] thiophene sulfone or




## Objectives

**1-Design scheme to synthesize new carbazole based conjugate polymers having:**

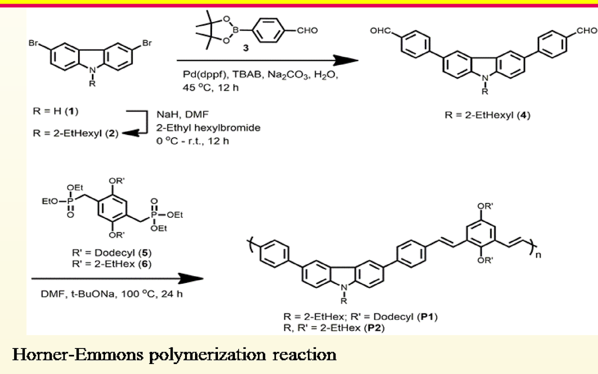
- Good conducting properties
- absorption in Visible region
- Low Bandgap
- High solubility
- Good Stability

**2-Characterization of synthesized Carbazole Polymer:**

| $^1$H-NMR | FTIR | SEM |
|---|---|---|
| DR-UV-Vis | TGA | PL |

**Three Electrode System Integrated with Solar Simulator**

## Synthesis and Characterization of P1 and P2




**Scheme 1.** Synthesis of **P1** and **P2**

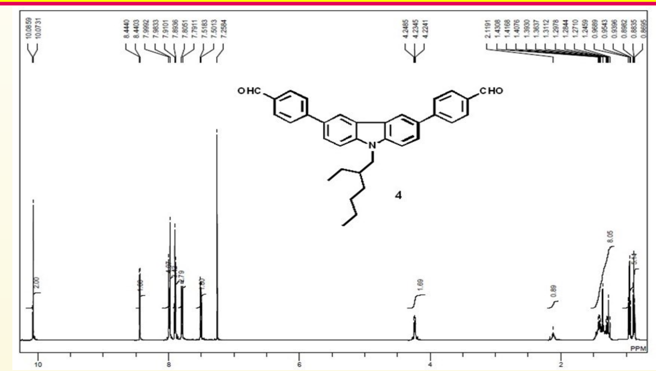


**Figure-1.** $^1$H-NMR of 4

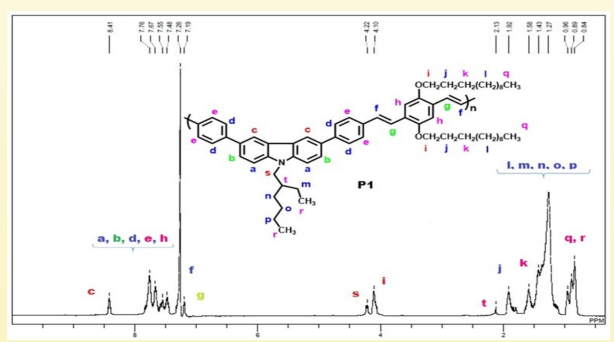


**Figure-2.** $^1$H-NMR of P1

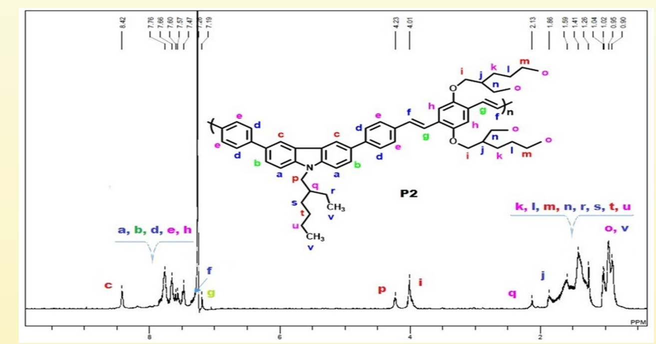


**Figure-3.** $^1$H-NMR of P2

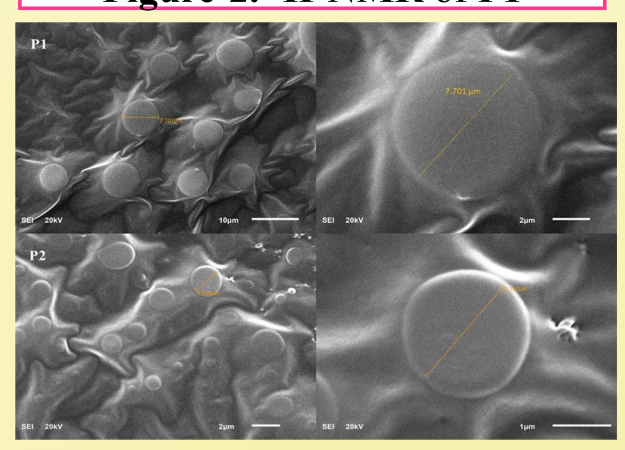


**Figure-4.** SEM images of **P1** and **P2**

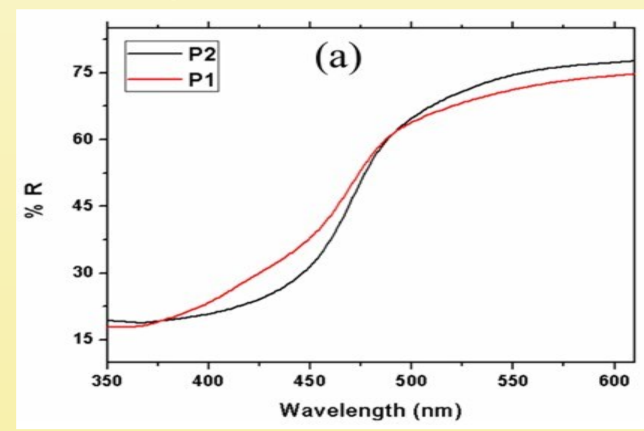



**Figure-5.** %R Vs nm of **P1** and **P2**

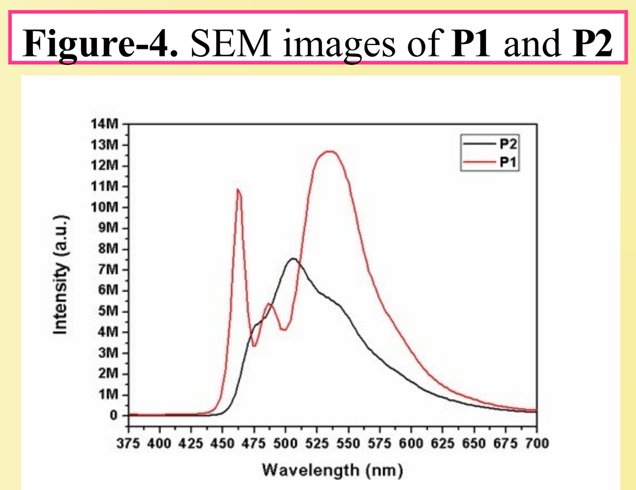



**Figure-6.** PL of **P1** and **P2**

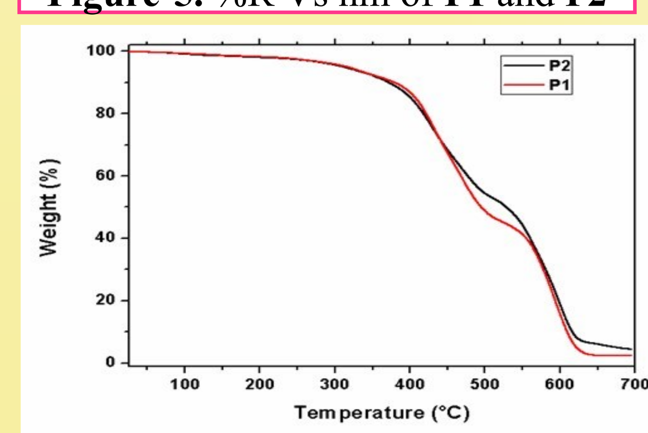
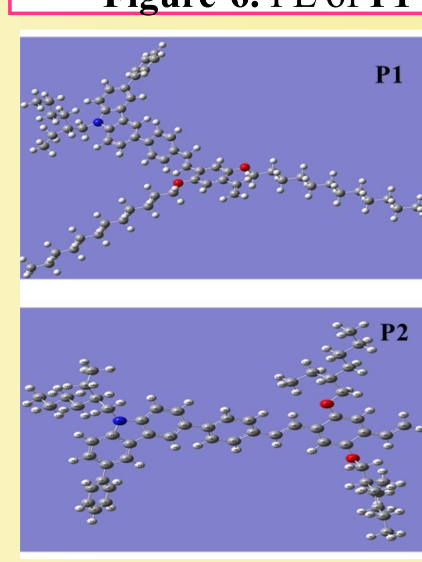



**Figure-7.** TGA of **P1** and **P2**




| | CV | B3LYP/ 6-311 |
|---|---|---|
| P1 | 2.52 eV | 2.57 eV |
| P2 | 2.36 eV | 2.41eV |

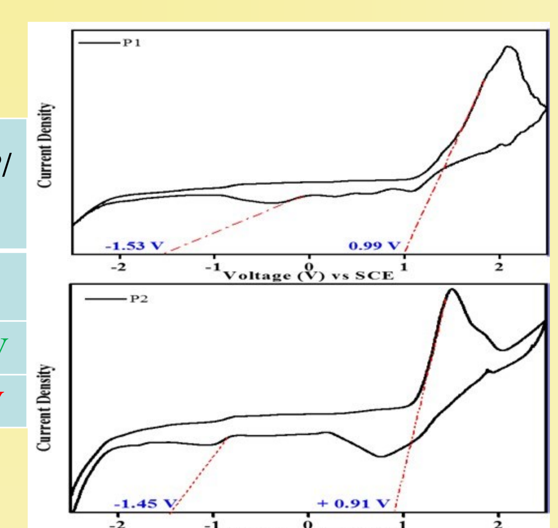
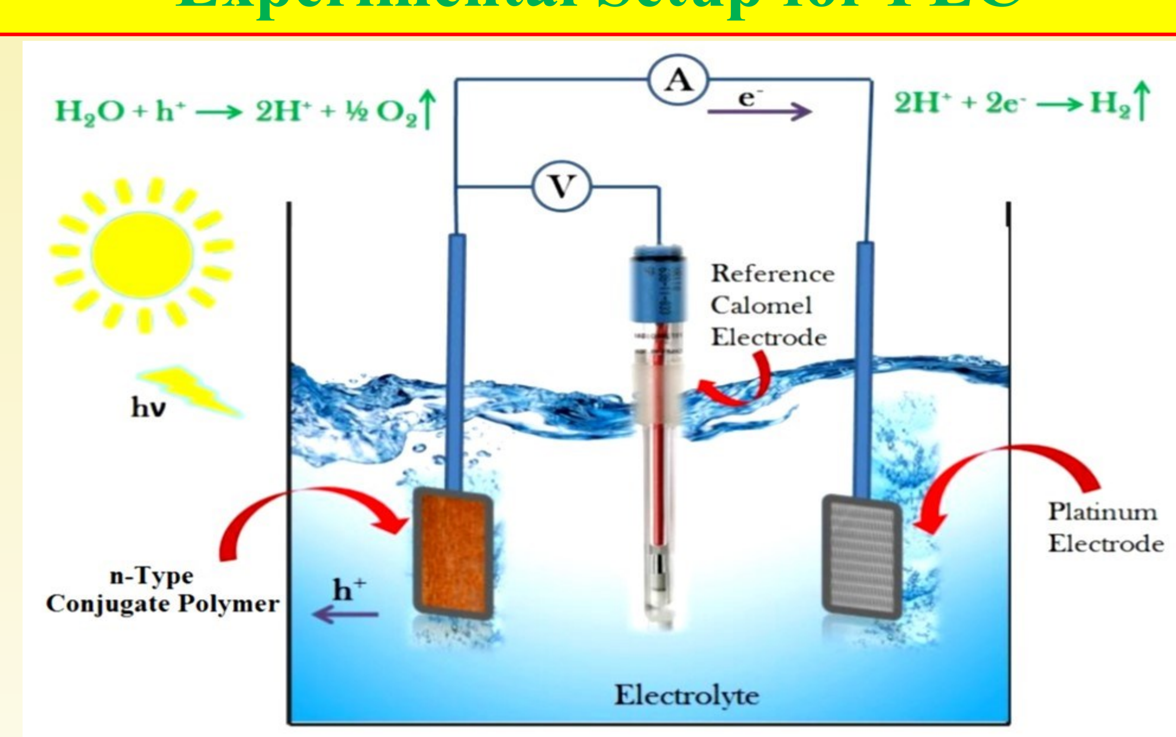



**Figure-8.** Bandgap measurement of **P1** and **P2** by **DFT** and **CV**

## Experimental Setup for PEC




**Scheme 2.** Plausible mechanism of water splitting

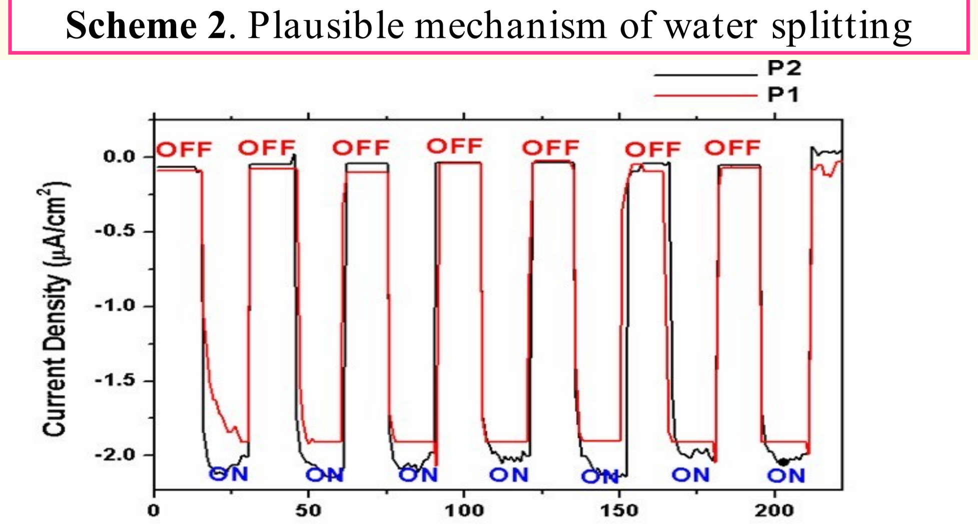



**Figure-9.** CA measurements of **P1** and **P2** coated on FTO glass @ 0V bias

⇨ **CA** measurements of **P1** and **P2** coated on FTO glass **0 V applied potential**, under dark and simulated solar light (**1 Sun**).

⇨ The stacked **CA** measurements revealed that the photocurrent density at

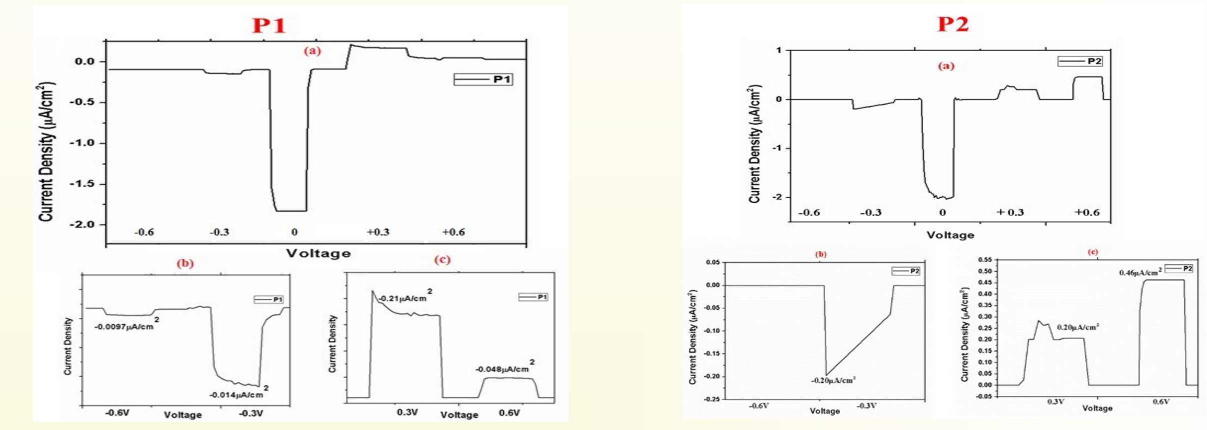



**Figure-10. A**). **P1** and **B**). **P2** current densities measurement of wa-

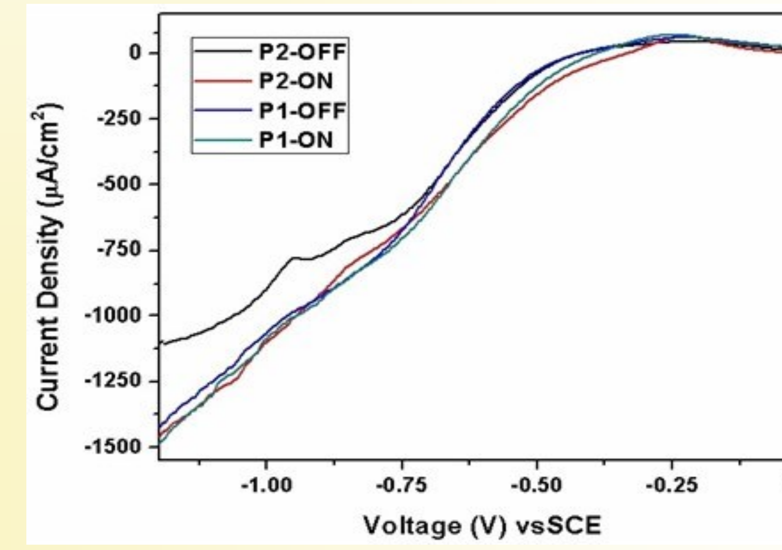



**Figure-11. LSV** of **P1** and **P2** coated on FTO glass with scan rate of - 2.45

⇨ **LSV** performed at a scan rate of **2.45 mV S$^{-1}$** under the dark and light conditions.

⇨ Under the **illumination of solar light**, the current density was maxi-

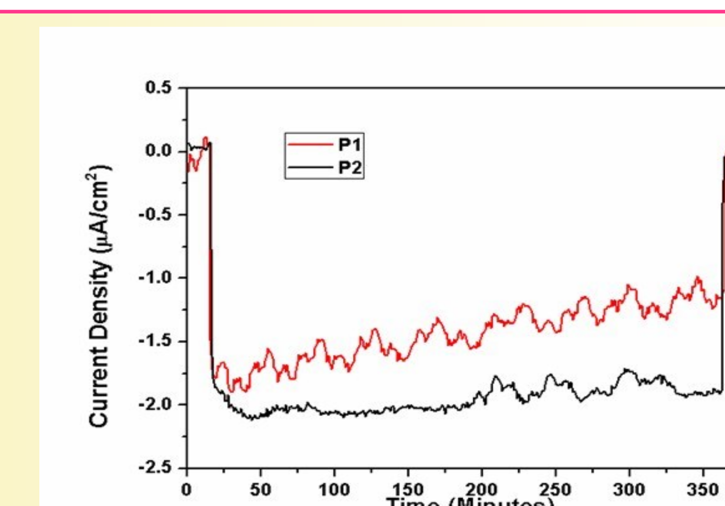



**Figure-12.** Long-term testing of **P1** and **P2** coated on FTO glass over a peri-

⇨ Stability of **P2** >**P1, 3%** decrease current density(2.1 to 2.0 mA/cm$^2$).

⇨ **P1** showed **33%** decrease in the current density(1.18 to 1.12 mA/cm$^2$).

## Conclusions

- Two new carbazole-containing conjugated polymers, **P1** and **P2**, have been synthesized by the **Horner-Emmons polymerization reactions**.
- **P2** and **P2** both have generated **good photo-current density.**
- **No co-catalyst is needed.**
- **No Sacrificial agent is needed.**
- **Excellent solubility** in organic solvents **P1** and **P2**

## References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## Acknowledgments


The financial support from KFUPM project # NUS15103/4 and research facilities provided by KFUPM are gratefully acknowledged.