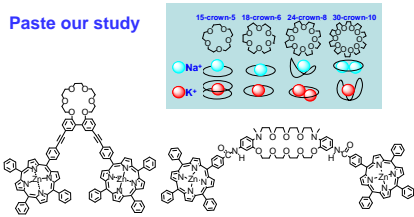


自己組織型キラルプローブを用いた光学活性化合物の絶対配置決定法の開発

久保 由治 (大学院理工学研究科)

Introduction

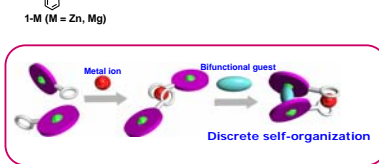
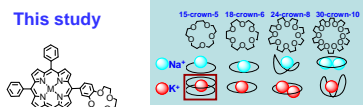
Paste our study



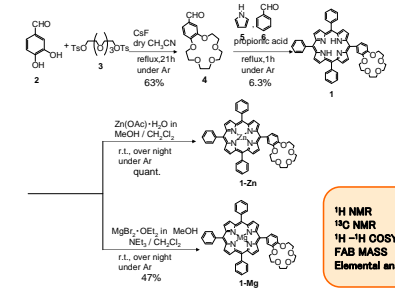
Y. Kubo, et al., *J. Am. Chem. Soc.*, 2001, 123, 12700-12701.

Y. Kubo, et al., *Chem. Commun.*, 2004, 1394-1395; *Org. Biomol. Chem.*, in press.

This study

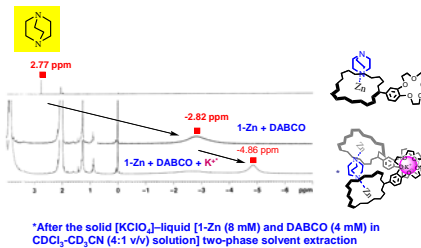
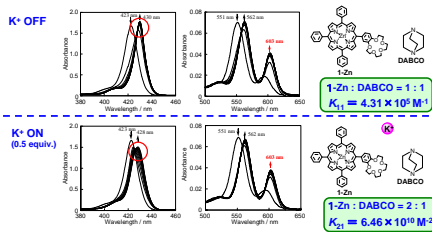


Synthesis of crowned metalloporphyrins

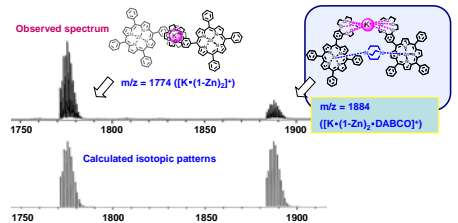


Investigation of self-assembly

UV-vis spectra of 1-Zn upon the addition of incremental amounts of DABCO in CH₂Cl₂-CH₃CN (9:1 v/v) at 25 °C, [1-Zn] = 4 μM

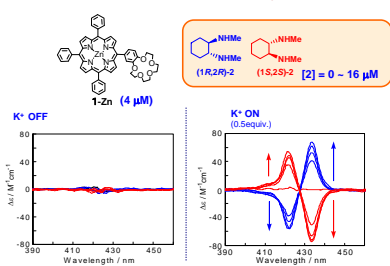


ESI MS study in CH₂Cl₂-CH₃CN (9:1 v/v) at a spray temperature of -30 °C [1-Zn] = 0.4 mM, [DABCO] = 0.2 mM, [KClO₄] = 0.2 mM.

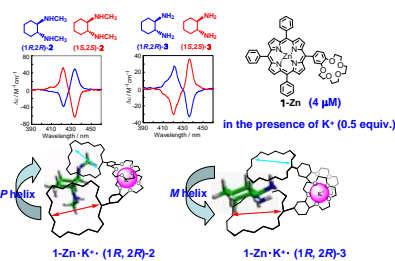


Function as chiral sensor

Cation-driven chirality induction using optically active *N,N'*-dimethylcyclohexane-1,2-diamines in CH₂Cl₂-CH₃CN (9:1 v/v) at 25 °C



Substituent effect on the chirality induction



Chirality induction using several diamines and aminoalcohols

Porphyrin	Guest	CD sign and peak position / nm		Total amplitude / M ⁻¹ cm ⁻¹
		1 st Cotton effect	2 nd Cotton effect	
1-Zn	(1 <i>R</i> ,2 <i>R</i>)-4	+ (433)	- (421)	+24.8
1-Zn	(1 <i>S</i> ,2 <i>S</i>)-4	- (433)	+ (421)	-23.2
1-Zn	(3 <i>R</i>)-5	- (433)	+ (423)	-91.4
1-Zn	(3 <i>S</i>)-5	+ (433)	- (423)	+86.8
1-Zn	(3 <i>R</i>)-6	- (434)	+ (422)	-31.9
1-Zn	(3 <i>S</i>)-6	+ (434)	- (422)	+34.3
1-Mg	(<i>R</i>)-7	+ (429)	- (421)	+43.8
1-Mg	(<i>R</i>)-8	+ (432)	- (420)	+70.7
1-Mg	(<i>S</i>)-8	- (432)	+ (420)	-71.4
1-Mg	(<i>R</i>)-9	+ (432)	- (420)	+68.5
1-Mg	(<i>S</i>)-9	- (432)	+ (420)	-67.6

Conclusion



1) 15-Crown-5-appended metalloporphyrin causes a K⁺-driven self-organization to bind a bifunctional guest ditopically, thereby allowing the circular dichroism (CD) detection of chirality induced in the ensemble when chiral amines are employed as the guest.

2) This insight may provide a new way to design chiral probes that can be produced easily since a versatile organization would be achieved based on various synthetic modifications of the porphyrin unit.

Acknowledgement

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References

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- Y. Ishii, K. Soeda, and Y. Kubo, *Chem. Commun.*, 2007, 2953-2955.