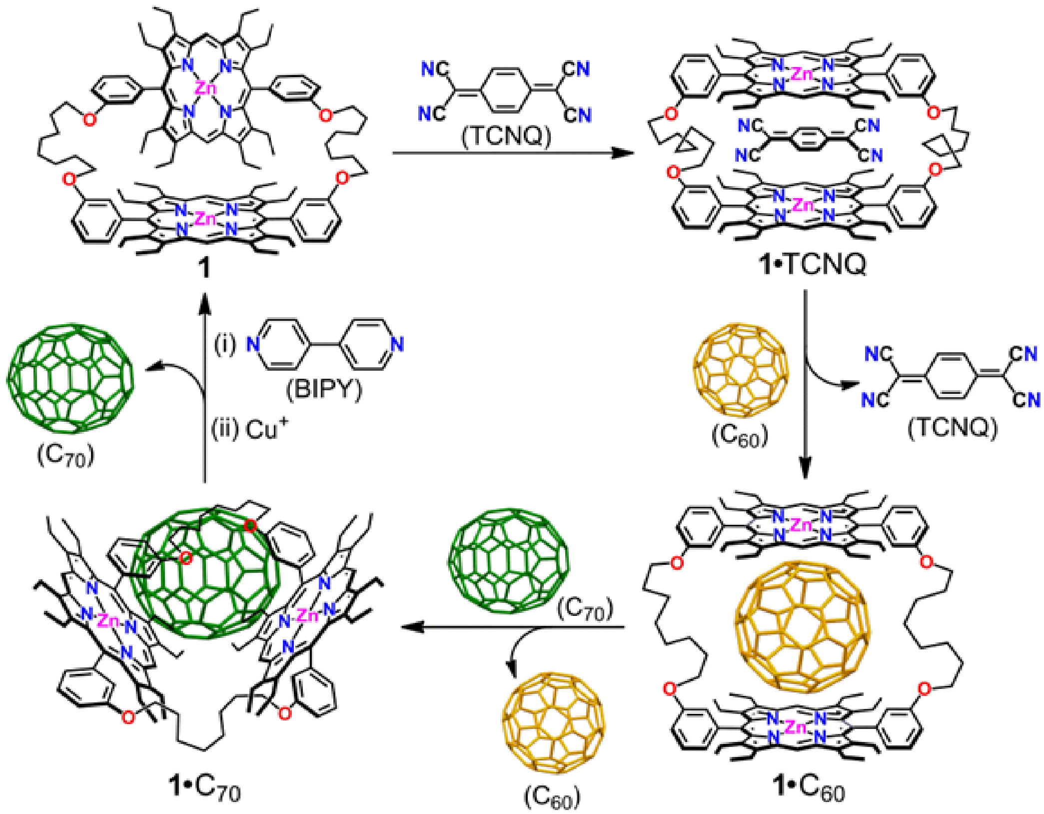
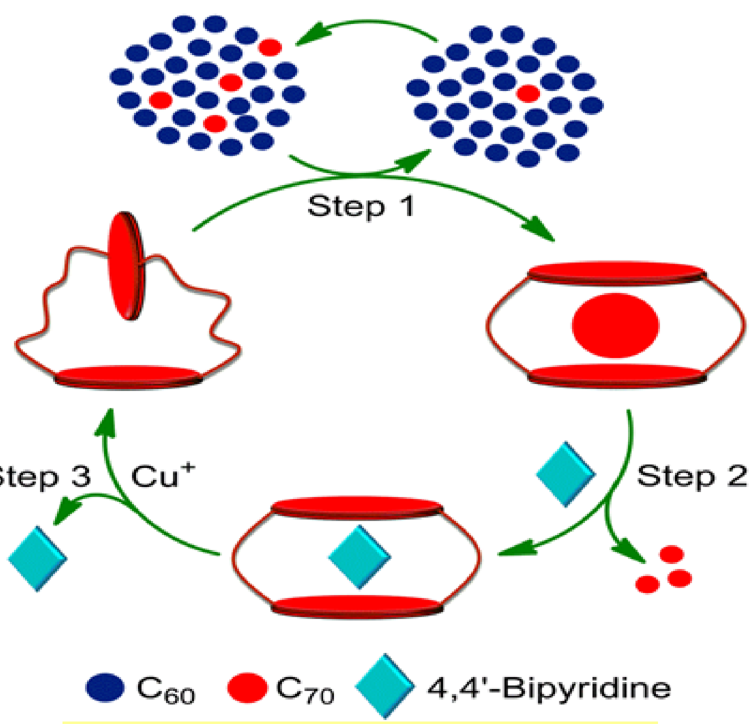
Artificial Cavity for Enzymatic Reactions

Enzymes, nature's creation of catalysts, encapsulate multiple functionalities within their cavity where the catalytic conversion takes place, and can be extremely active and selective for a range of chemical conversions. Therefore, in recent years, species with well-defined inner void spaces able to accommodate guests, also defined as molecular containers, have been extensively studied. The interest in such systems is driven in part by their potential utility in areas as diverse as catalysis, recognition, separation, and transport. Generally, the inner cavity of the molecular container offers an isolated microenvironment wherein encapsulated guests are exposed to a reduced number of interactions compared to the bulk solution. Whereas bound guests may interact only with the host or other co-encapsulated guests, in the bulk guests display a high number of interactions with solvent molecules or other guests. As a consequence, the properties of the bound guests are usually altered leading to applications for the resulting encapsulation complexes in different areas of chemical research. In this regard, the design of molecular container incorporating covalently linked bisporphyrins has enticed a great deal of attention recently, because of the cofacial arrangement through rigid/flexible linkers, which can act as molecular clefts for the binding and activation of a variety of substrates. Of particular interest to us is the design of bisporphyrins appropriate for applications involving efficient molecular recognition and catalysis. Bisporphyrin cavities of different shapes and sizes can recognize the substrates for various practical applications, whereas the presence of metal centers would facilitate further scope.

A Tunable Cyclic Container

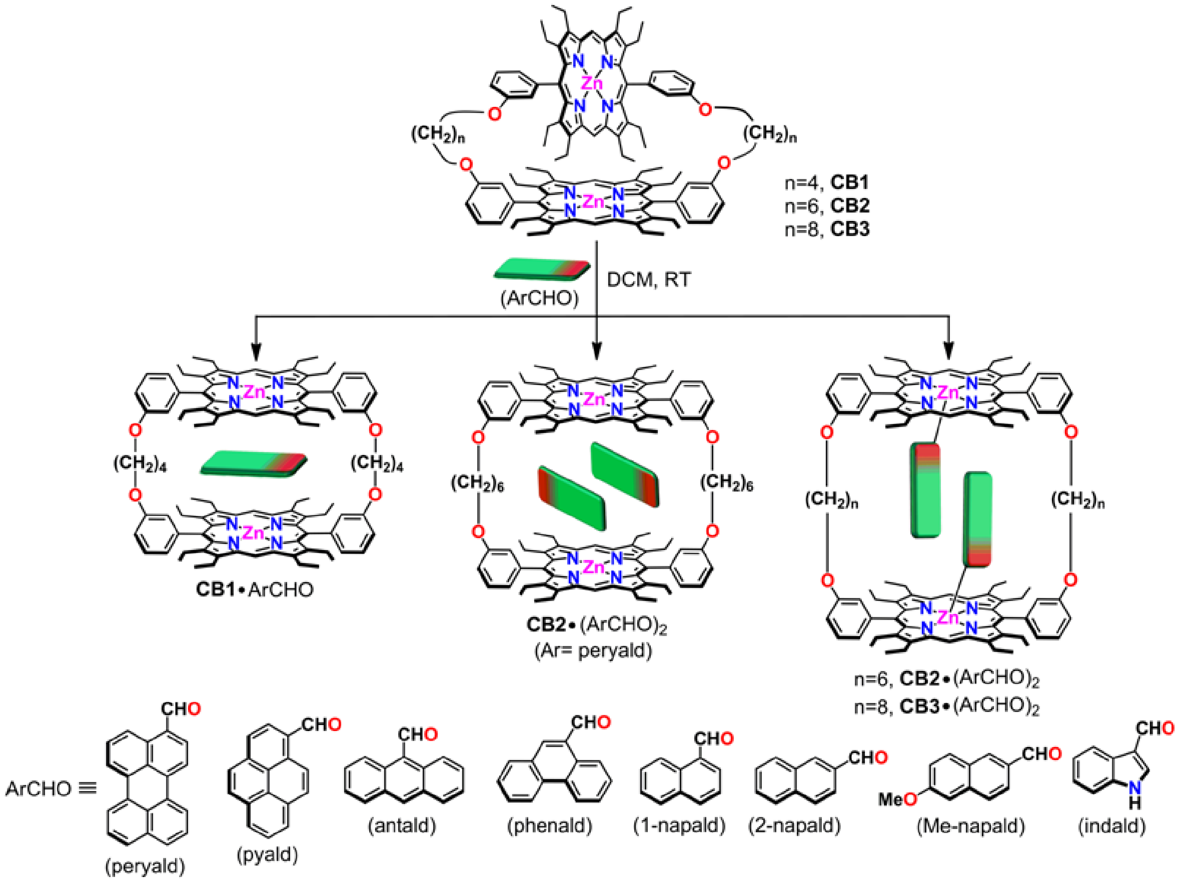


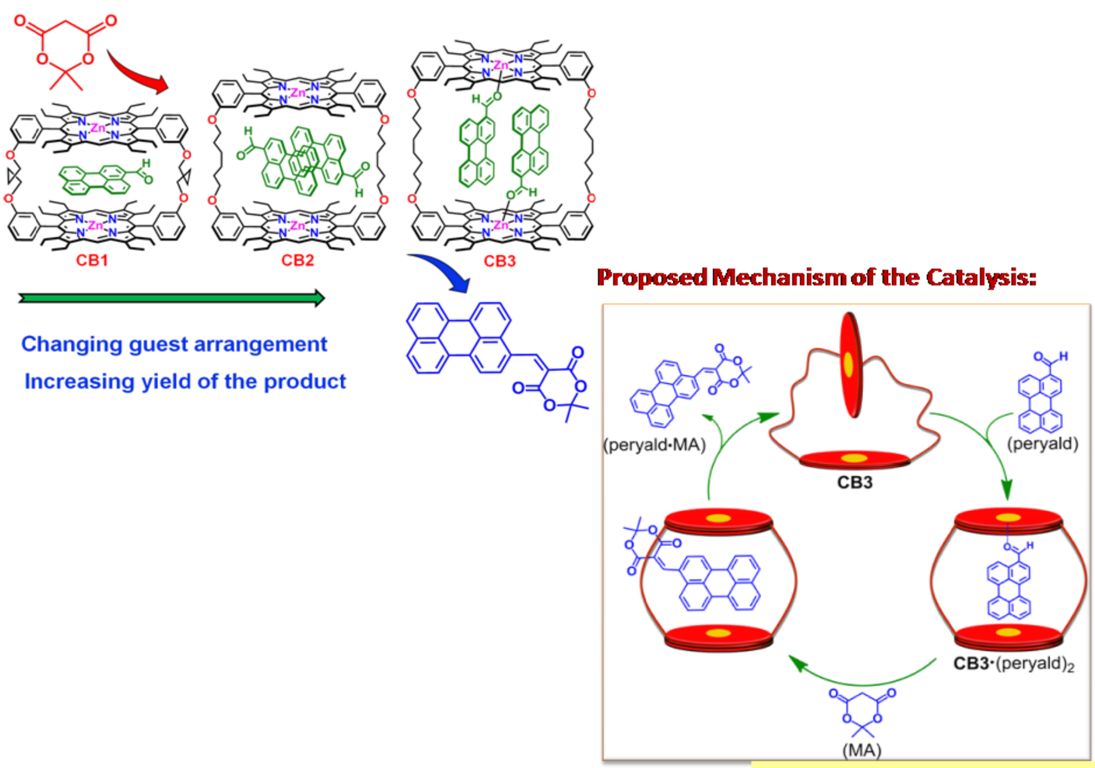
Schematic Presentation of the Selective C_{70} Isolation from the Mixture



Chem. Asian. J. **2017**, *12*, 0000

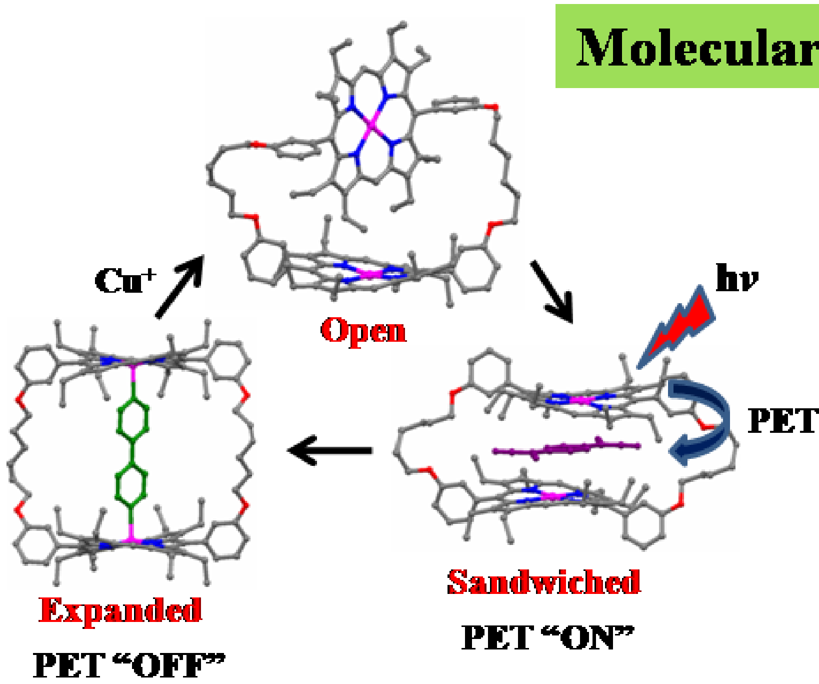
Cyclic Bisporphyrin Based Flexible Molecular Containers: Controlling Guest Arrangements and Supramolecular Catalysis by Tuning Cavity Size

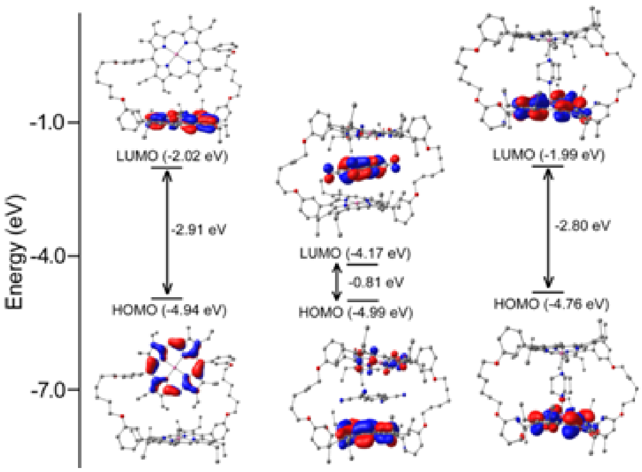




Chem. Eur. J. **2017**, *23*, 7093

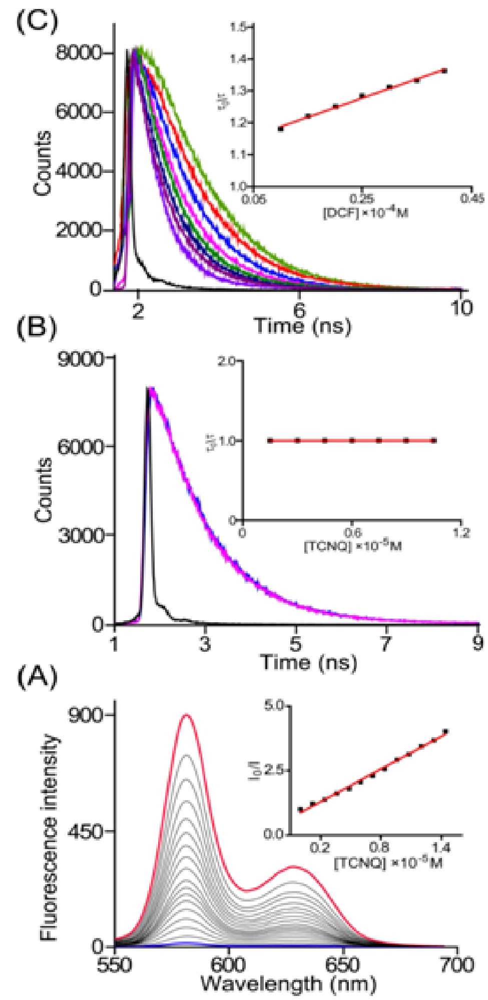
Molecular clip





Energy-level diagrams

Emission lifetime



Chem. Eur. J. **2016**, *22*, 5607

Molecular Cleft for Selective Binding

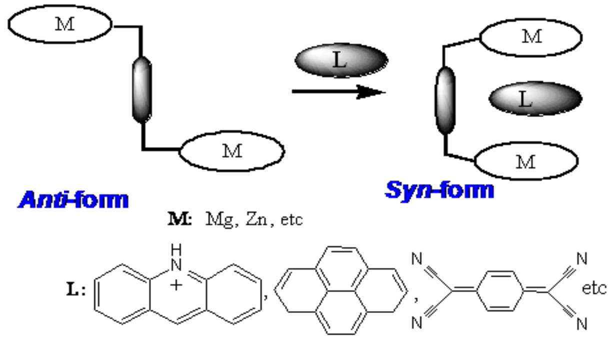
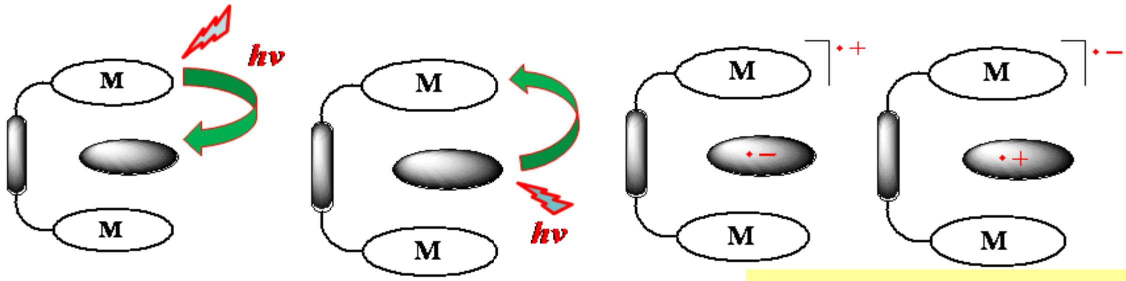
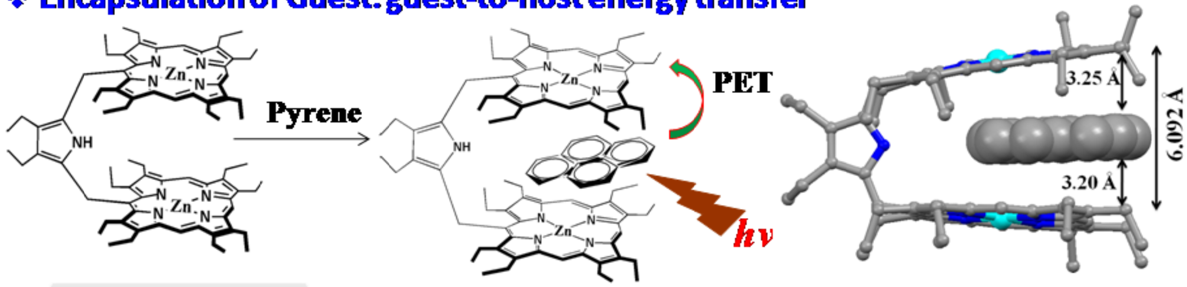


Photo-induced Energy Electron Transfer

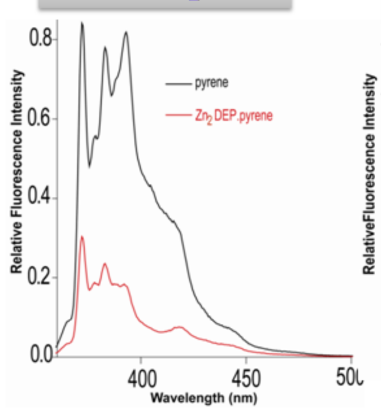


Chem. Eur. J. **2012**, *18*, 7404.
Chem. Eur. J. **2011**, *17*, 11478.
Dalton Trans. **2013**, *42*, 12381.

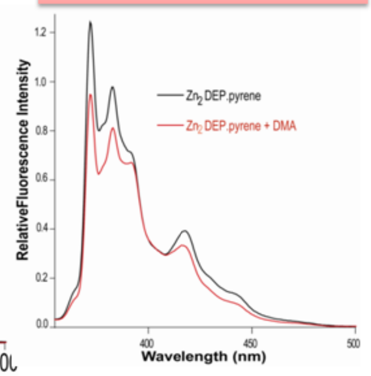
❖ Encapsulation of Guest: guest-to-host energy transfer



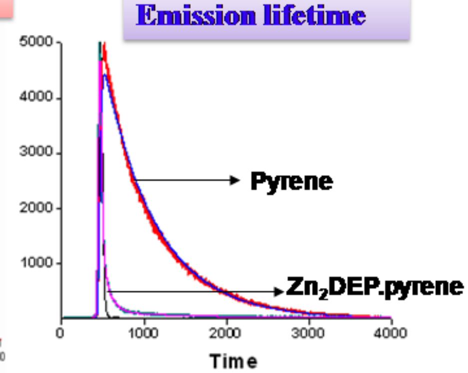
Emission spectra



No Exciplex formation

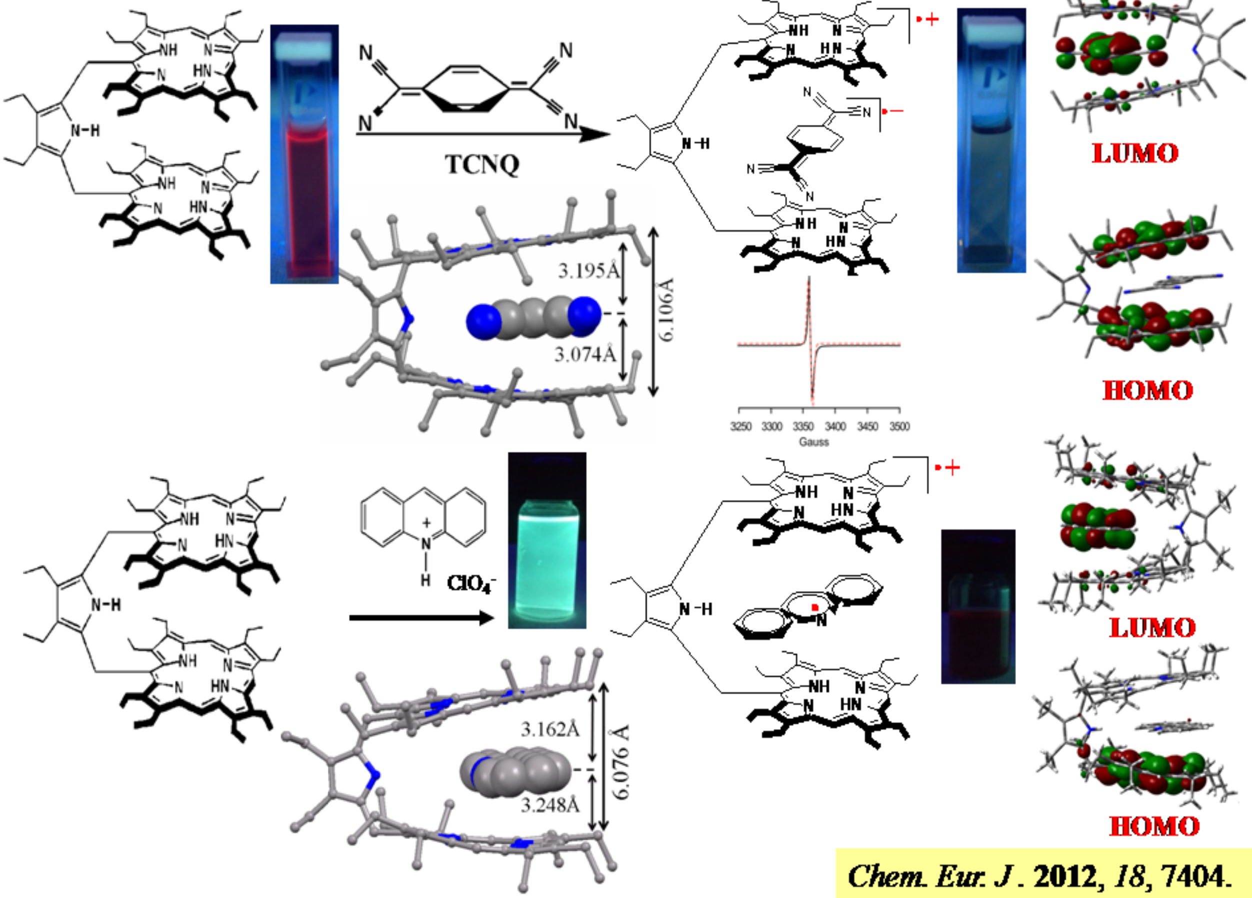


Emission lifetime



Chem. Eur. J. **2011**, *17*, 11478.

❖ **Encapsulation of Guest: host-to-guest electron transfer**



Representative Publications:

1. **Cyclic Bisporphyrin Based Flexible Molecular Containers: Controlling Guest Arrangements and Supramolecular Catalysis by Tuning Cavity Size**

   P. Mondal, S. Sarkar and S. P. Rath*

   Chem. Eur. J. **2017**, *23*, 7093-7103.

   Highlighted in Synfacts **2017**, *13(08),* 0816.

2. **A Tunable Cyclic Container: Guest-Induced Conformational Switching, Efficient Guest Exchange and Selective Isolation of C_{70} from Fullerene Mixture**

   P. Mondal and S. P. Rath*

   Chem. Asian J. **2017**, *12,* 1824-1835.

3. **Cyclic Zn(II)bisporphyrin Based Molecular Switch: Supramolecular Control of Complexation Mediated Conformational Switching and Photoinduced Electron Transfer**

   P. Mondal and S. P. Rath*

   Chem. Eur. J. **2016,** *22*, 5607-5619.

4. **Effect of Two Interacting Rings in Metalloporphyrin Dimers upon Stepwise Oxidations**

   S. Dey, D. Sil, Y. A. Pandit and S. P. Rath*

   Inorg. Chem. **2016**, *55*, 3229-3238.

5. **Metal-coordination-driven Mixed Ligand Binding in Supramolecular Bisporphyrin Tweezers**

   Sk. A. Ikbal, A. Dhamija and S. P. Rath*

   Chem. Commun., **2015**, 51, 14107 - 14110.

6. **Highly Selective and Sensitive Detection of Picric Acid Explosive by a Bisporphyrin Cleft: Synergistic Effects of Encapsulation, Efficient Electron Transfer, and Hydrogen Bonding**

   P. Mondal and S. P. Rath*

   Eur. J. Inorg. Chem. **2015**, 4956-4964.

7. **Building-up Remarkably Stable Magnesium Porphyrin Nano-Structures in One Pot: Synthesis, Structure, Surface Morphology and Effect of Bridging Ligands**

   Sk A. Ikbal, S. Brahma and S. P. Rath*

   Inorg. Chem. **2012,** *51*, 9666 - 9676.

8. **Syn-Anti Conformational Switching in an Ethane-bridged Co(II)bisporphyrin Induced by External Stimuli: Effects of Inter-macrocyclic Interactions, Axial Ligation and Chemical and Electrochemical Oxidations**

   S. Dey and S. P. Rath*

   Dalton Trans. **2014**, *43*, 2301 - 2314.

9. **Encapsulation of TCNQ and Acridinium Ion within Bisporphyrin Cavity: Synthesis, Structure, Photophysical and HOMO-LUMO Gap Mediated Electron Transfer Properties**

   A. Chaudhary and S. P. Rath*

   Chem. Eur. J. **2012**, *18,* 7404 - 7417.

10. **Efficient Complexation of Pyrrole-bridged Di-Zinc(II) Bisporphyrin with Fluorescent Probe Pyrene: Synthesis, Structure, and Photoinduced Singlet-Singlet Energy Transfer**

    A. Chaudhary and S. P. Rath *

    Chem. Eur. J. **2011**, *17*, 11478 - 11487.