The Ring Launching Solar Cell: The RING matters

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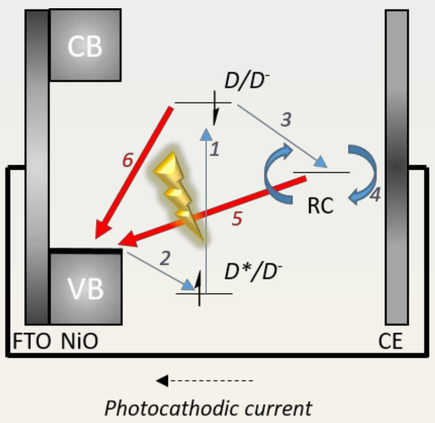
Introduction

Today, *n*-type Dye-sensitized solar cells (DSSCs) are a well-established exceeding 14% photonconversion efficiency (PCE). The complementary *p*-type DSSC opens new avenues to tandem solar cells to have greater PCE for future application in both photovoltaics and solar-driven fuel generation. However, *p*-type DSSCs are relatively unexplored and the efficiency remains low due to charge recombination.

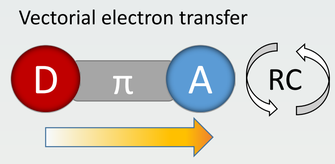


Blue arrows => the forward electron propagation
red arrows => the unfavorable recombnation

How to solve this recombination issue?

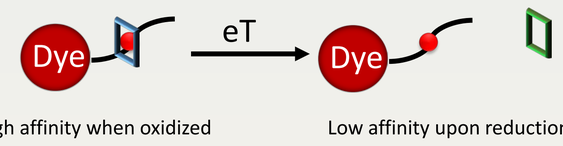
Spatial separation of charges

→ Donor–π–Acceptor



Alternative strategy:

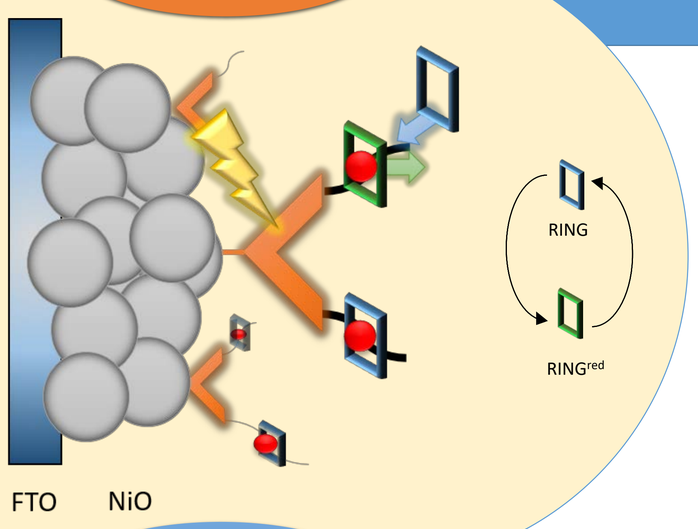
→ Supramolecular approach of pre-organization of the redox mediator



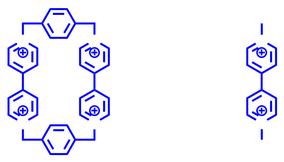
Pre-organization of the redox mediator leads to increased photocurrents in DSSCs

What is the difference between a cationic or neutral ring in photovoltaic properties of the solar cell?

Design



1. Cationic Ring

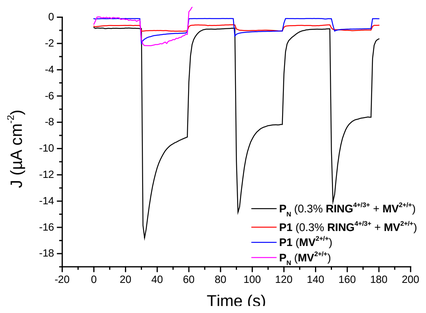


Binding studies show that

- The **RING^{4+}** has a high binding affinity for the DNP recognition sites: $K_{ass} = 3.4 \times 10^4\ M^{-1}$ $\alpha = 0.7$
- The **RING^{4+}** is able to quench in total 83% of the toal fluorescence of the dye at 630 nm.

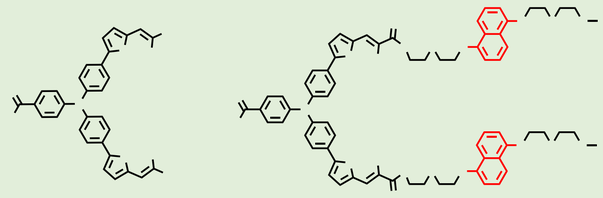
Photovoltaic properties

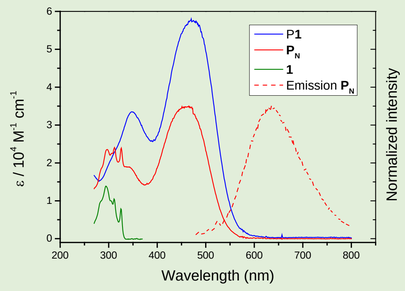
100 mW · cm^{-2} irridiation



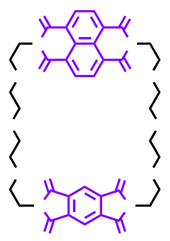
➢ Pre-organization of the redox mediator by pseudorotaxane formation leads to DSSC exhibiting 10 x higher photocurrents.

Dye





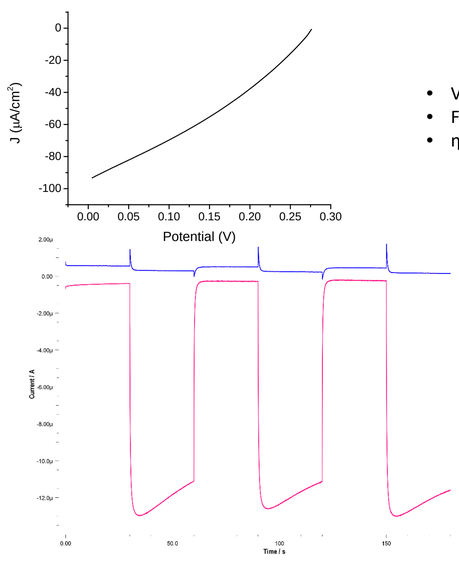
2. Neutral Ring



- **NDI–RING** has a low binding affinity
  - (~100 M^{-1})
- The reduction potential is more negative than **MV–RING^{4+}**
  - (380 mV and 50 mV versus NHE)

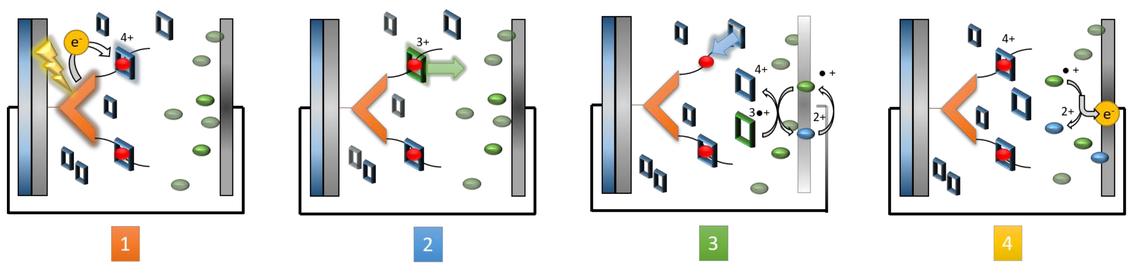
Photovoltaic properties

50 mW · cm^{-2} irridiation



- V_{OC} = 307
- FF = 0.35
- η = 0.02%

Proposed operational mode



Excitation of the P_N dye leads to eT to the **RING^{4+}**.

Reduction of **RING^{4+}** to **RING^{3+}** leads to ring dissociation.

Upon dissociation **RING^{4+}** will bind the the DNP and the e$^-$ can hop from **RING^{3+}** to **MV^{2+}**.

Regeneration of the redox couple to complete the circuit.

➢ The operational principle of the **NDI–RING** is supposed to proceed via a similar mechanism

Conclusions and Outlook

- New type of *p*-type DSSC is made where the redox acceptor is pre-organized to the dye. This **P_N** dye is based on the **P1** dye functionalized with DNP moeities that can form pseudorotaxanes with the electron acceptor **MV–RING^{4+}** (K_{ass} = 3 x 10^4 M^{-1}) or **NDI–RING** (K_{ass} ≈ 1 x 10^2 M^{-1}).
- Solar cells based on pseudorotaxanes afforded photocurrents of one order of magnitude higher compared to the control experiments (no pseudorotaxane formation).
- Neutral **NDI–RING** shows 50 x higher photocurrents than the cationic **MV–RING^{4+}**.
- Future research will focus on characterization and optimization of system

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4. T. Bouwens, S. Mathew, J. N. H. Reek, *Faraday Discuss.*, **2019**, *accepted*.