The Synthesis and Photophysical Properties of Alkene- and Stilbene-Linked Fullerene-Porphyrin Dyads

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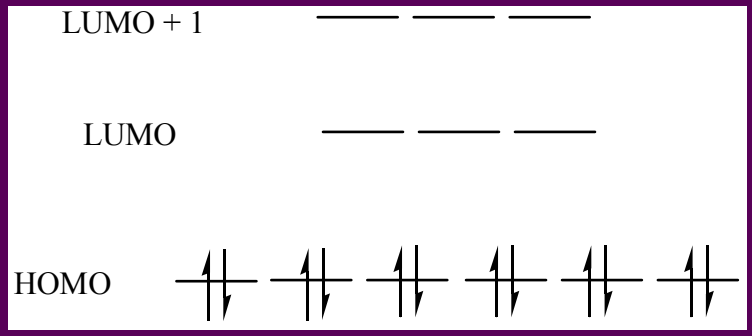
Donor / Acceptor Systems

Donors

- Metal complexes (e.g. ferrocene)
- Pre-Aromatics (e.g. tetrathiafulvalene)
- PORPHYRINS

Acceptors

- Quinones
- Imides
- FULLERENES



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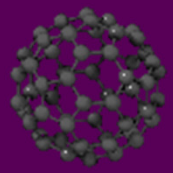
Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.*, **1999**, 2445-2457.



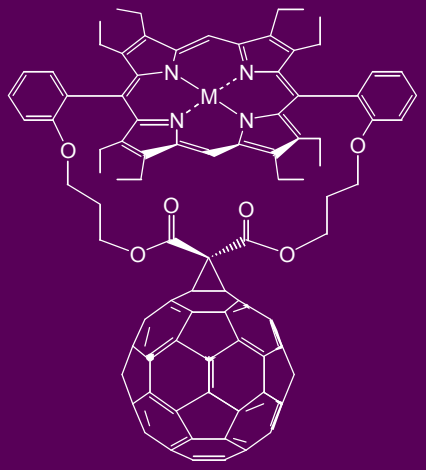
Fullerene-Porphyrin Dyads

- **Donor-Linker-Acceptor Systems**

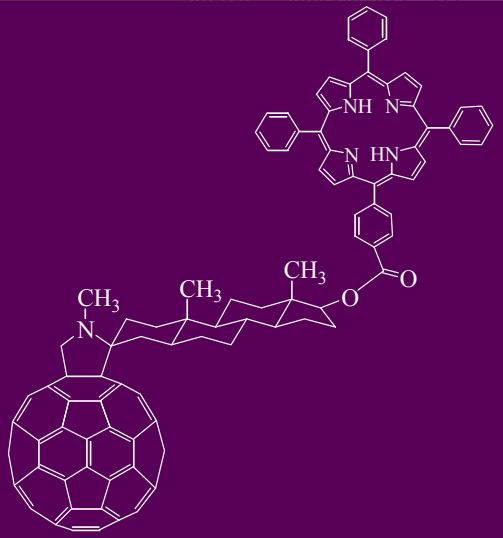
Goals:

- **Understanding Photophysical Properties as a function of Molecular Topology.**
- **Long-lived Charged Transfer States.** Electron transfer from the porphyrin to the fullerene mimics the process of photosynthesis in plants.
- **Development of Agents for Use in Photodynamic Therapy (PDT).** Light-absorbing species that photosensitize the formation of singlet molecular oxygen ($^1\Delta_g$) are being used against tumors in cancer treatment.

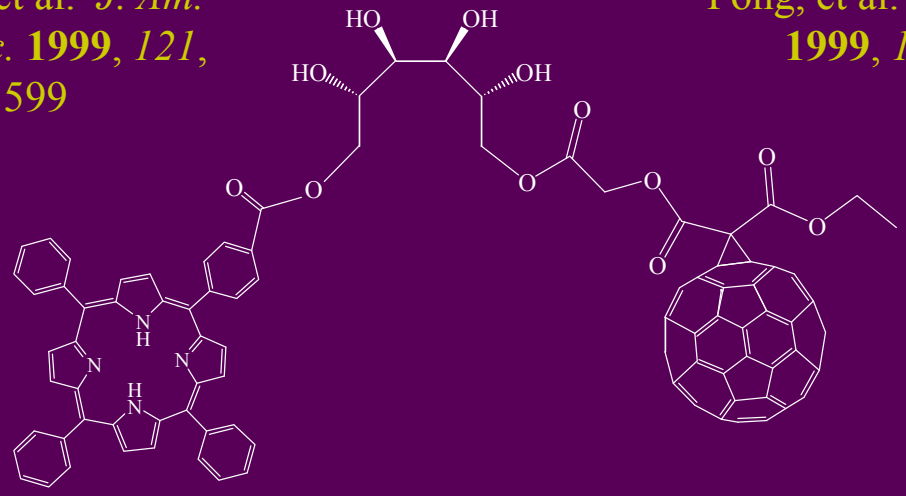
Past NYU Dyads



Schuster, et al. *J. Am. Chem. Soc.* **1999**, *121*, 11599

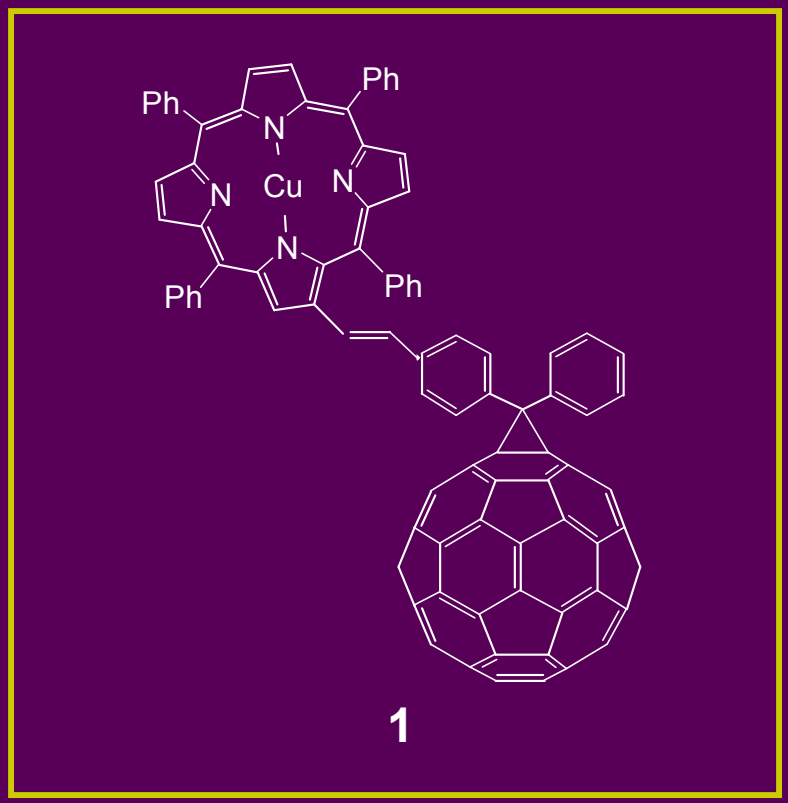


Fong, et al. *Org. Lett.* **1999**, *1*, 729.



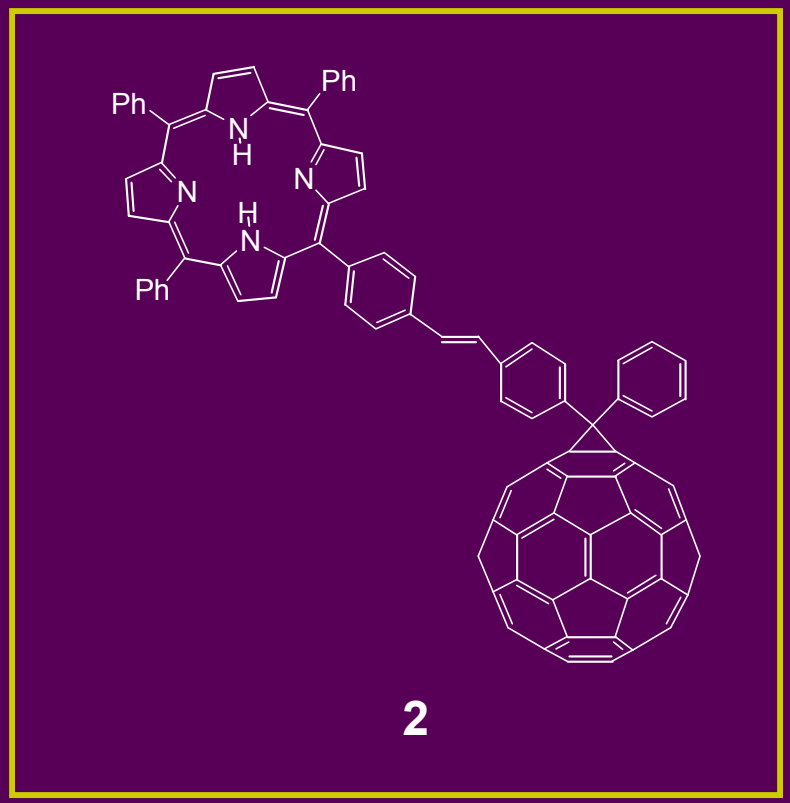
MacMahon. Unpublished results.

The New Alkene-Linked Dyads



1

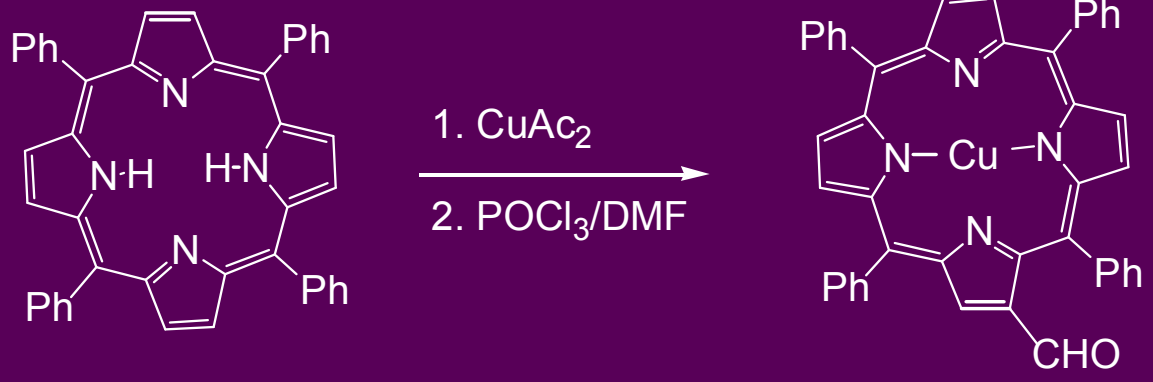
- Alkene linkage through a pyrrole ring.

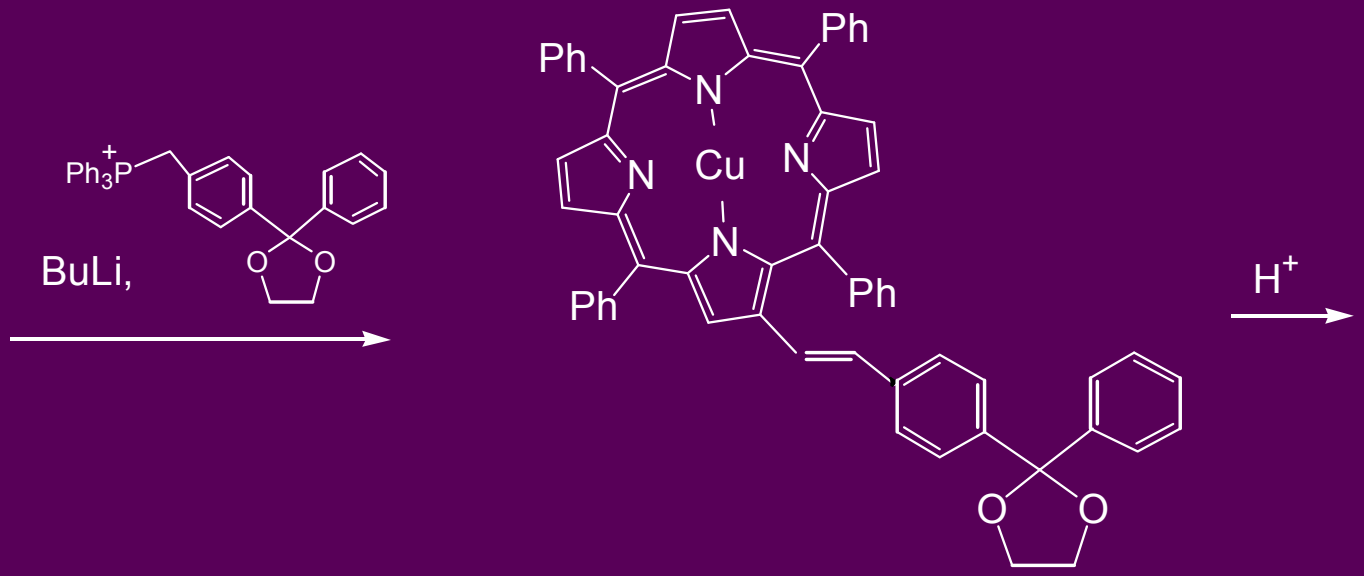


2

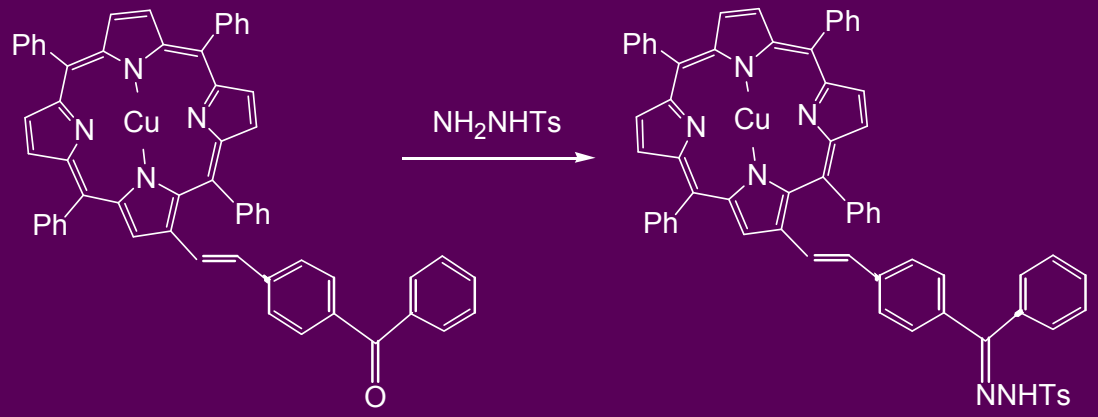
- Stilbene linkage through one of the porphyrin phenyl groups

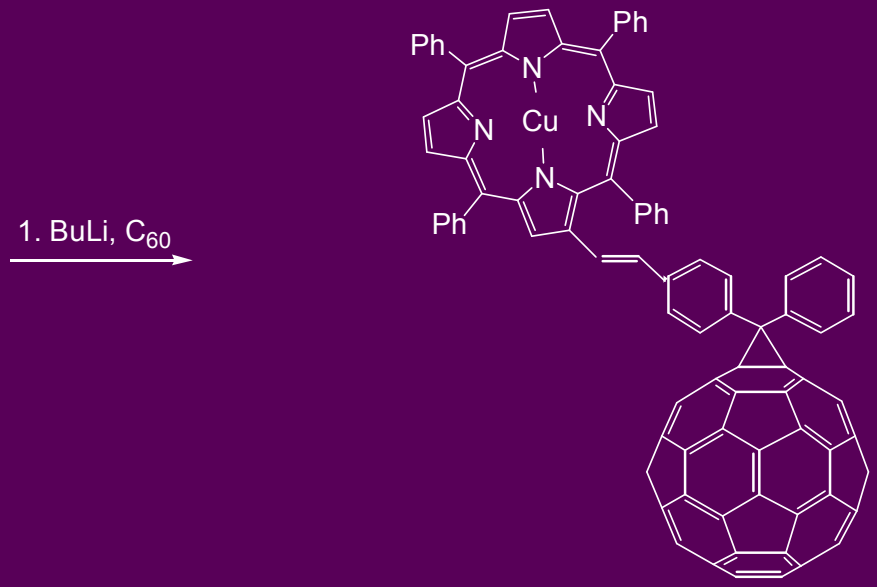
Synthesis of Dyad 1



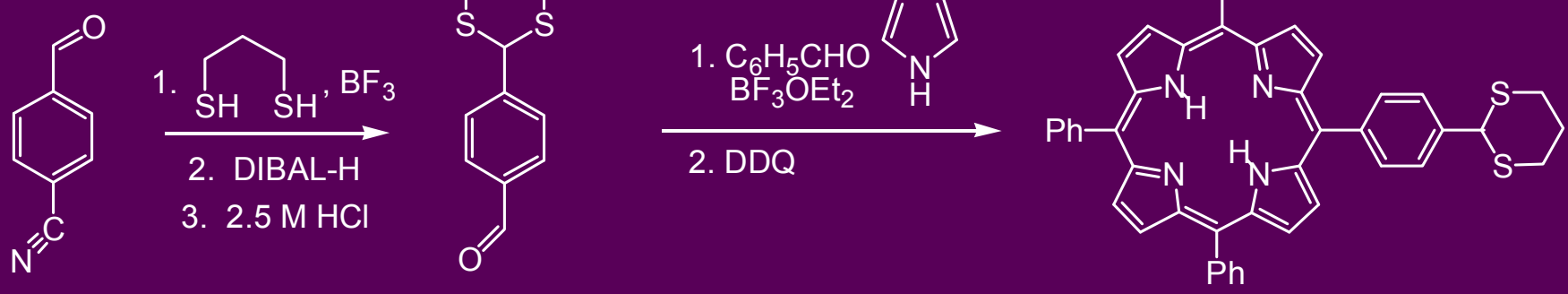


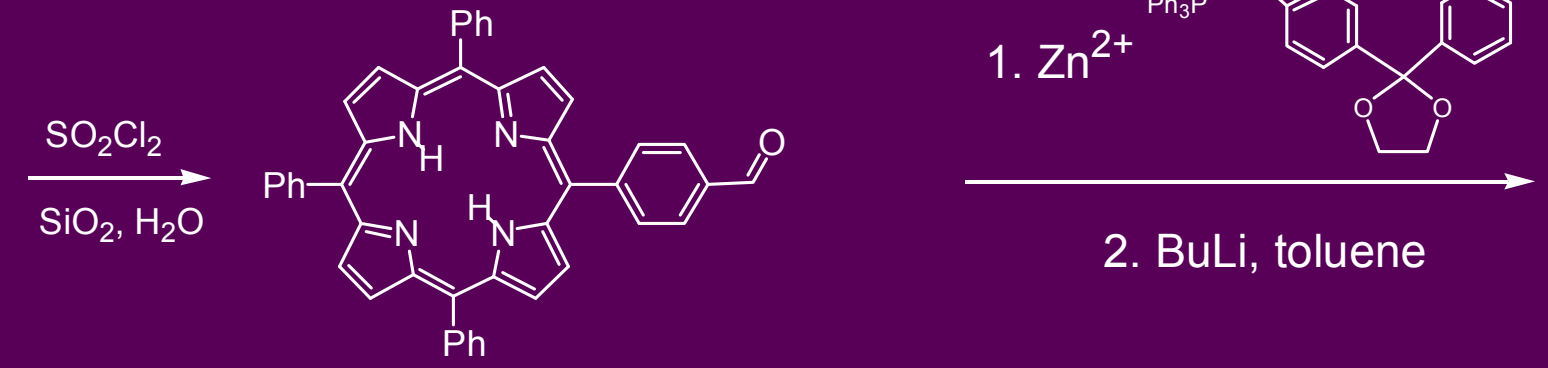
Synthesis of Dyad 1, ctd.



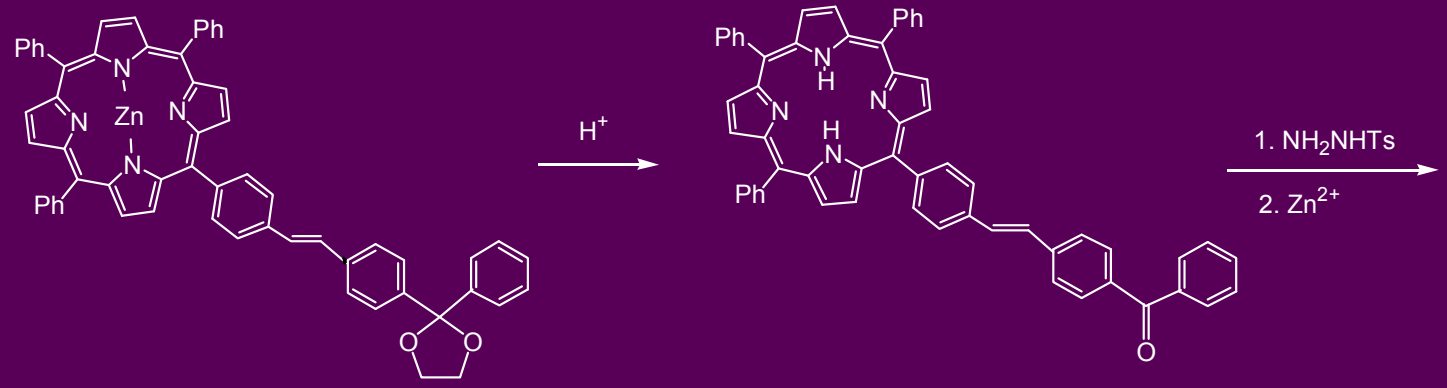


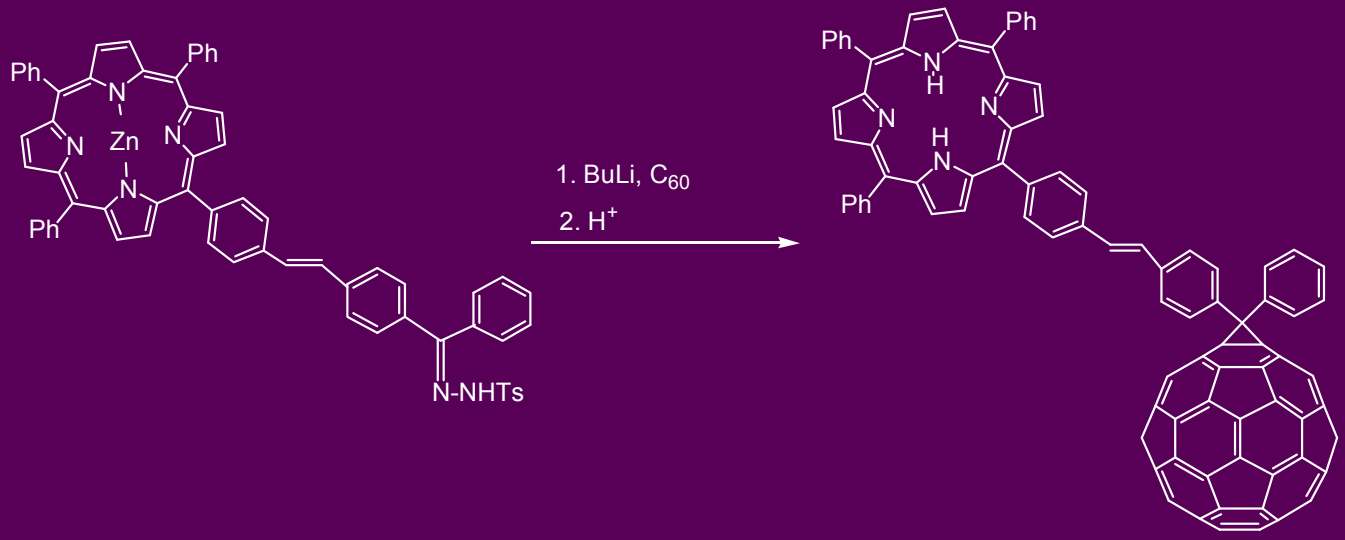
Synthesis of Dyad 2

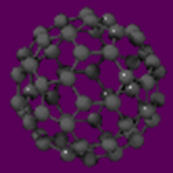




Synthesis of Dyad 2, ctd.



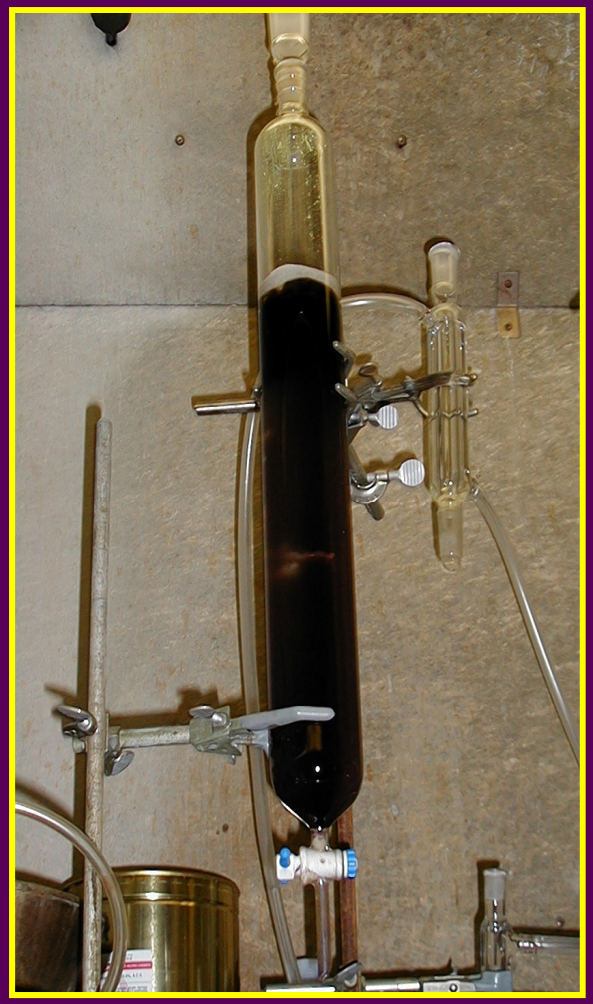




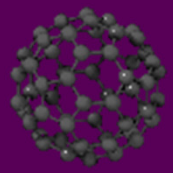
Characterization

- **NMR Spectroscopy**
  - All reactions involve the appearance or vanishing of easily recognizable functional groups, so NMR suffices despite the presence of the copper, which broadens the peaks.
- **UV-vis Spectroscopy**
  - The linker and dyads show similar absorption spectra in the UV-vis region

Porphyrin Synthesis Hurdles



- Low Solubility
- Low Reaction Concentrations
- Messy Extractions
- Arduous Column Chromatography
- Poor Yields (10-25% total)



Planned Studies

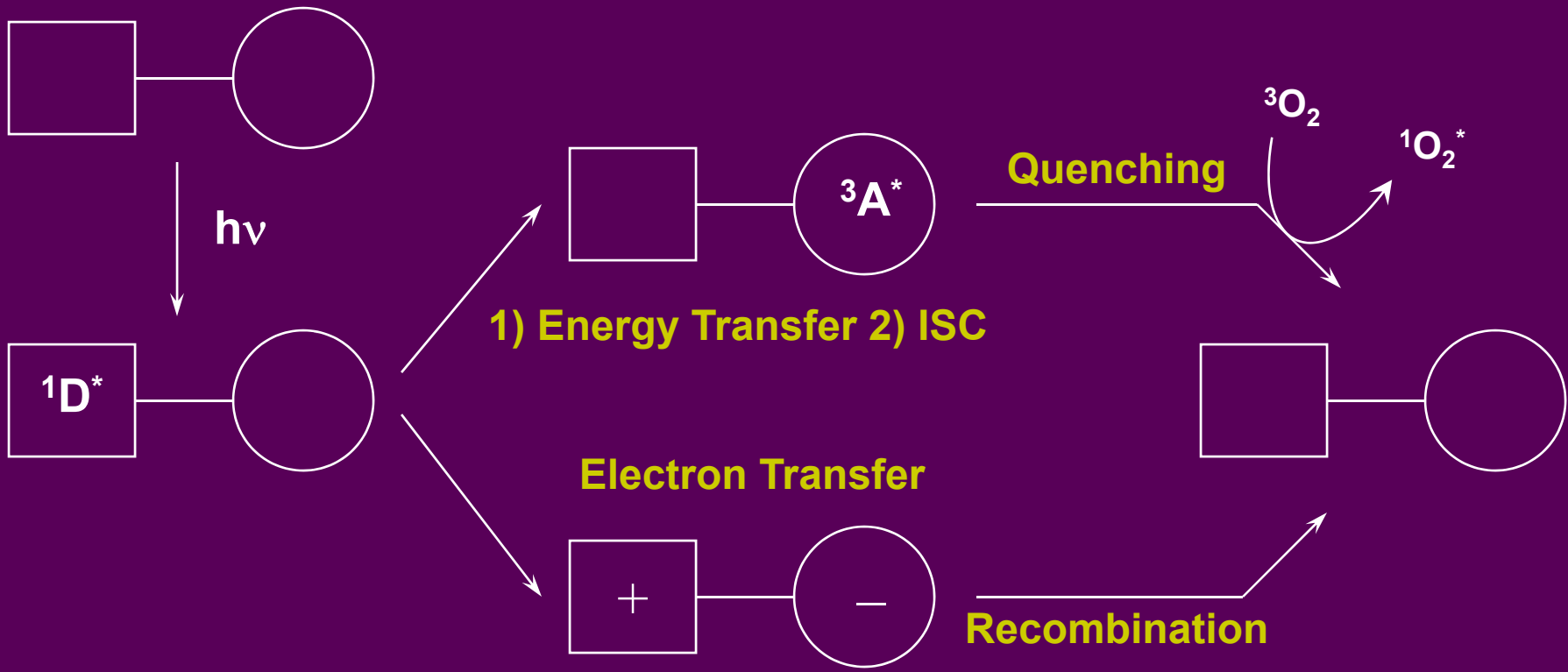
Synthetic:

- Synthetic generation of pure *cis* and *trans* linked forms of both dyads.

Photophysical:

- UV-vis & Fluorescence spectroscopy
- Transient absorption study of the excited states
- Singlet oxygen photosensitization quantum yields
- Photoinduced *cis-trans* isomerization in the linker moieties

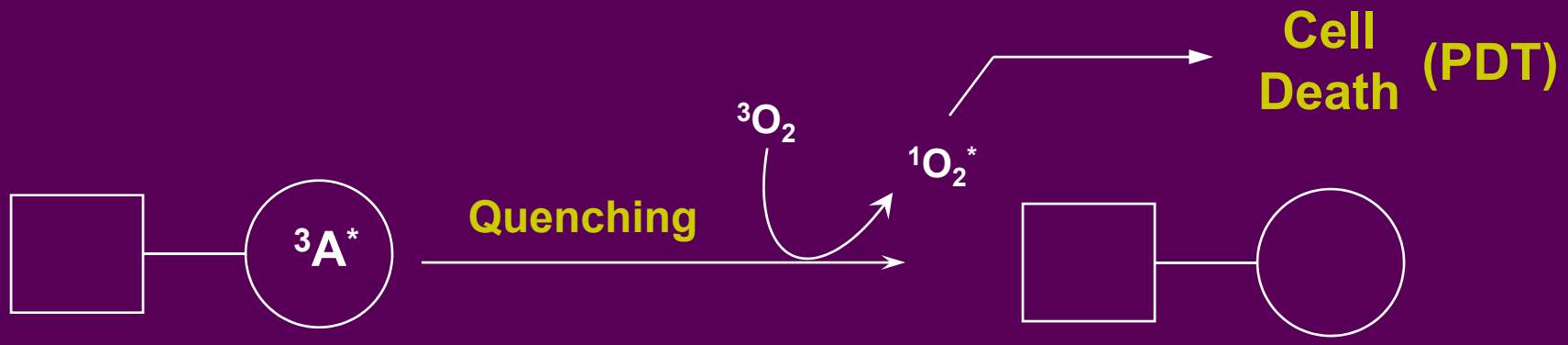
Photophysical Pathways



Porphyrin
(e^- donor)

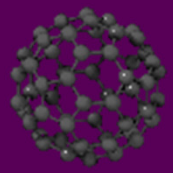
Fullerene
(e^- acceptor)

Energy Transfer Pathway



- Triplet excited C_{60} photosensitizes the formation of singlet oxygen ($^1\Delta_g$) with Φ_Δ=1
- Singlet oxygen decay ($^1\Delta_g \rightarrow {}^3\Sigma^-_g$) at 1270 nm can be detected using ultra-sensitive Ge-diode near-IR spectroscopy.

Khan, et al.. *Proc. Natl. Acad. Sci. USA*, **1979**, 6047-6049.



Photodynamic Therapy (PDT)

Procedure:

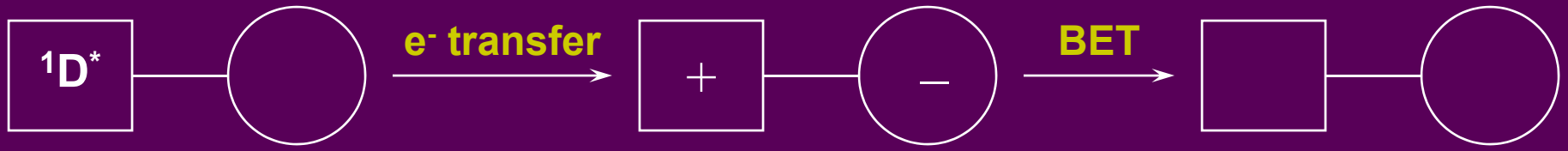
1) Chromophore is injected into patient
2) The tumor-diseased area is irradiated
3) Cell death results from the generation of singlet oxygen

- Recently, the FDA approved Photofrin®, a concoction of porphyrins, as a cancer-treatment agent for photodynamic tumor therapy (PDT).
- Studies in Japan concluded that a C_{60} derivative suppressed tumor growth better than Photofrin® in mice.

Tabata, et al.. *Jpn. J. Cancer Res.*, **1997**, 1108-1116.

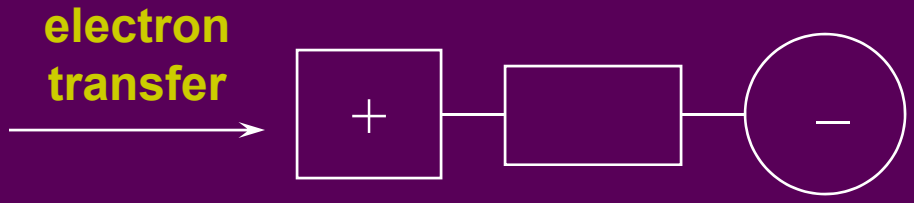
Electron Transfer Pathway

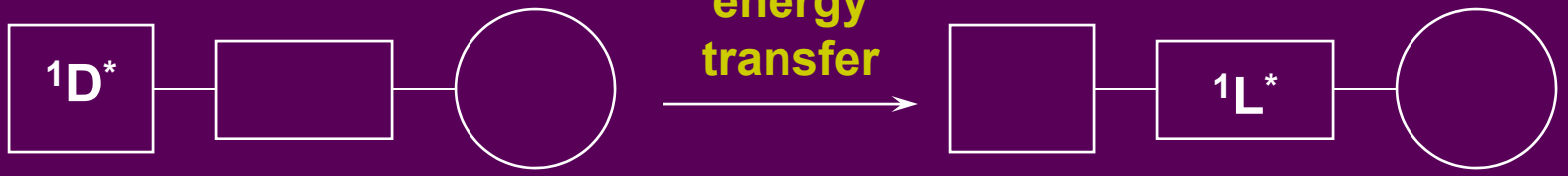
Following Irradiation:

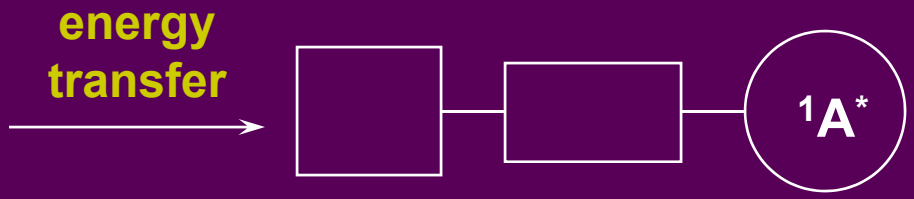


- The pathway can be monitored by transient absorption spectroscopy with the 670 nm decay of the porphyrin radical cation and the 1060 nm decay of the C_{60} radical anion.
- The goal is to produce long-lived charge-transfer states to mimic the photosynthetic reaction centers which are responsible for harvesting solar energy in plants.

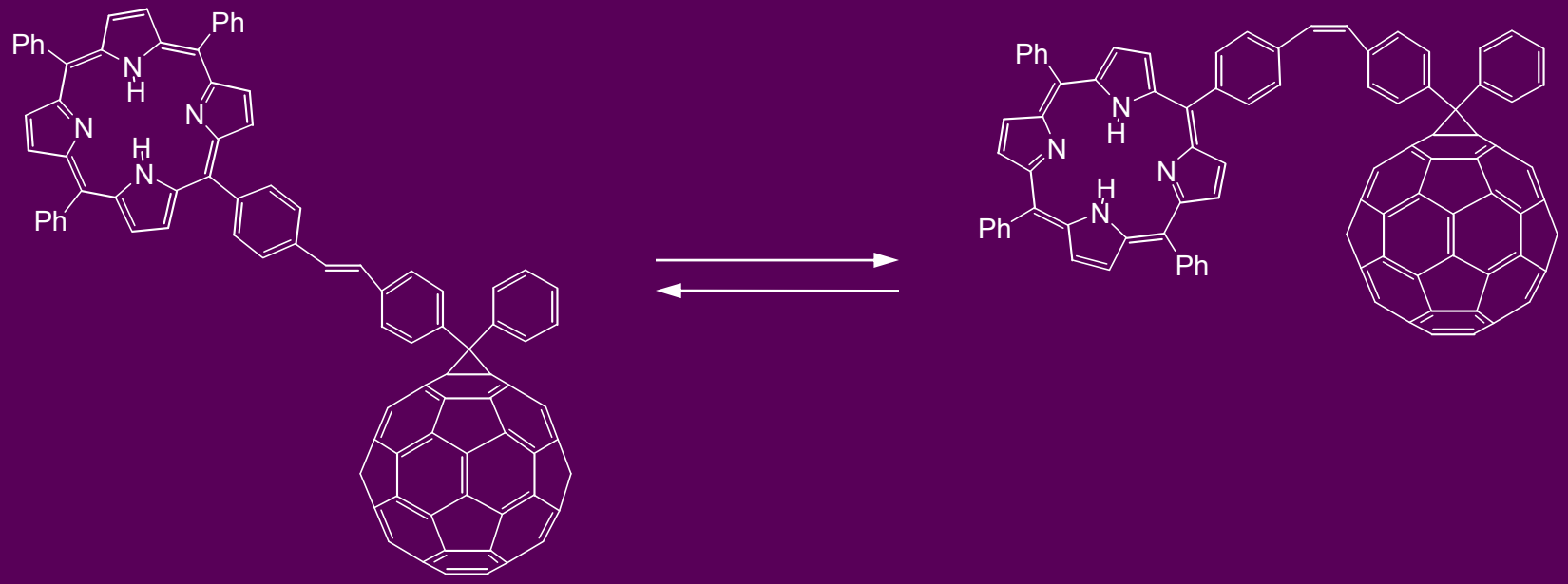
Stilbene Triad Pathways ??







cis-trans Photoisomerization



2a **2b**

- Introduces a significant change in molecular topology
- Separable by HPLC
- Such isomerization holds the potential for practical application as a molecular switch

Acknowledgments

- Technical Assistance & Helpful Discussions
  - Shaun MacMahon
  - Prof. Nicholas Geacintov (NYU), for providing access to his fluorimeter and the Ge-diode IR spectrometer
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- Funding
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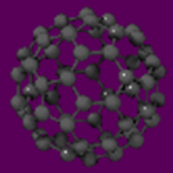
  - NYU College of Arts and Science, S.F.B. Morse Grant

THE ELECTROCHEMICAL SOCIETY



Paramagnetic Energy Plot

E

S_1

T_1

S_0

D_3

D_2

D_1

Q_2

Q_1

D_0

$P-{}^{*}C_{60}$

$P^{+\bullet}-C_{60}^{-\bullet}$

?