Photoactive Metallosupramolecular Squares

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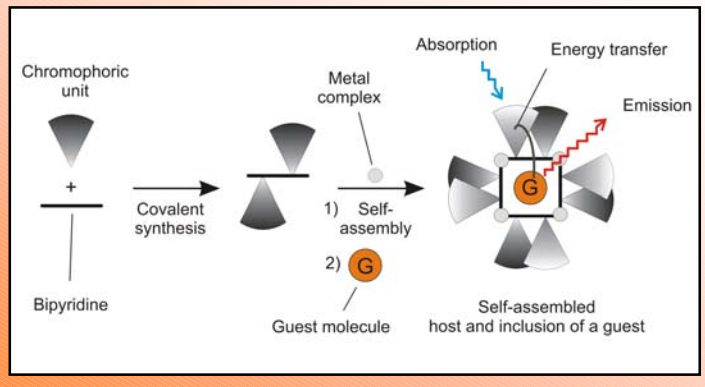
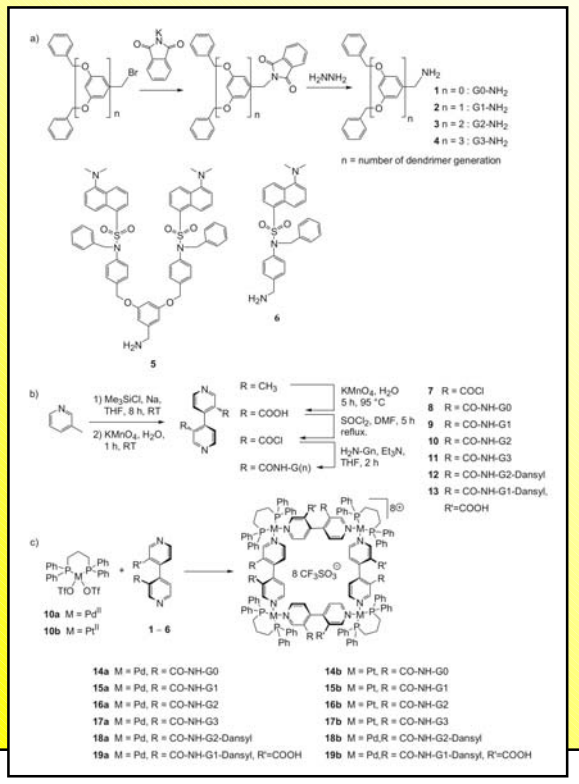
I. Synthetic strategy to photoactive assemblies

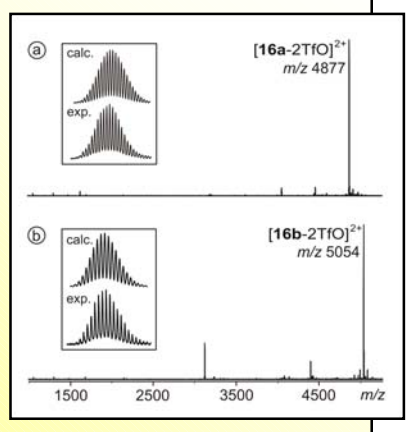


Programmed formation of dendritic architectures under thermodynamic control reduces synthetic efforts needed and provides a nm-sized cavity[1,2] for host-guest chemistry. Energy transfer from the peripherical units to the guest located inside of the cavity could be possible.

II. Synthesis of dendron-decorated self-assembling metallo-supramolecular squares[3-5]

Non-covalent synthesis allows high yields of squares with eight amide groups around the seam of the cavity capable of molecular recognition through hydrogen bonding.





ESI-MS chracterization of squares: only squares are formed, no other polygons or open chain oligomers are observed[5]

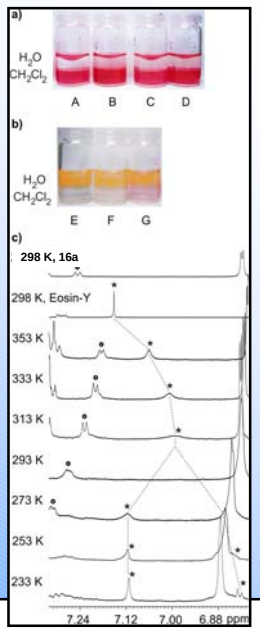
Mass spectral data permits to analyze the presence of defects in the dendrimer structure

III. Extraction of eosin-Y with Fréchet-type dendronized squares

a) Extraction of eosin-Y by squares; A = **15a**; B = **15b**; C = **16a** and D = **16b**. All dendritic squares are capable of extracting eosin from the water phase into dichloromethane

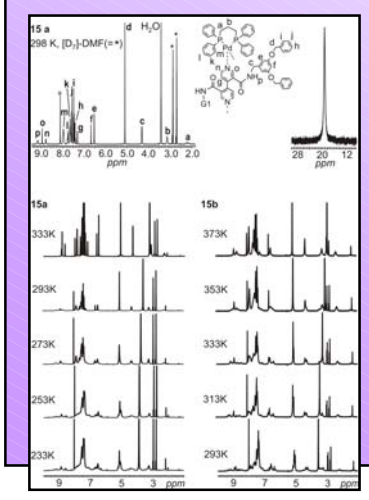
b) E = blind sample, extraction of eosin-Y by dendron-decorated bipyridine ligands; F = **9**; G = **10**. Very limited extraction is observed for the larger dendritic ligands.

c) Room-temperature ^{1}H NMR in [D_7]-DMF (top) of **16a**, and (second spectrum from the top) of eosin-Y. Series of temperature-dependent ^{1}H NMR spectra of the complex formed by mixing **16a** and 8 eqv. of eosin-Y. The presence of two sets of signals at lower temperatures is likely due to both free eosin and its complex with **16a** (labeled with asterisks). These results indicate that eosin is bound to **16a**, even though it is hard to determine its location within the dendrimer structure.



IV. Dynamic NMR and Isomerism

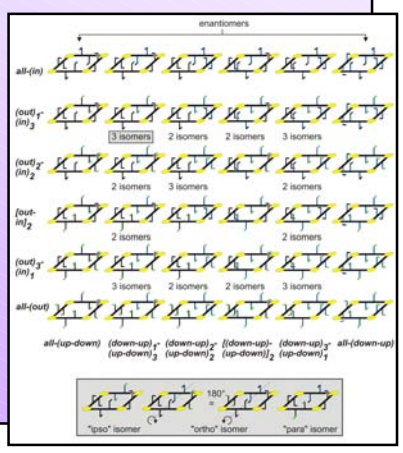
Only at elevated temperatures squares show a transition into simple spectra with one single set of signals. This points to the presence of up to 54 different isomers due to the orientation of the dendrons above or below up-down) the square plane and toward or away from the cavity (in-out).



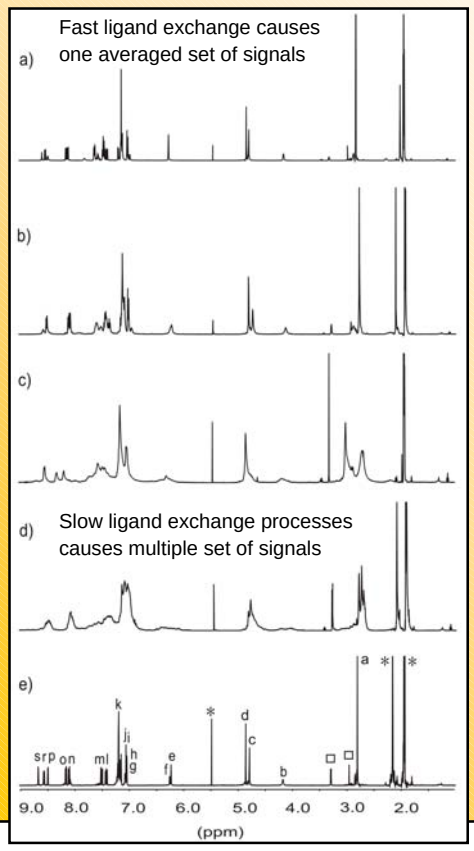
These isomers interconvert under thermodyamic control in what can be considered a dynamic library.

Different exchange mechanisms may contribute (e.g. ligand racemization, ligand exchanges, and its rotation).

Isomer interconversion is faster for Pd than for Pt squares indicating that ligand exchanges contribute to the exchange[6]



V. ^{1}H NMR and ^{31}P {H} NMR of dansylated Pd(II) assemblies



18a at T = 323 K

18a at rt.,

18b at T = 323 K

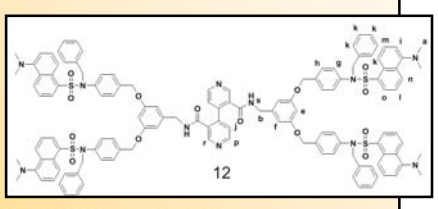
18b at rt.

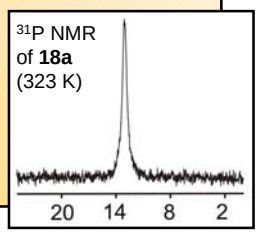
free ligand 12 at rt. in [D_3] acetonitrile

Assemblies with dansyl-functionalized ligands exhibit very similar dynamic properties as observed for the Fréchet-type dendronized squares.

Although the mass spectrometric characterization still needs to be done, we speculate that squares are formed in analogy to these.

Dynamic exchange processes are also indicated by the slightly broadened ^{31}P NMR signal for the assemblies

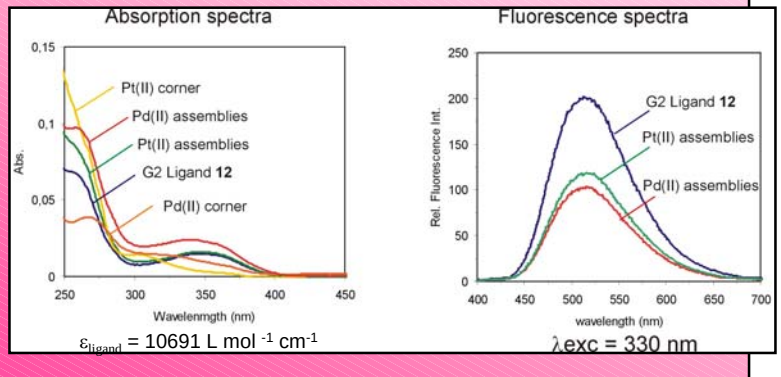




VI. UV-VIS and fluorescence spectra of dansylated Pd(II) and Pt (II) self-assemblies

Absorption spectra represent the superposition of ligand and corner spectra

Quenching is observed either due to the close vicinity of the chromophores incorporated in the self-assembled structures or due to the influence of the heavy transition metal; quenching may involve the ^{3}MLCT [Pt-π*(L)] excited state



ε_{ligand} = 10691 L mol $^{-1}$ cm^{-1}

λexc = 330 nm

VII. Conclusions

- Dendrimers can be self-assembled and form a nanometer cavity as a suitable host for molecules.
- Temperature dependent NMR and extraction experiments reveal eosin-Y to be extracted by dendrimeric metallosupramolecular squares into organic solvents
- At low temperature, the complexity of 1H NMR spectra of assemblies indicates isomer interconversion and the formation of a dynamic library
- Different temperature regimes for Pd(II) and Pt(II) squares indicate ligand exchanges to contribute to the isomer interconversion
- Preliminary spectroscopic results indicate fluorescence emission to be strongly effected by the formation of self-assembled structures

VIII. Literature

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