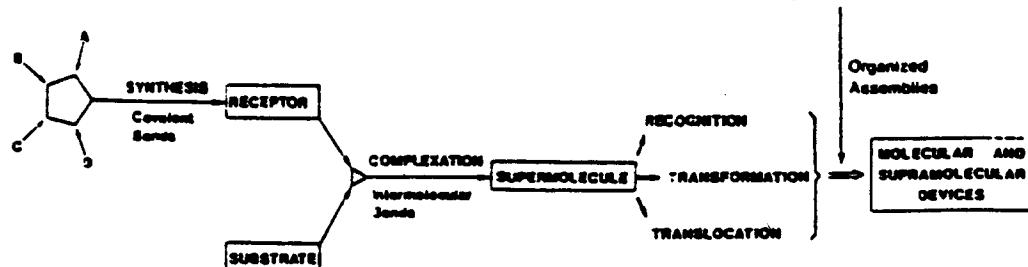


# CHEMISTRY

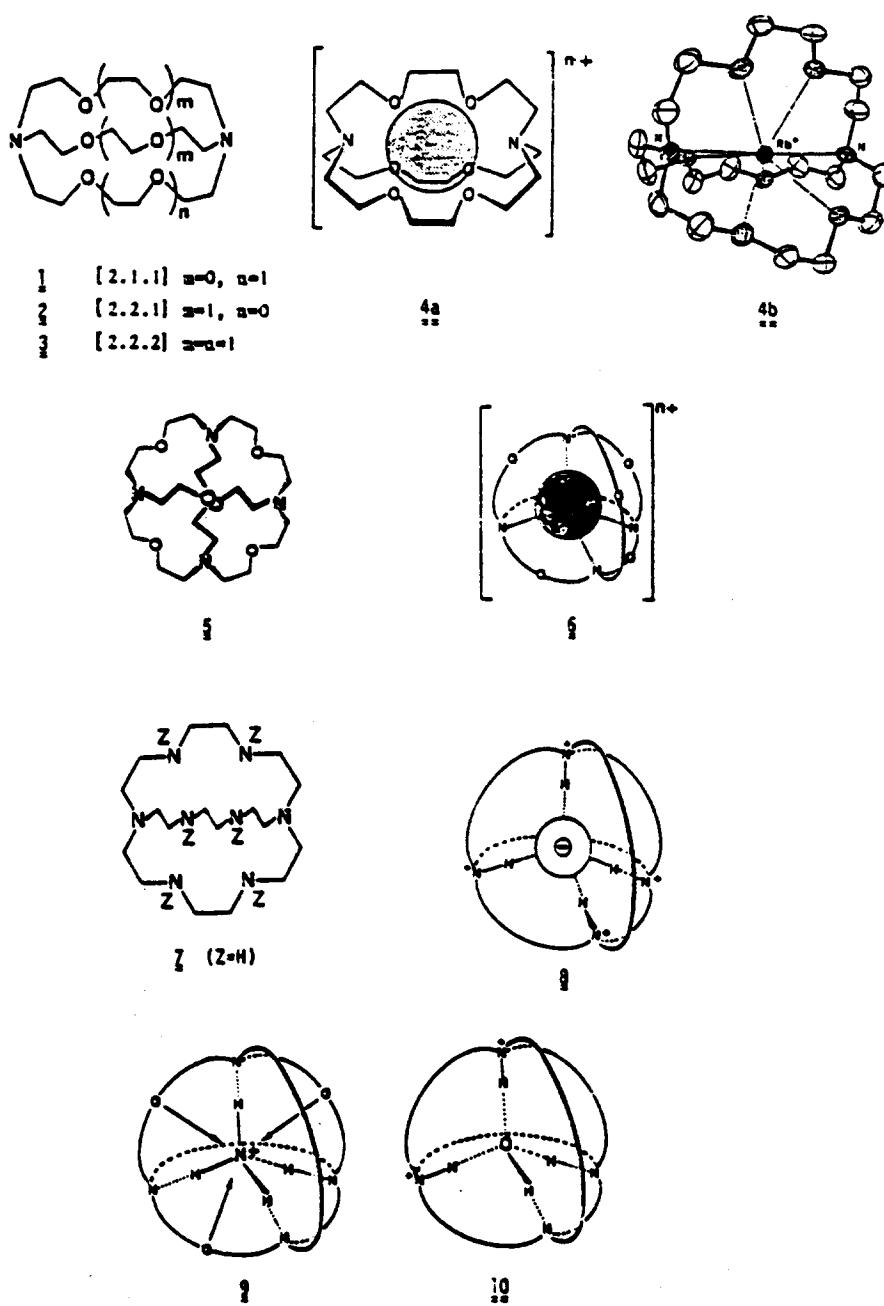
## MOLECULAR

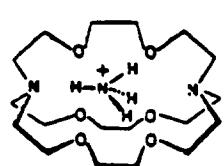
## SUPRAMOLECULAR

## POLYMOLECULAR

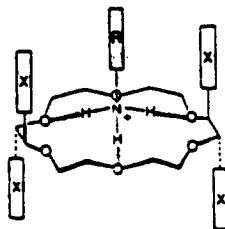


**Scheme 1.** From molecular to supramolecular chemistry; molecules, supermolecules, molecular and supramolecular devices.

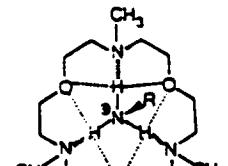




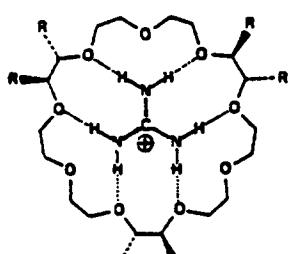
11



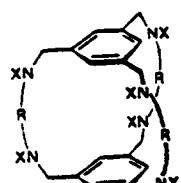
12  
1 X=H  
2 X=CO<sub>3</sub><sup>-</sup>  
3 X=CONYY'



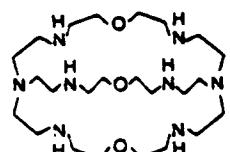
13



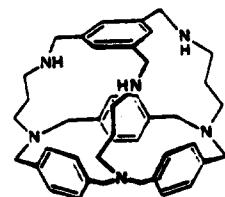
14 (R-CO<sub>3</sub><sup>-</sup>)



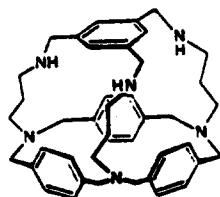
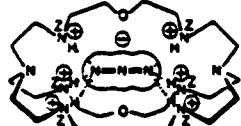
15 (X=N, R=(CH<sub>2</sub>)<sub>3</sub>)



16



17



19

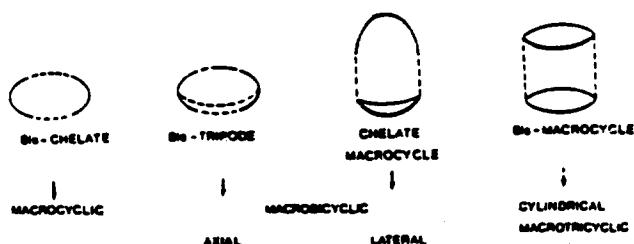
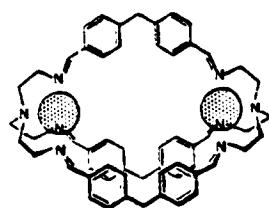
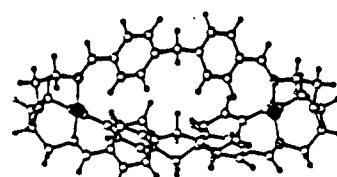


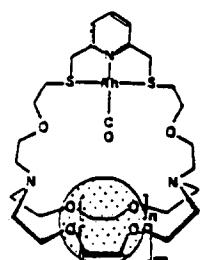
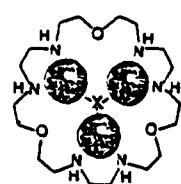
Fig. 2. Combination of chelating, tripodal and cyclic subunits into di-nuclic co-receptors of macrocyclic, axial and lateral macrobicyclic and cylindrical macrotricyclic types (from left to right).



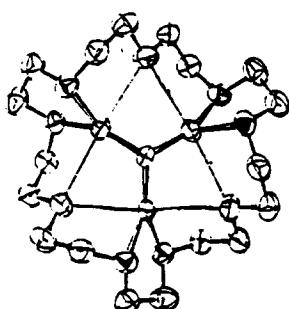
19



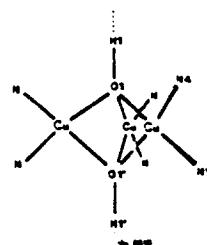
20

21 ( $m, n=0, 1$ )

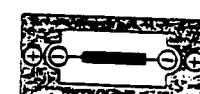
22



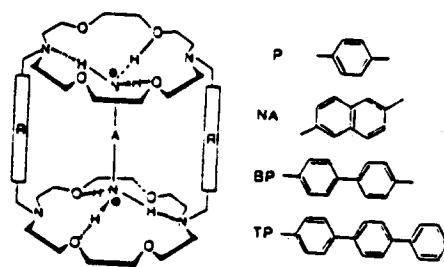
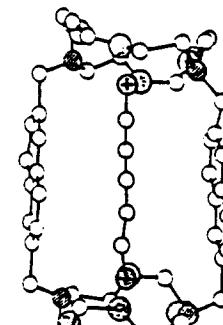
23



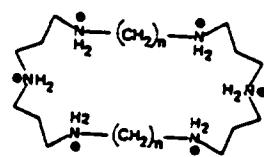
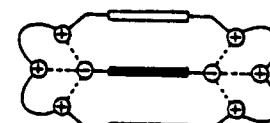
24



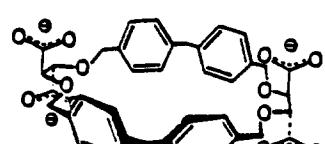
25

26 ( $R=P, NA, BP, TP$ )

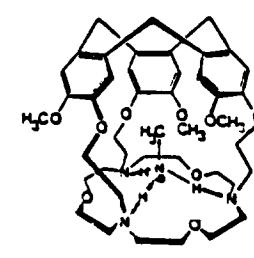
27

28 ( $n=7, 10$ )

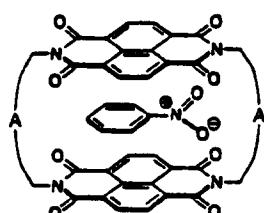
29



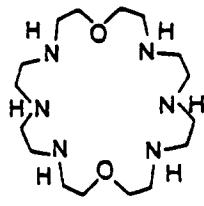
30



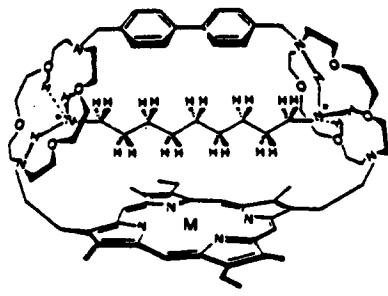
31



32 ( $A=(CH_2)_8$ )



33



34 ( $M=Zn$ )

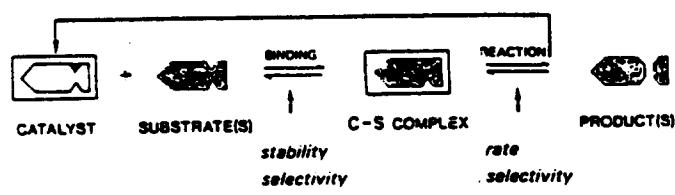
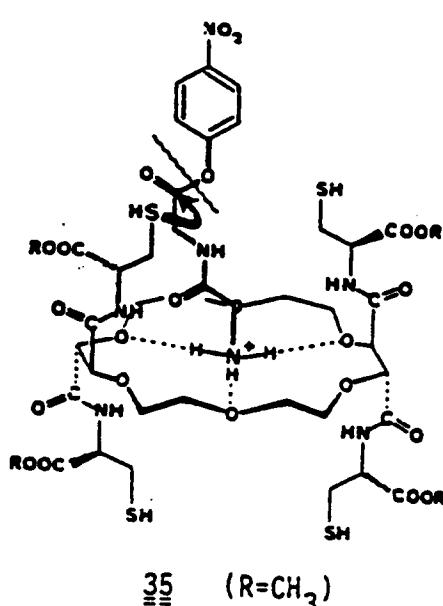
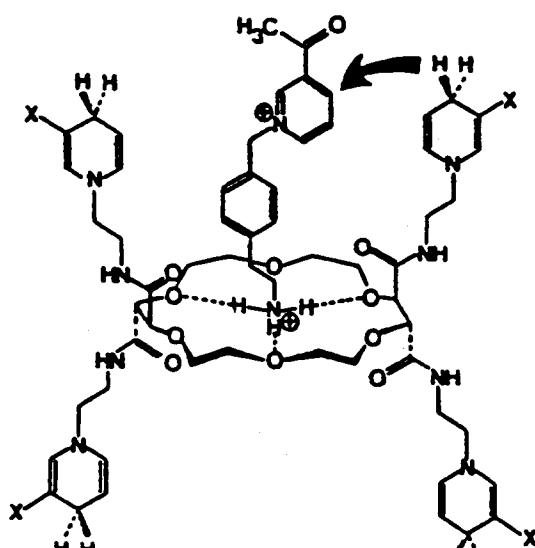


Fig. 3. Schematic representation of the supramolecular catalysis process.



35 ( $R=CH_3$ )



36 ( $X=CONHnBu$ )

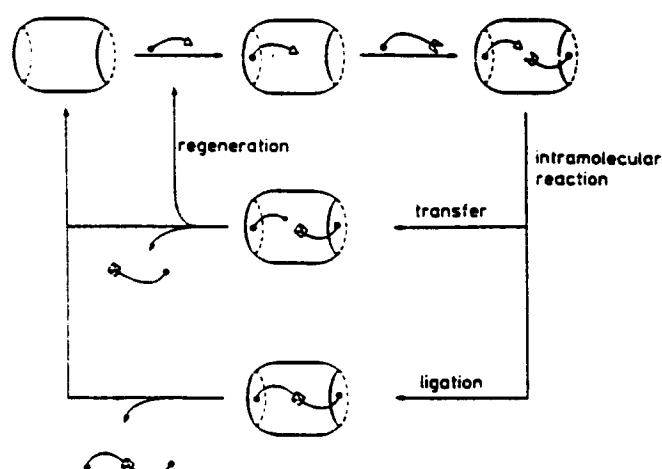


Fig. 4. Schematic illustration of cocatalysis processes: group transfer and ligation reactions occurring within the supramolecular complex formed by the binding of substrates to the two macrocyclic subunits of a macrotricyclic co-receptor molecule.

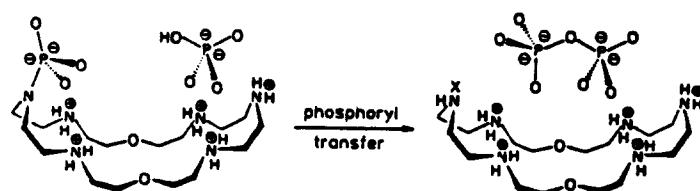


Fig. 5. Cocatalysis: pyrophosphate synthesis by phosphoryl transfer mediated by macrocycle 33 via the phosphorylated intermediate 38.

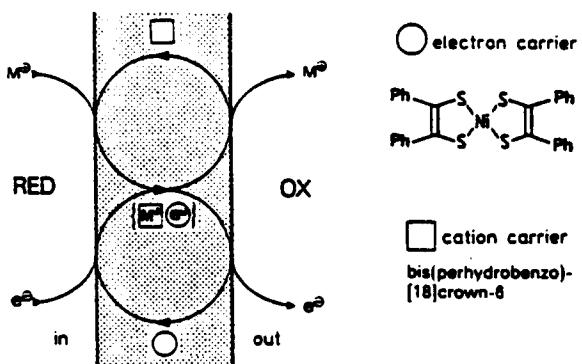


Fig. 7. Electron-cation coupled transport: a redox-driven electron-cation symport consisting of an electron carrier (nickel complex) and a selective cation carrier (macrocyclic polyether). RED, potassium dithionite; OX,  $\text{Na}_2[\text{Fe}(\text{CN})_6]$  [133].

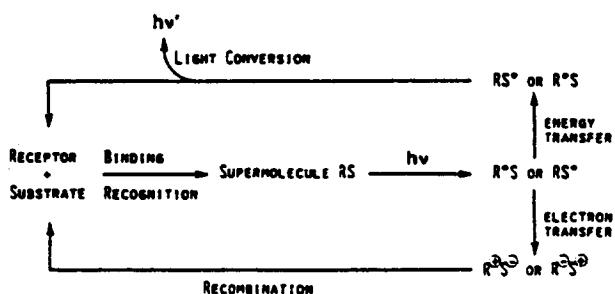
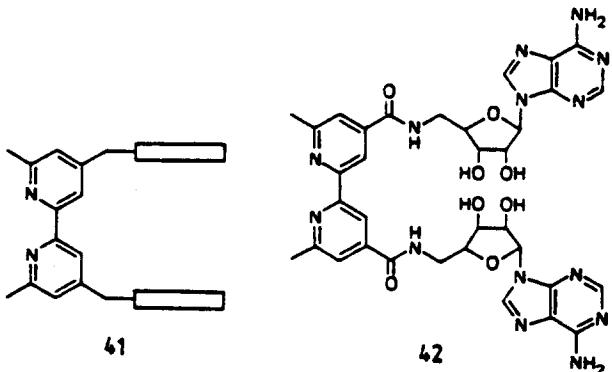
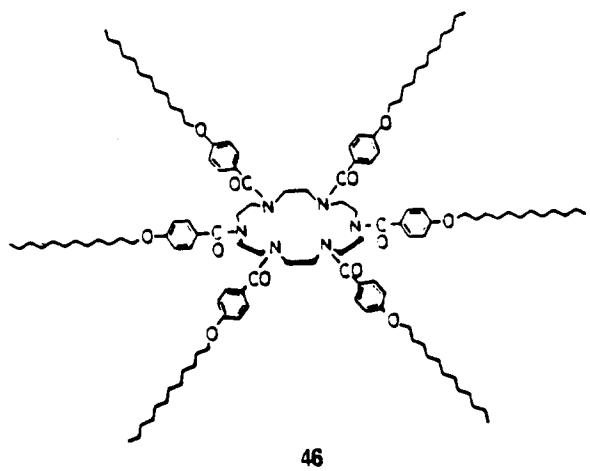
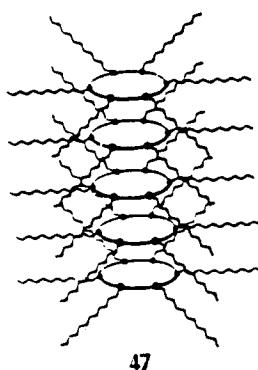


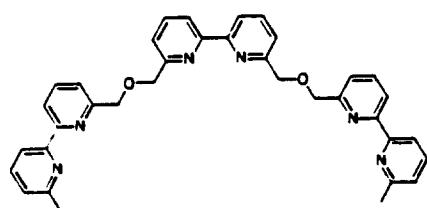
Fig. 10. Representation of the processes involved in supramolecular photochemistry. Generation of  $\text{R}^{\bullet}\text{S}$ ,  $\text{RS}^{\bullet}$ ,  $\text{R}^{\bullet}\text{S}^{\bullet}$ , or  $\text{R}^{\bullet}\text{S}^{\bullet}$  may be followed by a chemical reaction.



46



47



48



49