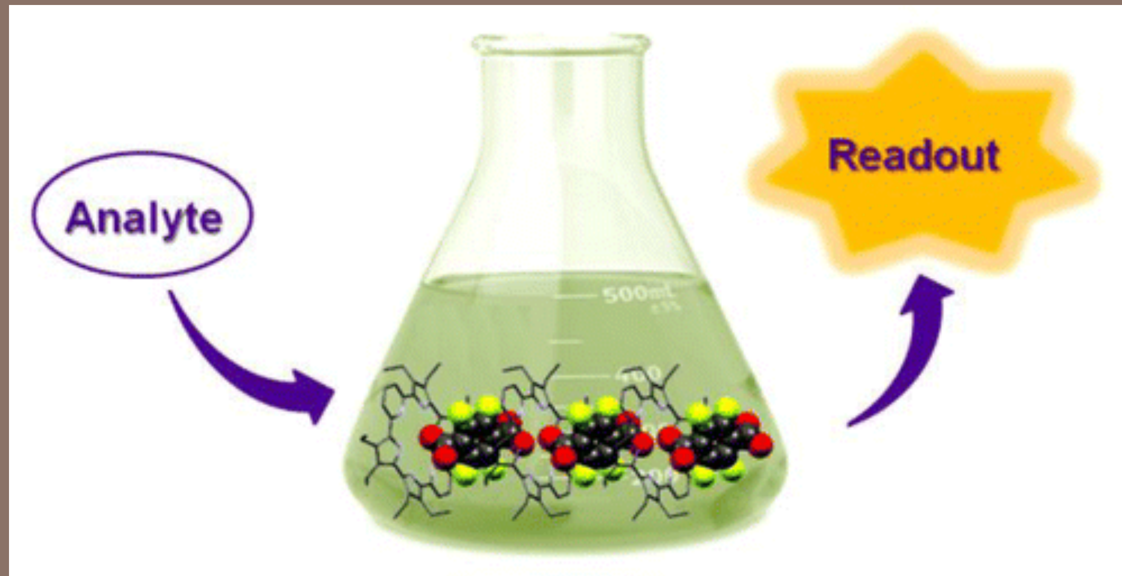


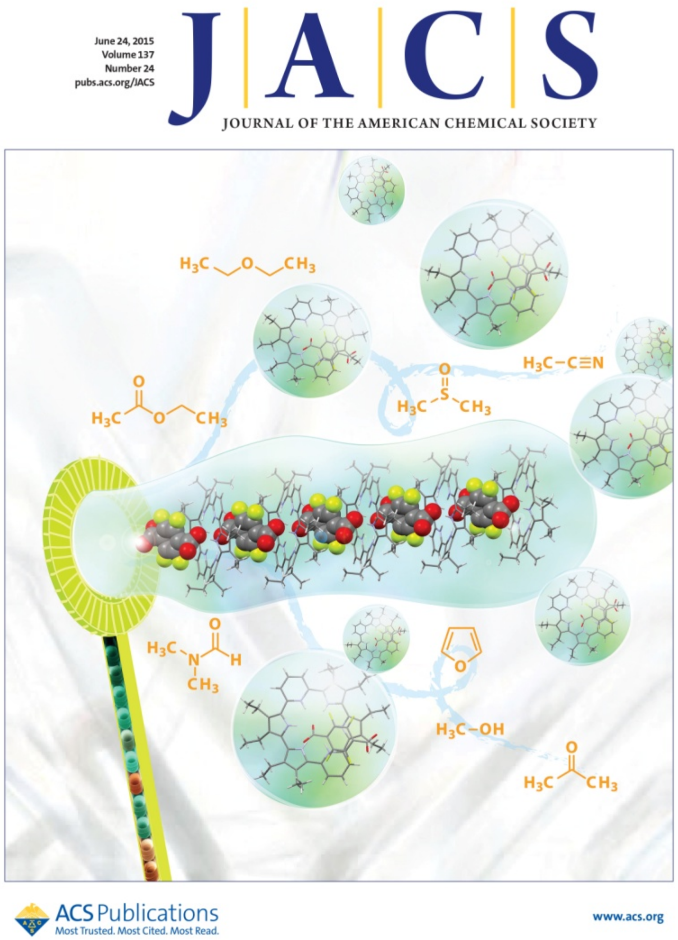
EXPANDED PORPHYRIN-ANION SUPRAMOLECULAR ASSEMBLIES: ENVIRONMENTALLY RESPONSIVE SENSORS FOR ORGANIC SOLVENTS AND ANIONS

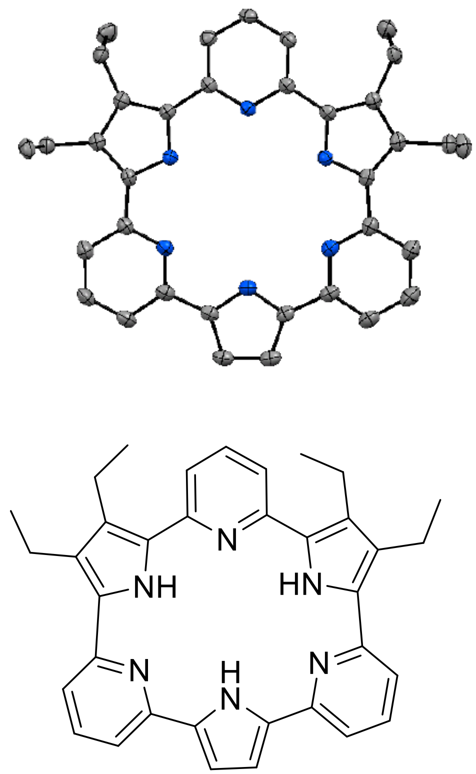
Zhan Zhang, Dong Sub Kim, Chung-yon Lin, Huacheng Zhang, Aaron D. Lammer, Vincent M. Lynch, Ilya Popov, Ognjen Š. Miljanić, **Eric V. Anslyn**, And **Jonathan L. Sessler**

Marina Kovaliov

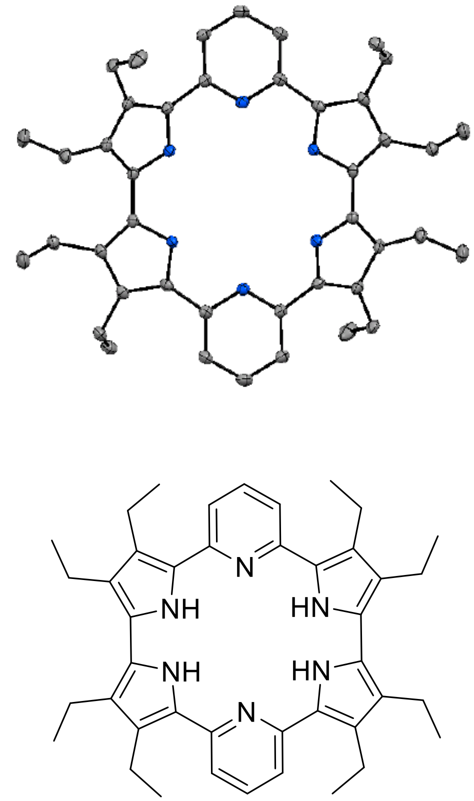
J. Am. Chem. Soc., **2015**, *137* (24), pp *7769–7774*

Cyclo[m]pyridine[n]pyrroles





Cyclo[3]pyridine[3]pyrrole

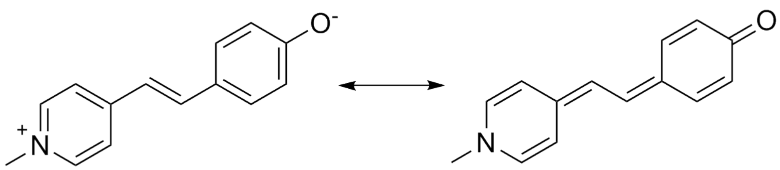


Cyclo[2]pyridine[4]pyrrole

Marina Kovaliov @ Wipf Group 29 December 2015

Chemosensing

- Solvatochromic Dyes (Brooker's merocyanine)

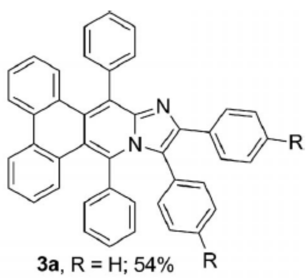


C. Reichart et al., *Chem. Rev.*, **1994**, 94, 2319

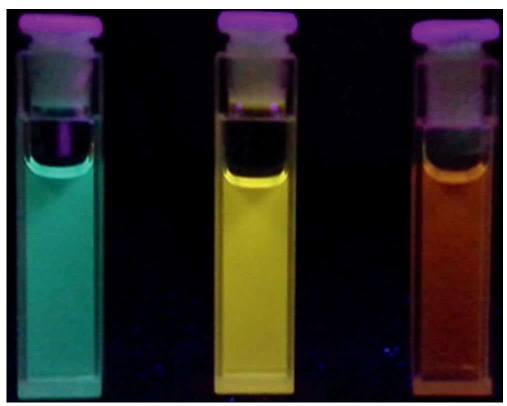
- Fluorescent chemosensors

(9,11,12,14-Tetraaryldibenzo[f,h]imidazo[1,2-b]isoquinolines)

Y. Wang et al., *Eur. J. Org. Chem.*, **2013**, 94, 7320



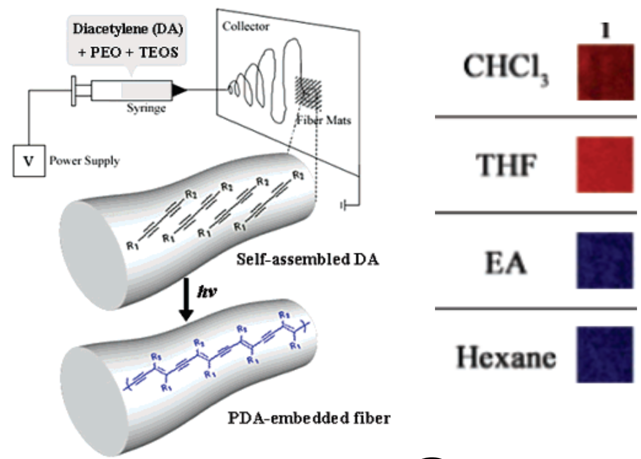
3a, R = H; 54%
3b, R = CH_3; 55%
3c, R = *n*Bu; 59%
3d, R = *t*Bu; 32%
3e, R = OCH_3; 60%
3f, R = OPh; 52%
3g, R = Br; 43%
3h, R = $N(CH_3)_2$; 51%



Chemosensing

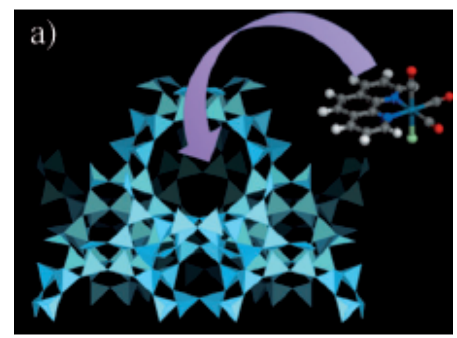
- Functional polymers

J. Kim et al., *JACS.*, **2007**, 129, 3038



- Solid metal complexes [Re(phen)$(CO)_3$Cl]@NaY

(zeolite framework for the supramolecular assembly of rhenium complexes with applications to vapor sensing)



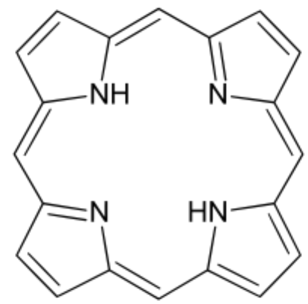
A. A. Marti at el, *Angew. Chem. Int. Ed.*, **2013**, 52, 12615

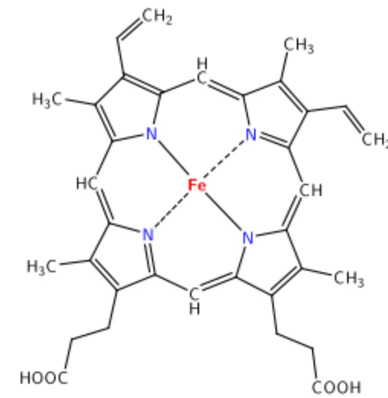
Marina Kovaliov @ Wipf Group 29 December 2015

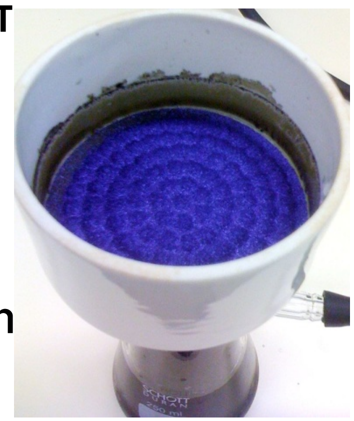
Porphyrins

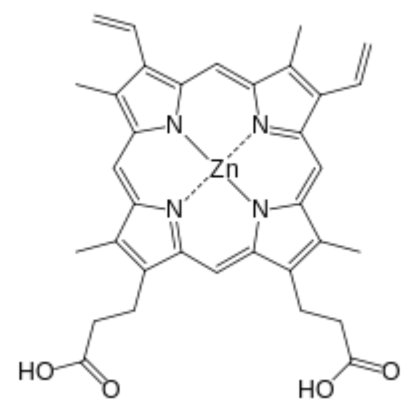
5

- Porphyrins are a group of heterocyclic macrocycle organic compounds, composed of four modified pyrrole subunits interconnected at their α carbon atoms via methine bridges.
- The porphyrin it is aromatic macrocycle has 26 (delocalized) π electrons in total.
- Porphyrin macrocycles are highly conjugated systems and characterized by intense absorption and emission features in UV, visible and IR regions.







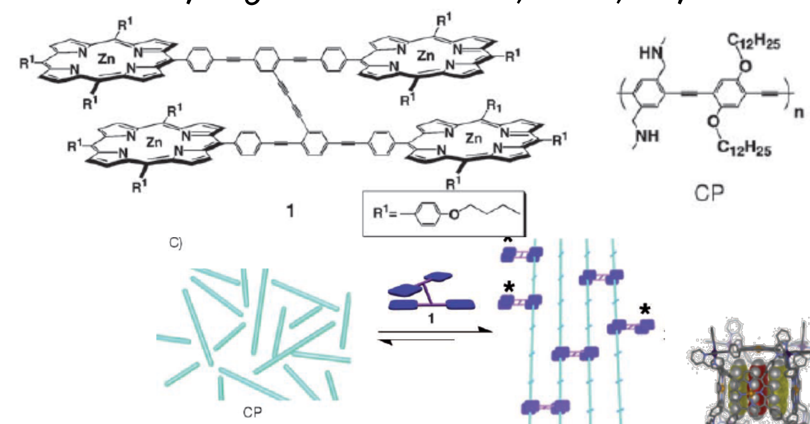


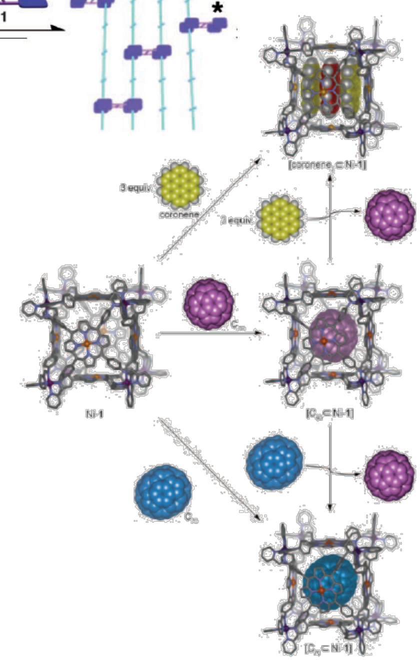
Marina Kovaliov @ Wipf Group 29 December 2015

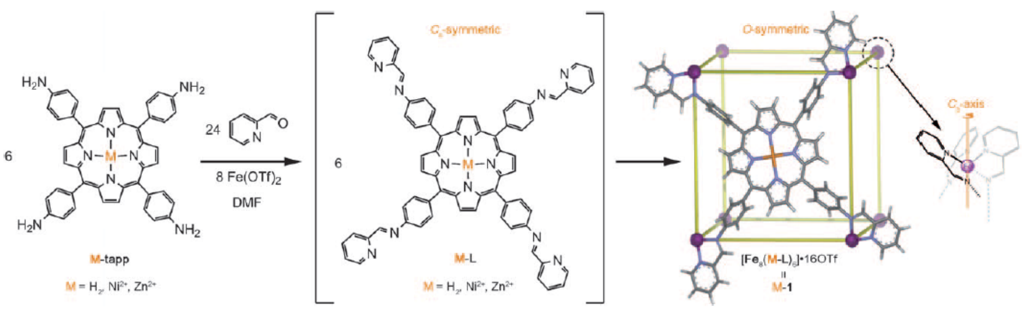
Self ensembled structures

- Porphyrins are attractive building blocks for the construction of self-assembled structures, π,π-donor–acceptor and π-ion interactions.
- The ability of porphyrins to coordinate cations allows for metaldirected self-assembly.
- Porphyrin-based supramolecular assemblies have been studied as promising chemical sensors, copolymers, hosts for planar aromatic guests and fullerenes.
- When functionalized with hydrogen bond donors/acceptors, porphyrin derivatives have been used to create linear polymers, cyclic oligomers, and cages.

Y. Kubo at el, *Angew. Chem. Int. Ed.*, **2006**, 45, 1548







J. R. Nitschke at el, *Angew. Chem.*, **2011**, 123, 3541

Expanded porphyrins

- As compared to porphyrins, expanded porphyrins typically display distinct optical features, more diverse π-conjugation pathways, greater flexibility, and, in many cases, a propensity to interact with anions, as opposed to cations.

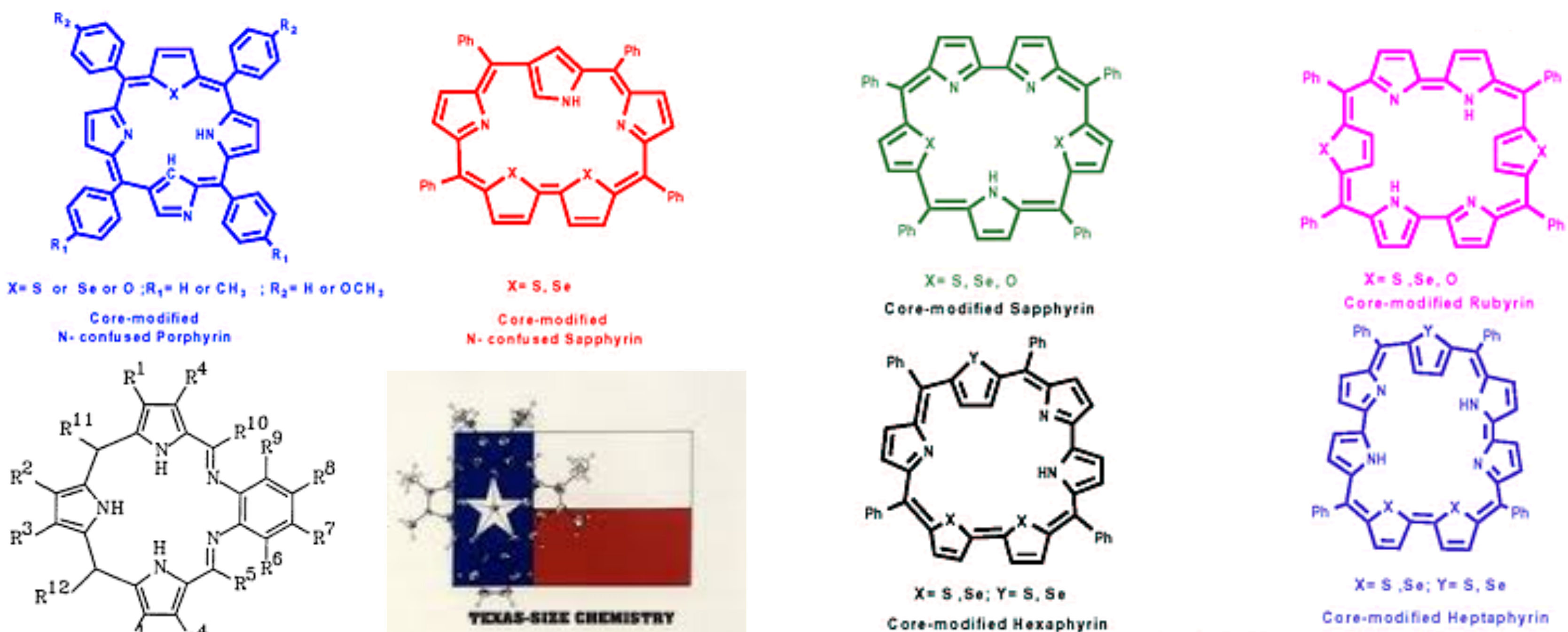
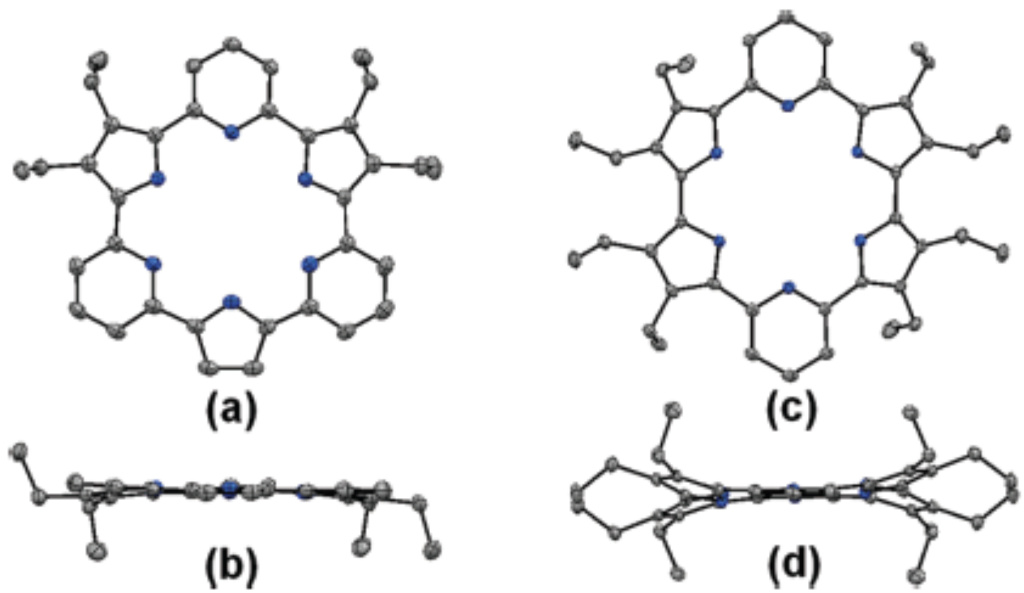


Figure1: Porphyrinoid macrocycles reported

C. Reichart et al., *Chem. Rev.*, **1994**, 94, 2319

Expanded Porphyrins- cyclo[m]pyridine [n]pyrroles

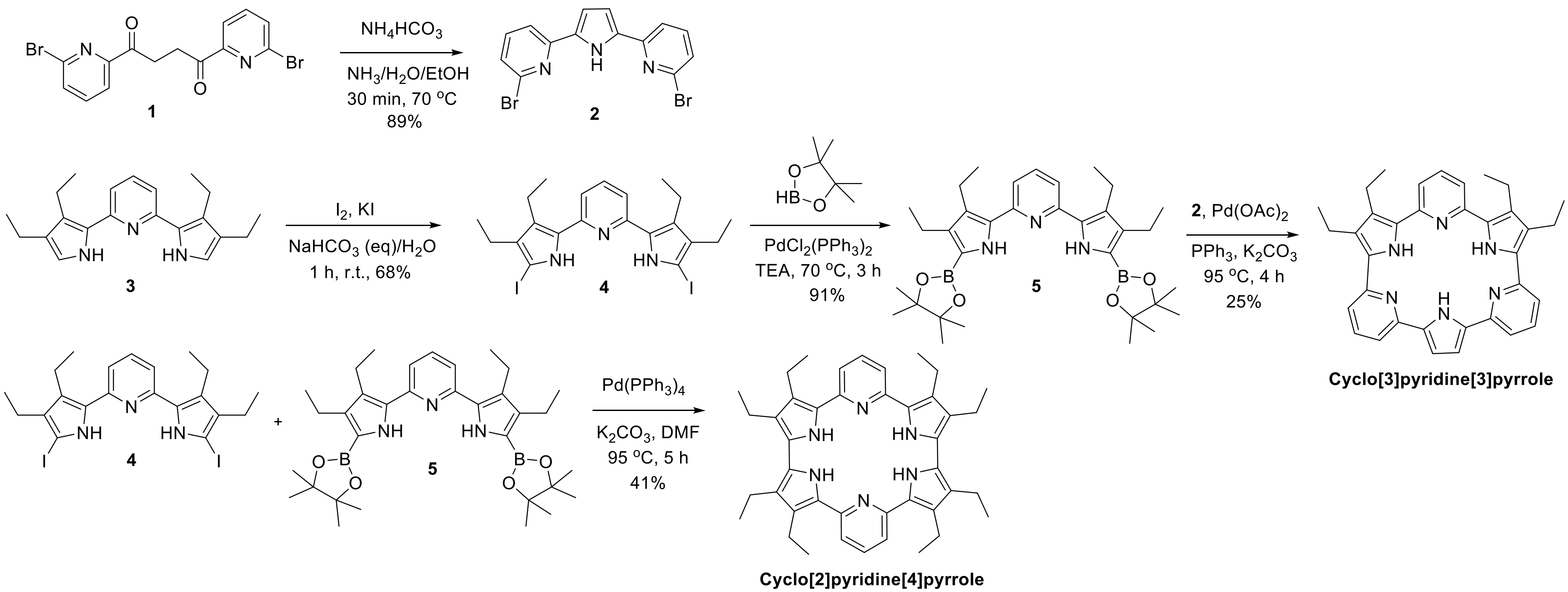
- **P_mP_n** expanded porphyrin, the cyclo[m]pyridine[n]pyrroles (m + n = 6), may be used to stabilize a new class of anion-derived selfassembled constructs.
- Pyridine containing analogs of cyclo[6]pyrrole.



J. L. Sessler et al., *JACS.*, **2012**, 134, 4076

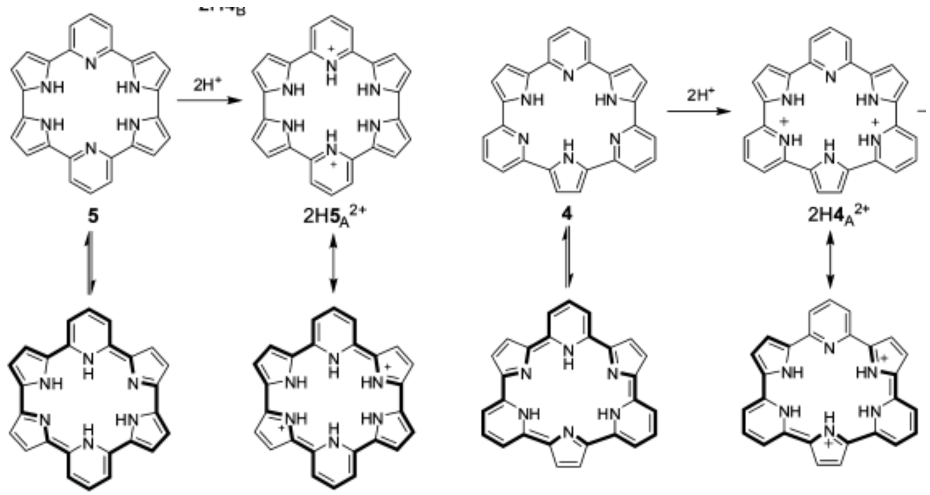
Synthesis

Cyclo[2]pyridine[4]pyrrole & Cyclo[3]pyridine[3] pyrole



J. L. Sessler et al., *JACS.*, **2012**, 134, 4076

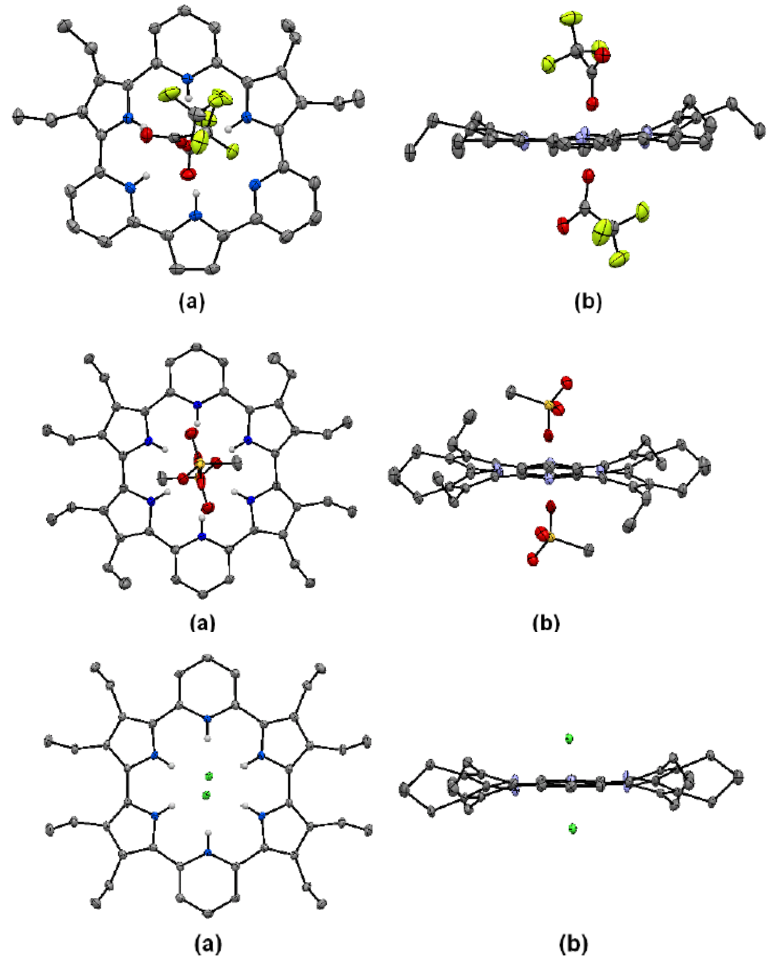
Design and Preparation of the Supramolecular Assemblies



P_2P_4 P_3P_3

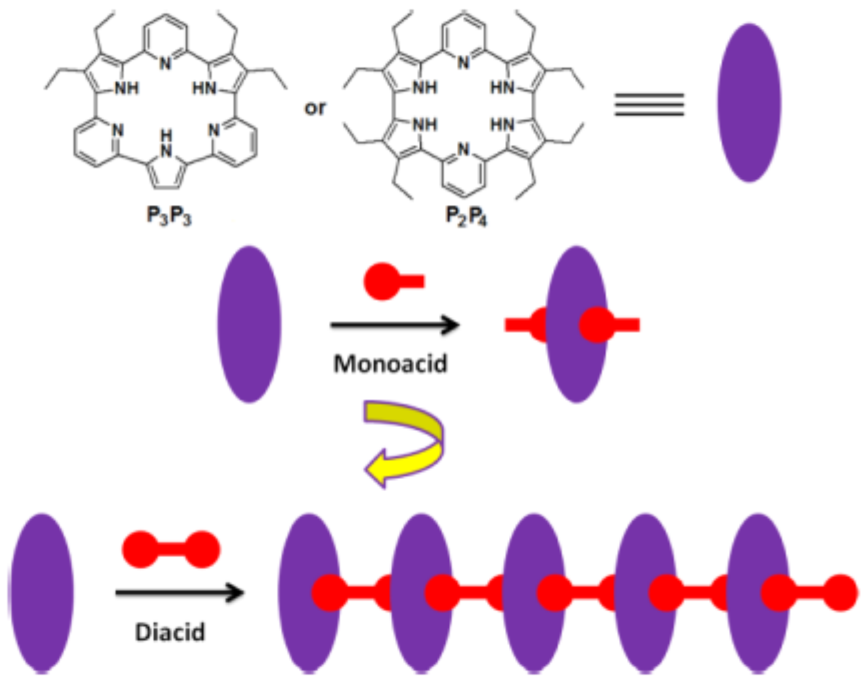
J. L. Sessler et al., *JACS.*, **2012**, 134, 4076

- Protonation of these nonaromatic compounds can lead to the expansion of π-conjugation, fully conjugated structure that reflects the presence of an electronically delocalized 24 π-electrons.



Expanded Porphyrins-Anion self-assembly

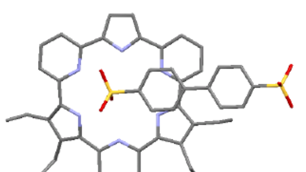
- **P_mP_n** expanded porphyrin, the cyclo[m]pyridine[n]pyrroles (m + n = 6), may be used to stabilize a new class of anion-derived selfassembled constructs.
- Pyridine containing analogs of cyclo[6]pyrrole.

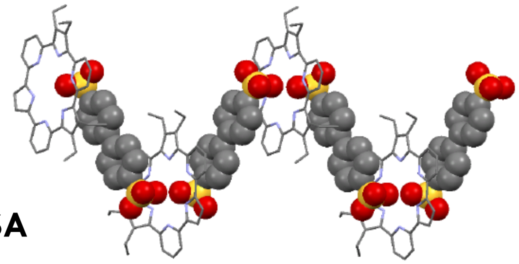


Preparation & Solid-State Characterization

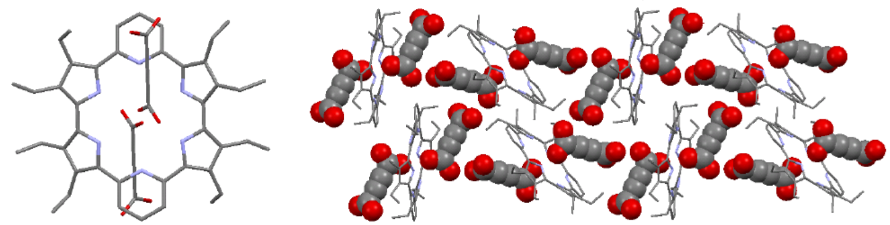
12

- **Preparation of 1:1 P_mP_n-diacid polymers.** The free-base form of the macrocycle, P_2P_4 or P_3P_3, (0.01 mmol) was dissolved in 80 mL CH_2Cl_2 and 1.2 equivalents of acid were added in solid form. The mixture was sonicated until all the granules were dissolved.
- **Preparation of 1:2 P_mP_n-diacid assembles.** These ensembles were prepared 2.4 molar equivalents of acid.

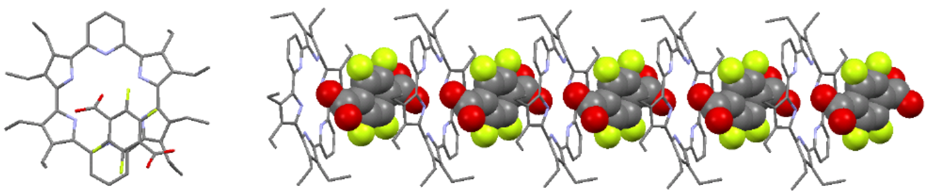




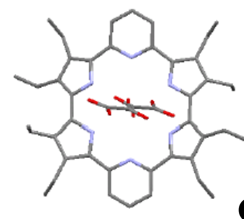
BPDSA

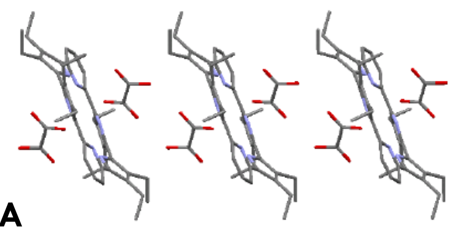


ADCA

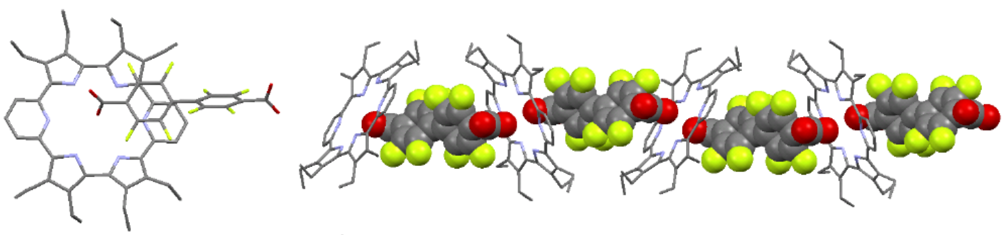


TFTPA





OA



OFBPA

pKa_1 of oxalic acid OA (1.2) enables to protonate a first PmPn macrocycle and relatively relatively high value of pKa_2 (4.1) precludes protonation of a second macrocycle.

In contrast, the pKa_2 values for BPDSA and TFTPA are around 2.0 (pKa_1 = 1.0) , one molecule of acid can protonate two macrocycles.

Marina Kovaliov @ Wipf Group 29 December 2015

Morphology of the Ensembles (SEM)

- In order to determine the morphology of the ensembles produced under conditions of fast evaporation, rather than slow crystallization, drop-cast samples were prepared and studied by scanning electron microscope (SEM)

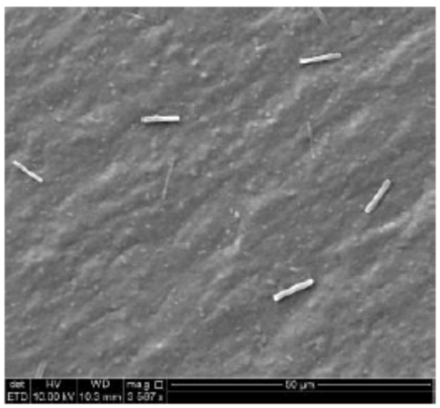


Figure S1. P_3P_3-BPDSA.

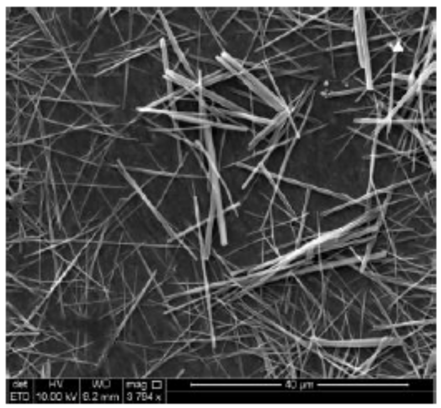


Figure S2. P_3P_3-TFTPA.

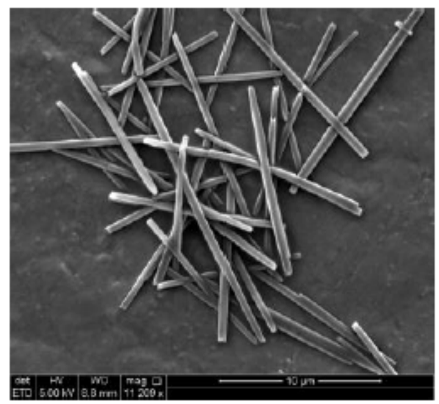


Figure S3. P_3P_3-OA.

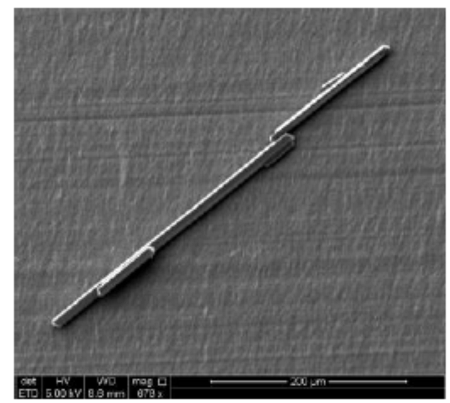


Figure S4. P_2P_4-ADCA.

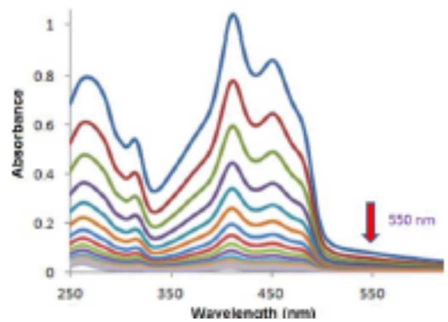
Solution-State Binding Studies

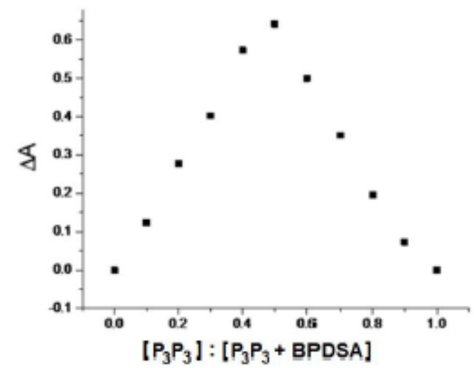
- **Stochiometry** (continuous variation (Job's) plots):

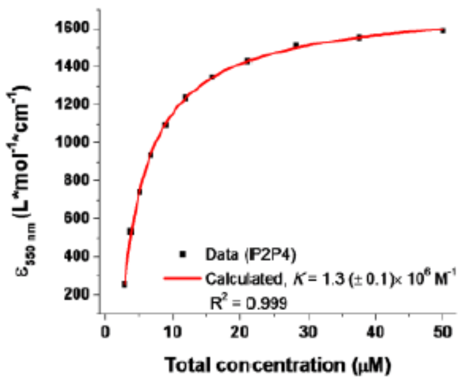
  1:1 mixture of P_2P_4 and BPDSA (absorption change at 451 nm and the mole fraction of P_2P_4 *vs* the mole fraction of P_2P_4 + BPDSA).

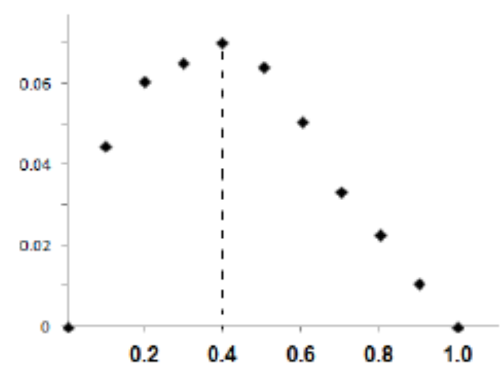
  1:2 mixture of P_2P_4 and OA (absorption change at 451 nm and the mole fraction of P_2P_4 *vs* the mole fraction of P_2P_4 + OA).

- **Binding affinities:** extinction coefficient as a function of the total concentration of an equimolar mixture of P_2P_4 and BPDSA



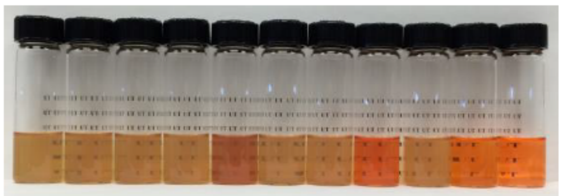


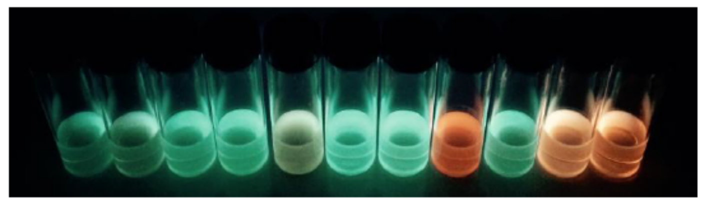


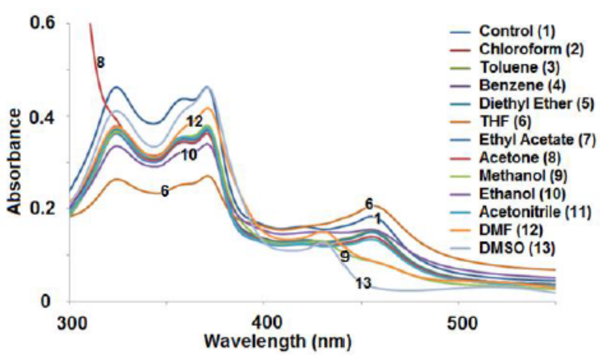


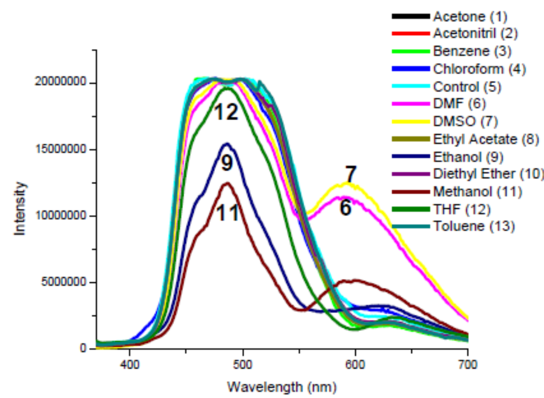
Solvent Response

- Solvent response observed for the P_3P_3-BPDSA assembly. 10% v. v. of polar solvents were added to a CH_2Cl_2 solution of the assembly. Top: color changes; bottom: fluorescence changes. From left to right: control (only CH_2Cl_2), chloroform, toluene, diethyl ether, THF, ethyl acetate, acetone, methanol, acetonitrile, DMF, and DMSO.







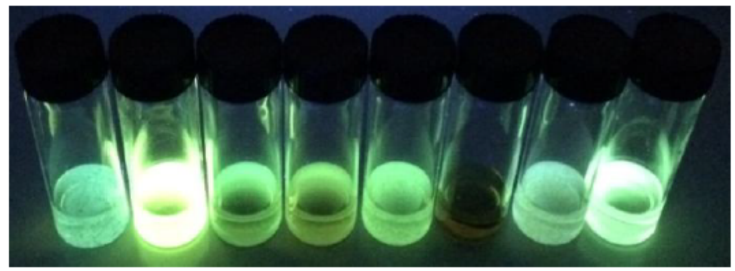


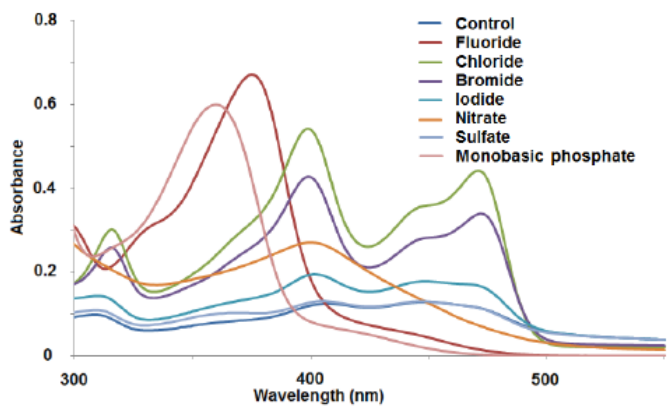
Supramolecular Assemblies —**Polar solvent**→ **Shorter Assemblies + Monomers**

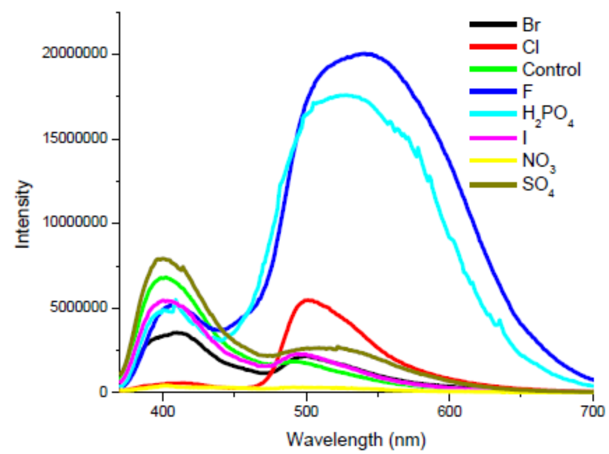
Anion Response

16

- Response of P_2P_4-BPDSA (in CH_2Cl_2) towards anions. Upper left: color change upon addition of an anion (control, fluoride, chloride, bromide, iodide, nitrate, sulfate and monobasic phosphate)







Marina Kovaliov @ Wipf Group 29 December 2015

Conclusions

- A series of expanded porphyrin-anion supramolecular assemblies using P_mP_n macrocycles and was successfully synthesized.
- These assemblies are characterized by highly ordered structures in the solid state. In the case of the 1:1 complexes strong interactions between the macrocycle and the various test anions were observed.
- The self assembled systems reported here are environmentally responsive and undergo distinct changes in solubility, color, and fluorescence intensity when exposed to polar solvents or Lewis basic anions.
- These systems could be used as chemosensors that allow certain salts and various solvents to be identified easily by optical or visual means.