Reversible Interconversion of a Static Metallosupramolecular Cage Assembly into a High-Speed Rotor

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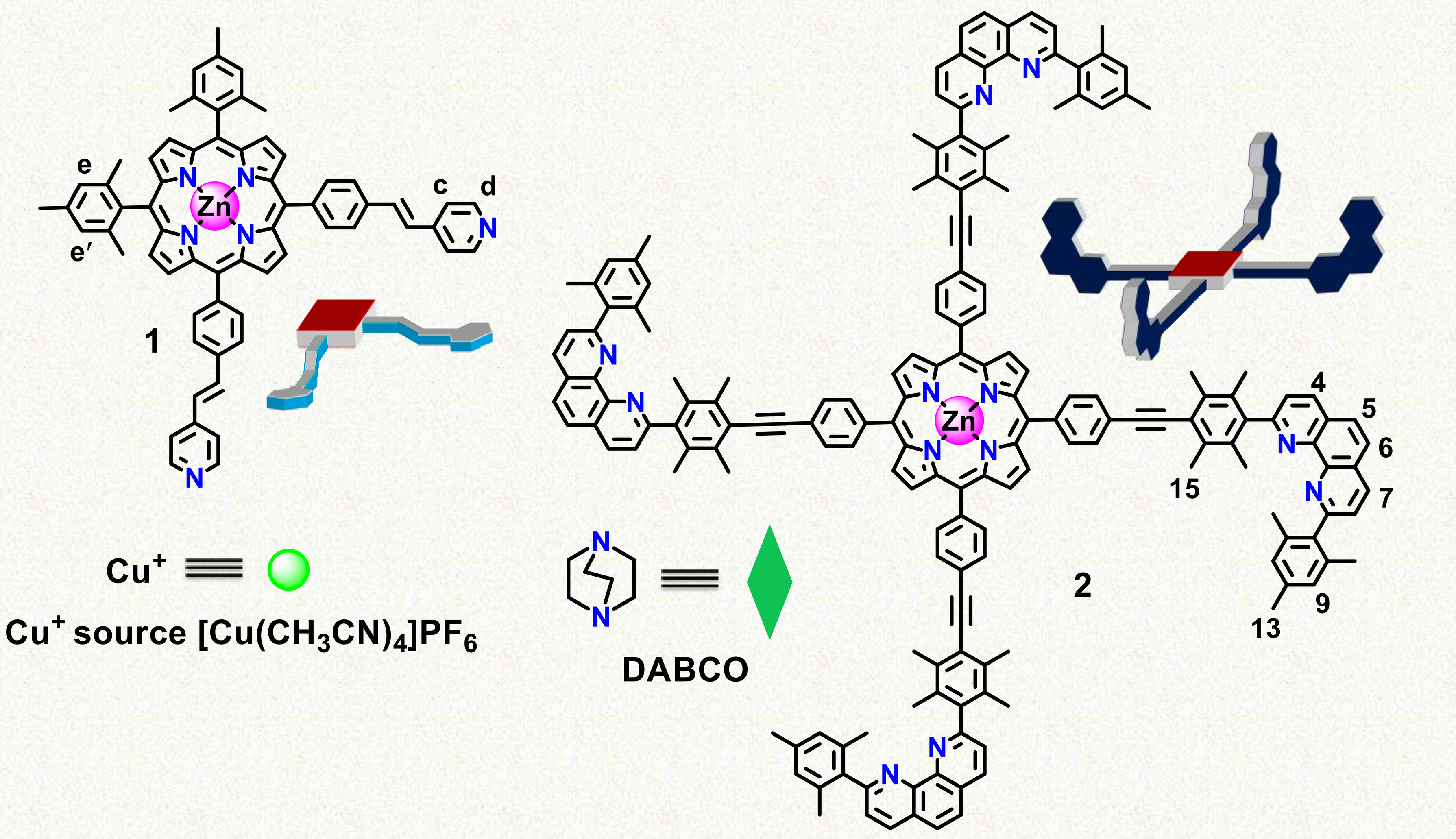
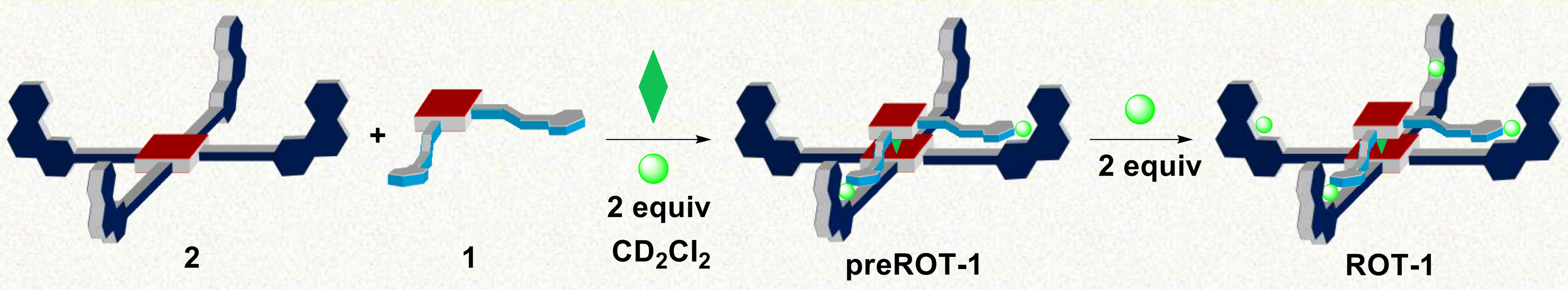
The multicomponent static metallosupramolecular cage **ROT-1** was synthesized in CD_2Cl_2 from: (a) stator **2**, (b) rotator **1**, (c) metal ions (Cu^+) and (d) DABCO as dynamic hinge. **ROT-1** can be reversibly converted to a high-speed rotor just by addition of nucleophiles (CD_3CN or I^-).[1] The fine tuning of the rotational frequency depends on the amount and nature of the added nucleophile. **ROT-1** was converted to the high-speed rotor **ROT-1**$_{16.7}^{CD_3CN}$ (k = 8000 s^{-1}) and **ROT-1**$_8^{I^-}$ (k = 20000 s^{-1}) just by addition of 16.7 (v/v)% of CD_3CN in CD_2Cl_2 and 8.0 equiv of iodide, respectively. The rotor can be converted back to the original cage by removal of CD_3CN or iodide by Ag^+ ion.

Different components of the supramolecular assembly



Synthesis of static cage ROT-1

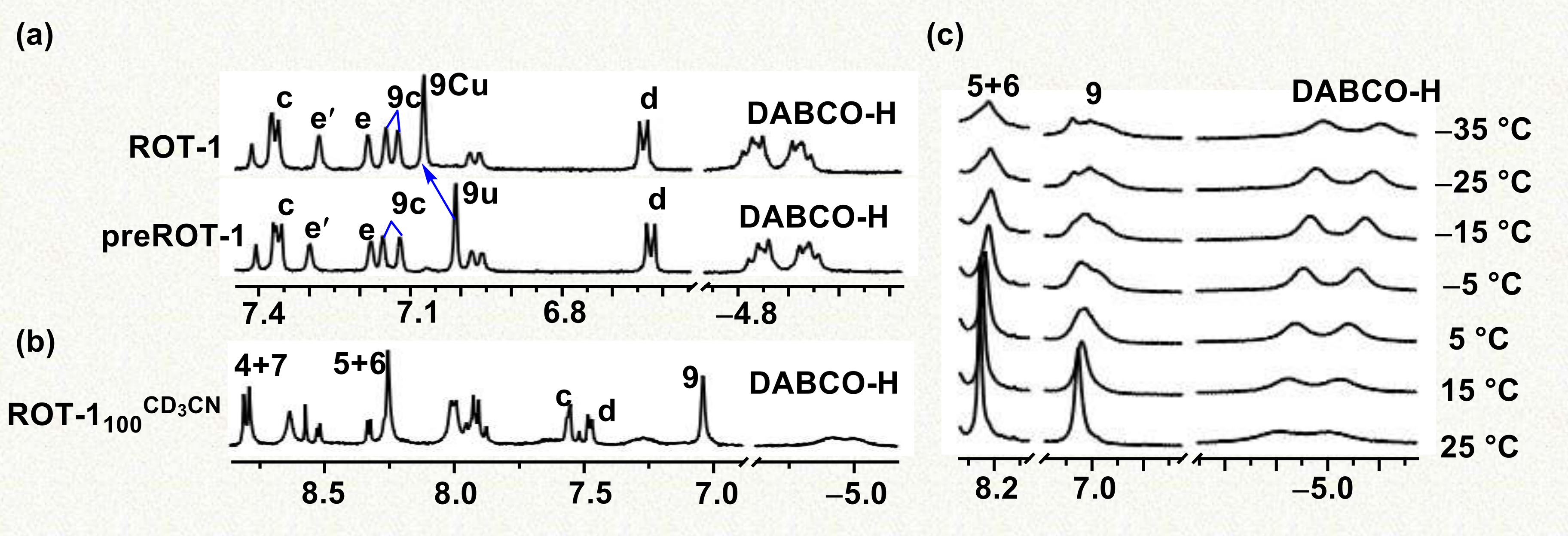


ROT-1 was synthesized quantitatively in CD_2Cl_2 by mixing stator **2**, rotator **1**, DABCO and $[Cu(CH_3CN)_4]PF_6$ in 1:1:1:4 ratio.

^{1}H NMR of PreROT-1, ROT-1 and ROT-1$_{100}^{CD_3CN}$

^{1}H NMR and ^{1}H-^{1}H ROESY of **ROT-1** in CD_2Cl_2 confirm that there is no rotation present in the system.

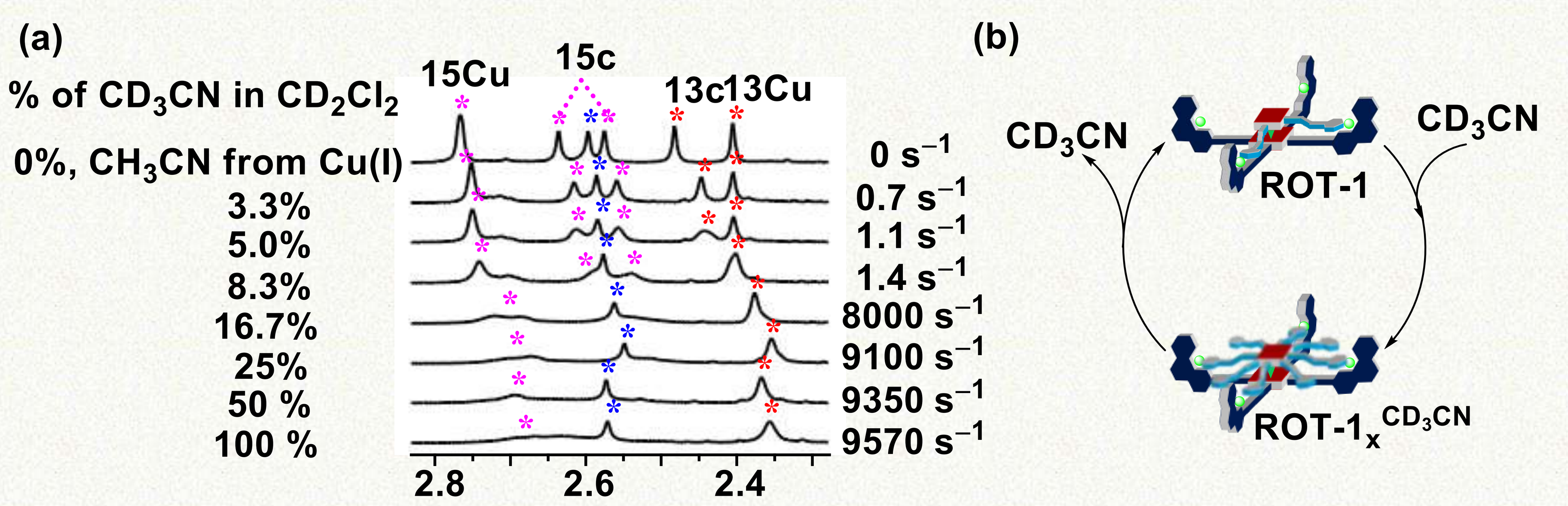
High-speed rotor **ROT-1**$_{100}^{CD_3CN}$ was prepared from **ROT-1** by changing the solvent from CD_2Cl_2 to CD_3CN.



(a) Comparison of partial ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K) of **preROT-1** and **ROT-1**. Mesityl protons 9-H are denoted as 9c-H, 9u-H and 9Cu-H for HETPYP-I complexed,[2] uncomplexed and Cu^+-loaded phenanthroline protons, respectively. (b) Partial ^{1}H NMR (CD_3CN, 400 MHz, 298 K) of **ROT-1**$_{100}^{CD_3CN}$. (c) Partial VT ^{1}H NMR (CD_3CN, 600 MHz) of **ROT-1**$_{100}^{CD_3CN}$ shows the broadening of 9-H.

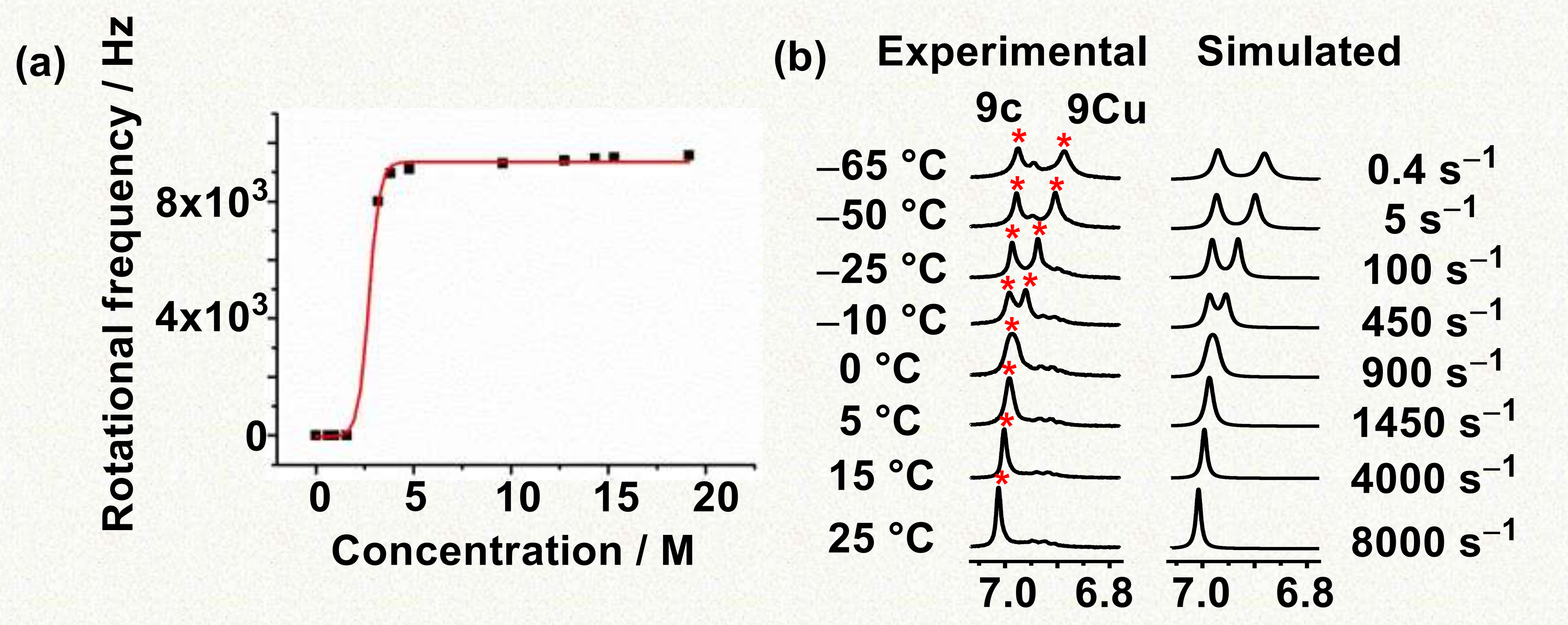
Titration from ROT-1$_{100}^{CD_3CN}$ to ROT-1

A titration of **ROT-1** with CD_3CN shows that the rotational frequency increases with increasing percentage of CD_3CN. The plot of rotational frequency vs concentration of added CD_3CN furnishes a sigmoidal relationship.



(a) Partial ^{1}H NMR (400 MHz, 298 K) of **ROT-1**$_x^{CD_3CN}$ (x is the (v/v)% of CD_3CN present in the solvent mixture of CD_3CN and CD_2Cl_2) at different ratio of CD_3CN and CD_2Cl_2. (b) Cartoon representation for the interconversion of **ROT-1** and **ROT-1**$_x^{CD_3CN}$.

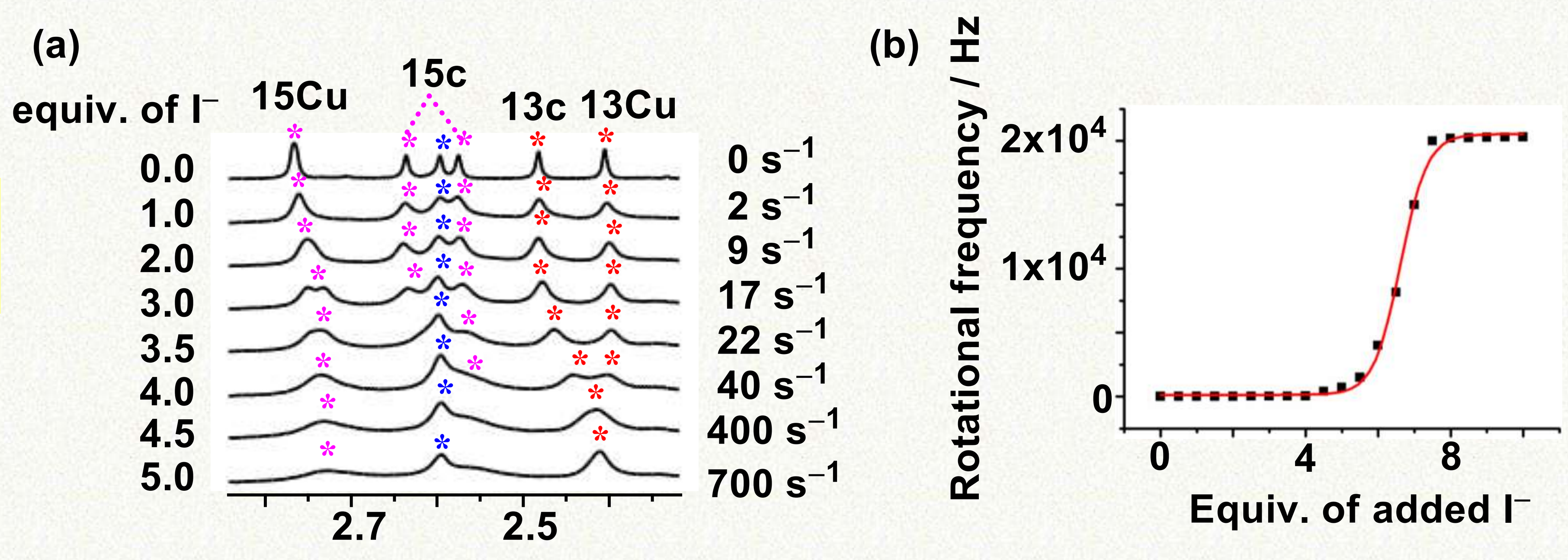
Rotational frequency varies with amount of CD_3CN



(a) Sigmoidal relationship of rotational frequency and concentration of added nucleophile (CD_3CN). (b) Partial VT ^{1}H NMR (600 MHz, CD_2Cl_2:CD_3CN = 5:1) of **ROT-1**$_{16.7}^{CD_3CN}$.

Effect of I^- on rotational frequency

To get further insights on the effect of nucleophiles on the rotational frequency, **ROT-1** was titrated with I^-. The plot of rotational frequency vs equivalence of added I^- furnishes a sigmoidal relationship.



(a) Partial ^{1}H NMR (400 MHz, 298 K) of **ROT-1**$_y^{I^-}$ (y is the equiv of I^- present in the solution). (b) Sigmoidal plot of exchange frequency of rotor (1 mM in CD_2Cl_2) vs equiv of added nucleophile (I^-).

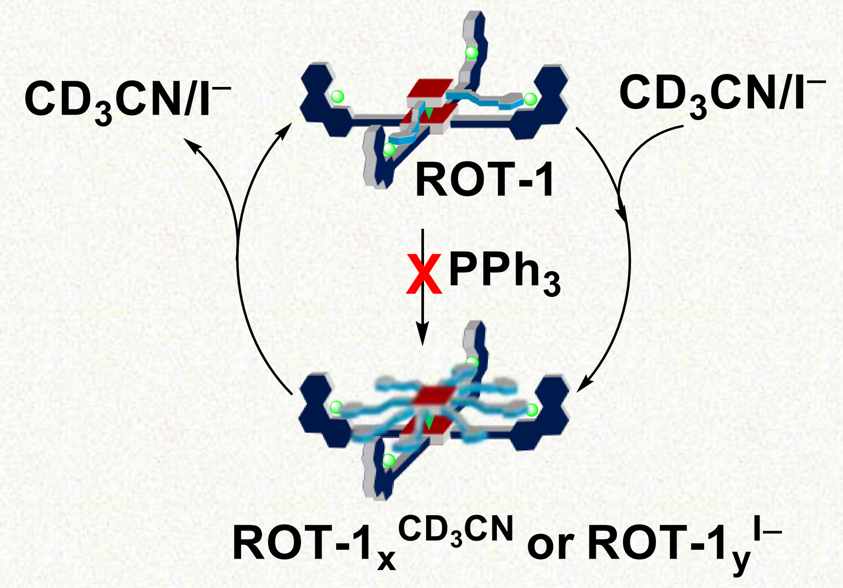
Comparison of CD_3CN and I^- on rotational frequency

The effect of I^- on the kinetics of rotation is much more pronounced compared to that of CD_3CN due to stronger nucleophilicity.

Added equiv of CD_3CN	Rotational rate of **ROT-1**$_x^{CD_3CN}$	$\Delta G^{‡}_{298}$ (kJ mol^{-1})	Added equiv of I^-	Rotational rate of **ROT-1**$_y^{I^-}$	$\Delta G^{‡}_{298}$ (kJ mol^{-1})
16	<0.1	> 79	0	<0.1	> 79
1590	1.4	72.2	2.0	8.5	67.9
3190	8000	50.9	6.5	8150	50.2
15310	ca. 9500		8.0	20200	48.7
19150	ca. 9500		10	20296	48.3

Effect of PPh_3 on rotational frequency

Interestingly, addition of the strong nucleophile PPh_3 to **ROT-1** does not increase the rotational frequency due to too strong binding to the Cu^+ center. As a consequence, rotational acceleration is only effective with ligands that are both good nucleophiles and nucleofuges.



References

[1] Saha, S.; Biswas, P. K.; Schmittel, M. *Inorg. Chem.* **2019**, just accepted.

[2] Schmittel, M.; He, B.; Fan, J.; Bats, J. W.; Engeser, M.; Schlosser, M.; Deiseroth, H.-J. *Inorg. Chem.* **2009**, *48*, 8192–8200.

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