Reversible Reconfiguration of Catalytic Networked Machinery: Resetting Machine Tasks By Dual-Component Exchange

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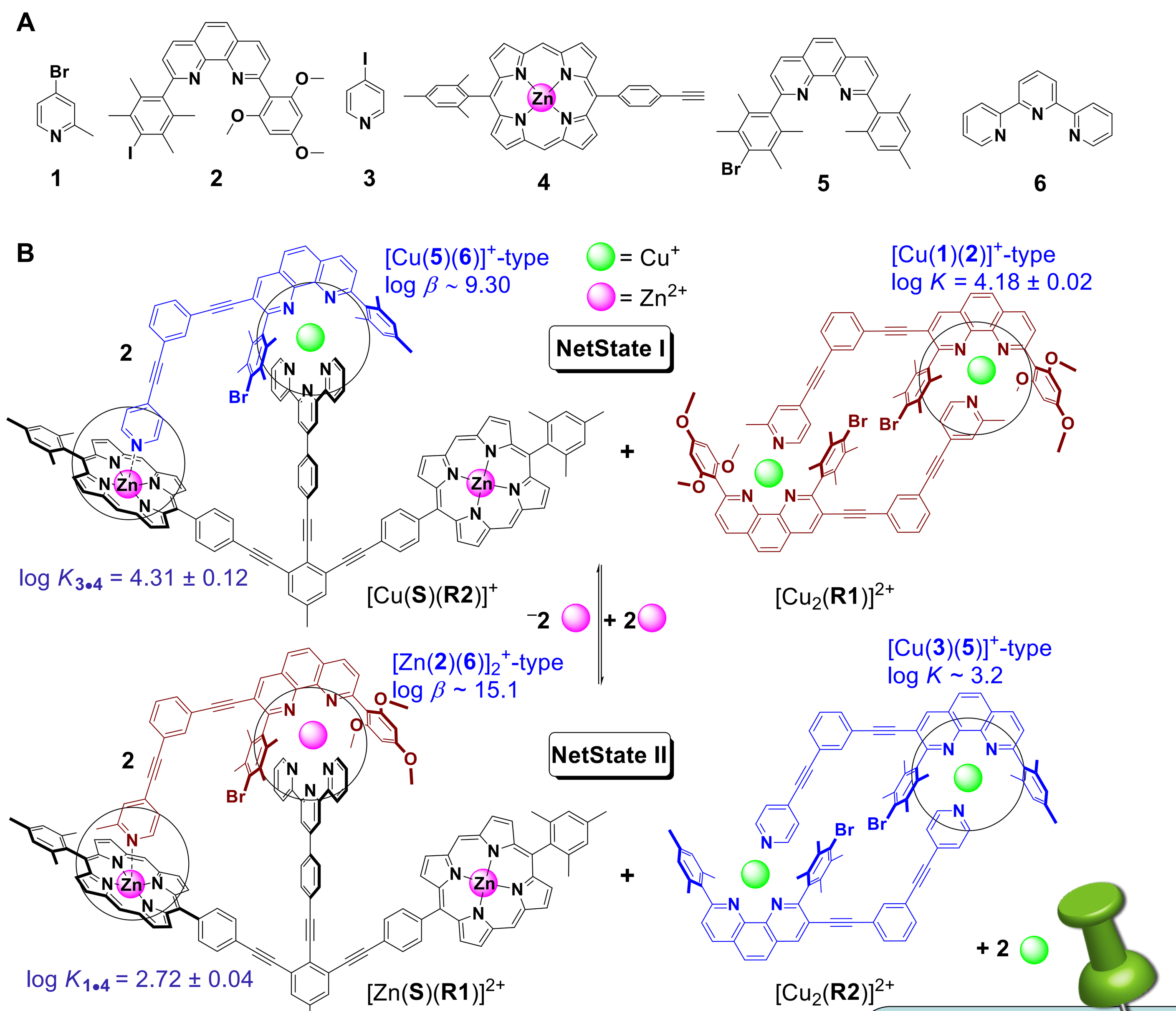
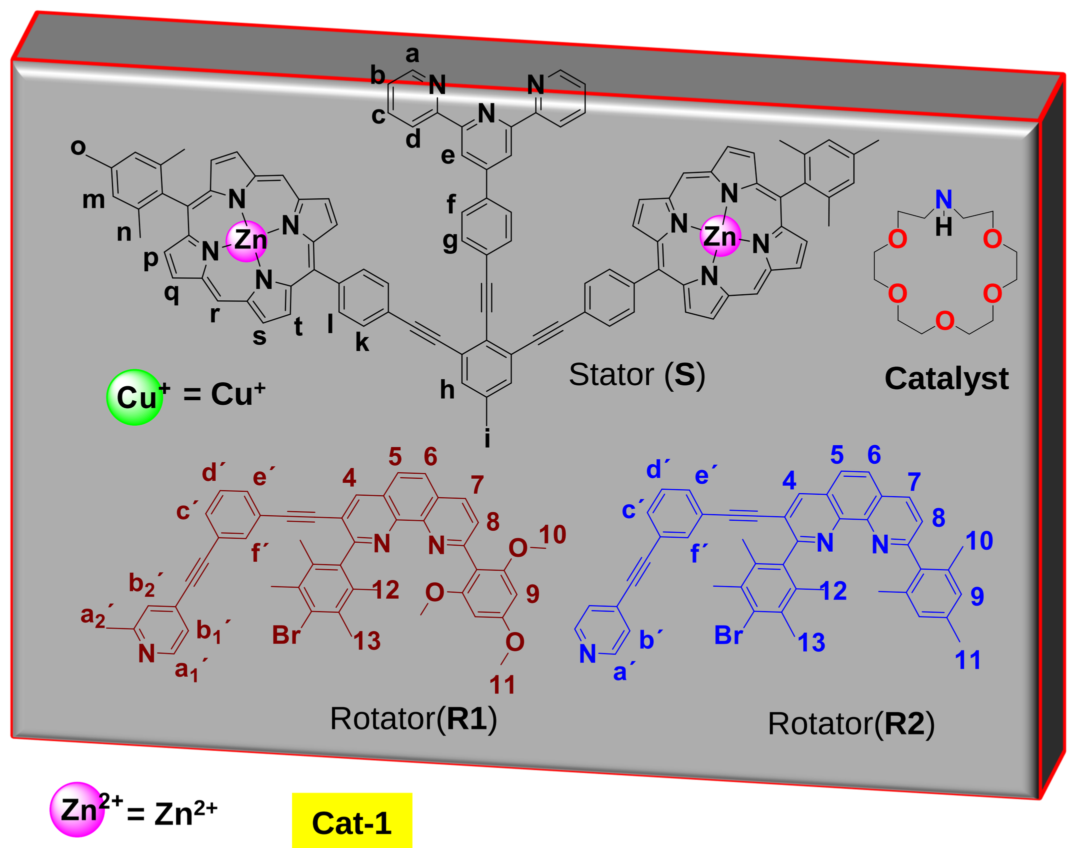
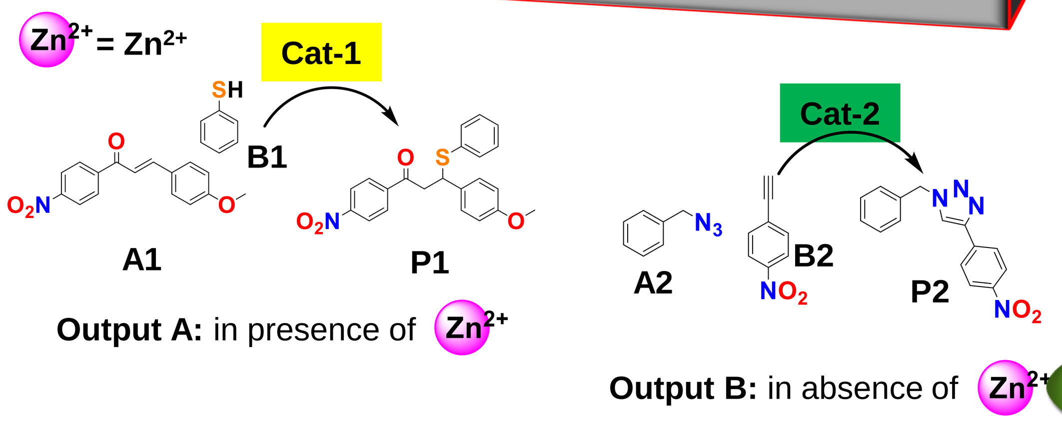
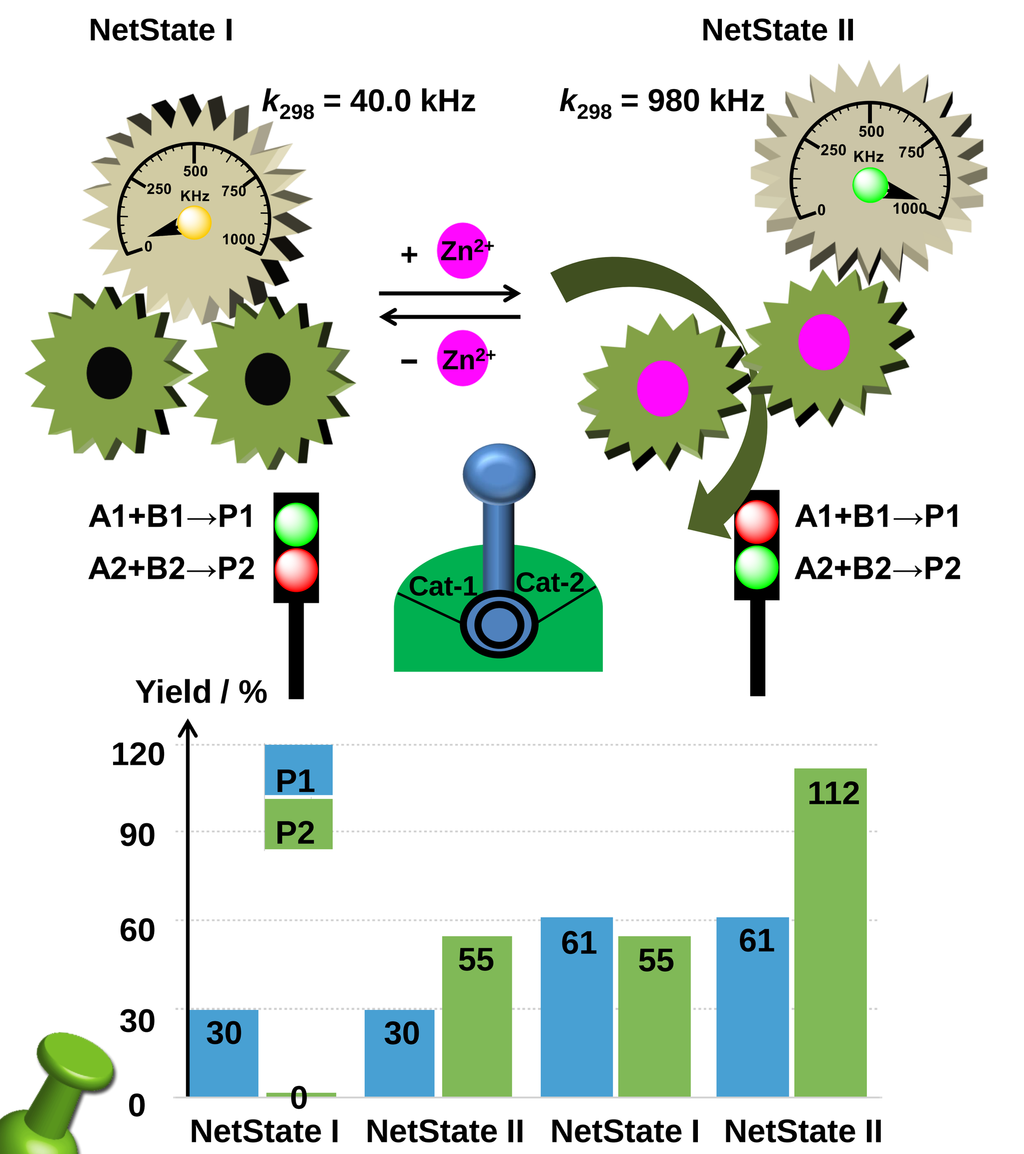
The present work demonstrates how the workflow of two multicomponent rotary catalytic machineries can be interlinked by the simultaneous shuffling of two components (metal and ligand) requiring perfect signaling in a twelve-component networked system. Addition and removal of zinc(II) ions trigger three distinct events in parallel: (i) self-assembly of three-component nanorotors and two-component parallelograms by resorting components, (ii) toggling between different rotational exchange rates in the assembled rotors, and (iii) toggling between two diverse catalytic reactions.







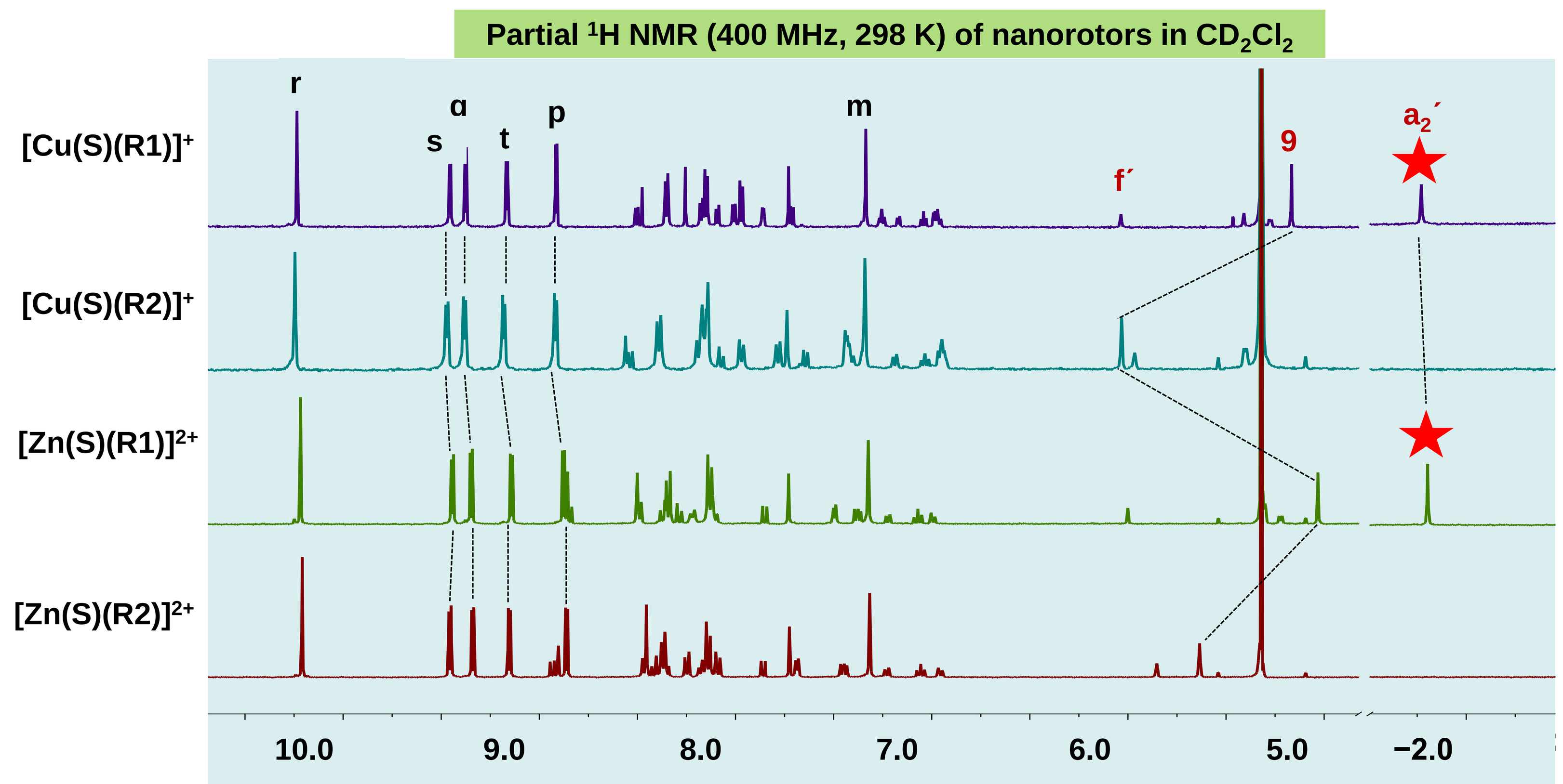


Control over:

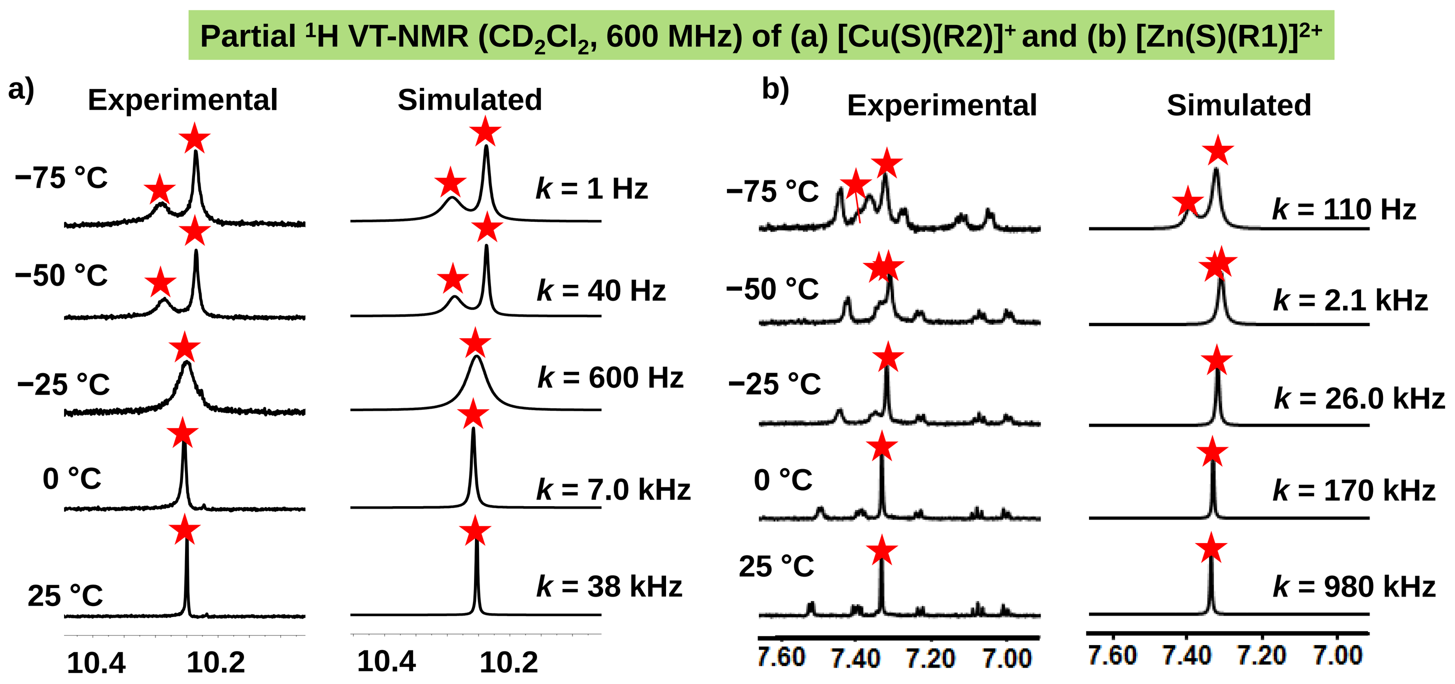
1. Rotational Speed
2. Self-assembly
3. Two alternate Catalysis (ON/OFF)

Characterization and kinetic analysis of nanorotors

Partial ^1H NMR (400 MHz, 298 K) of nanorotors in CD_2Cl_2



Partial ^1H VT-NMR (CD_2Cl_2, 600 MHz) of (a) $[Cu(S)(R2)]^+$ and (b) $[Zn(S)(R1)]^{2+}$

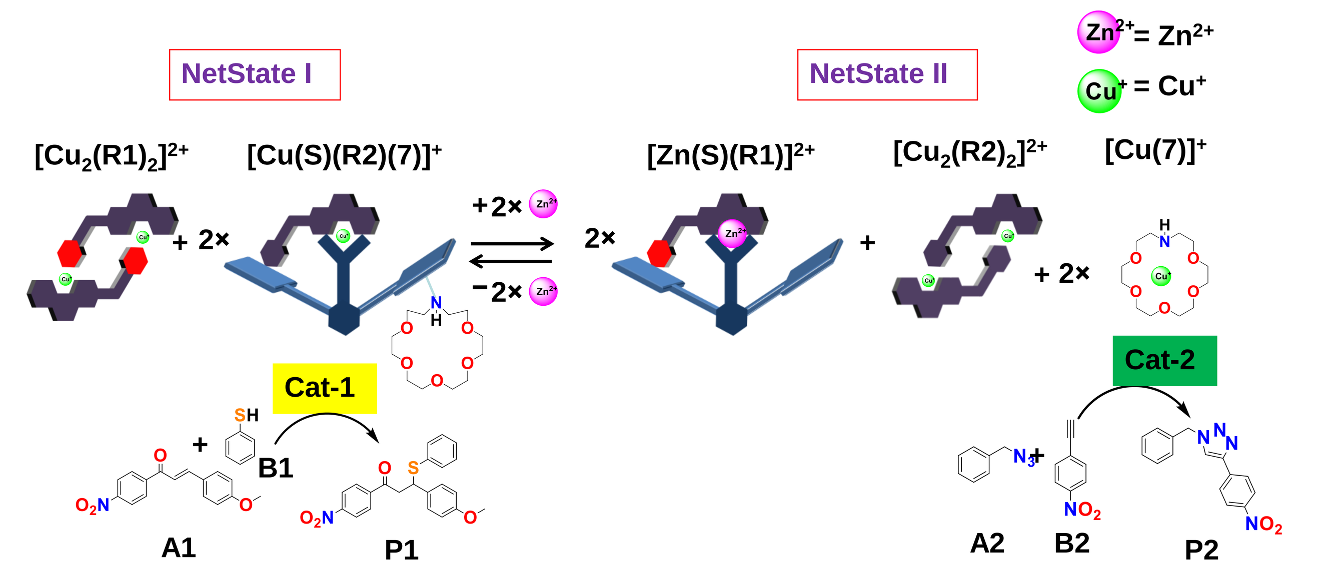


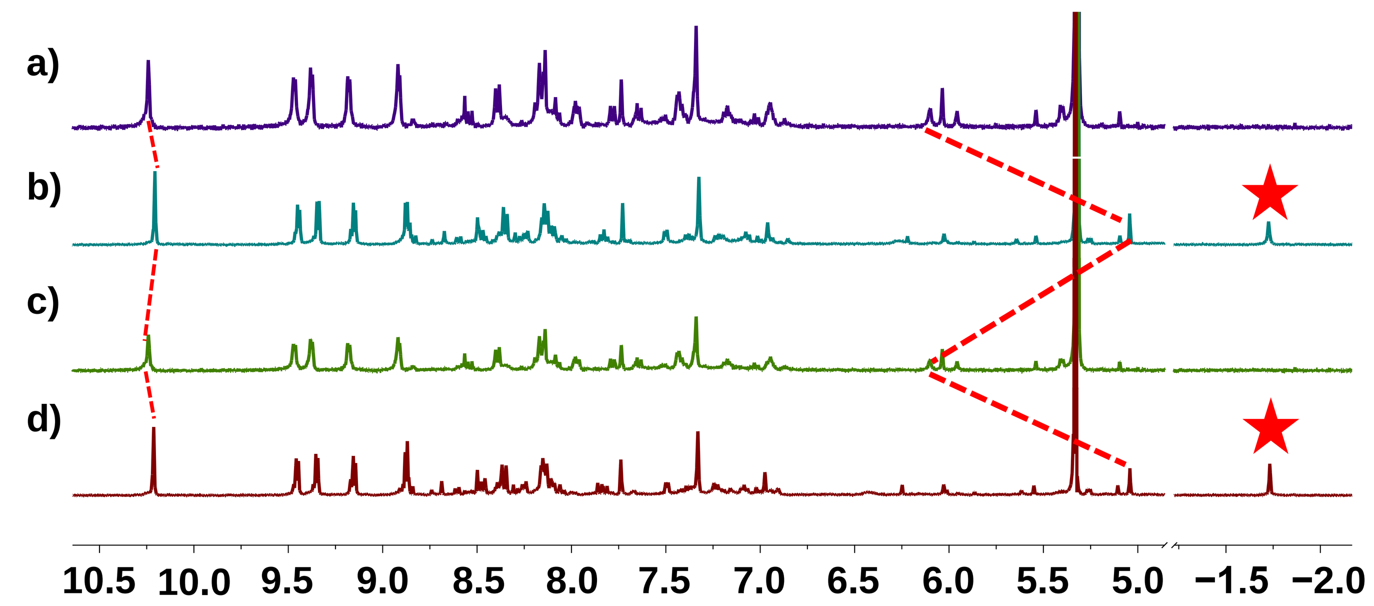
Rotational frequency and activation data of nanorotors

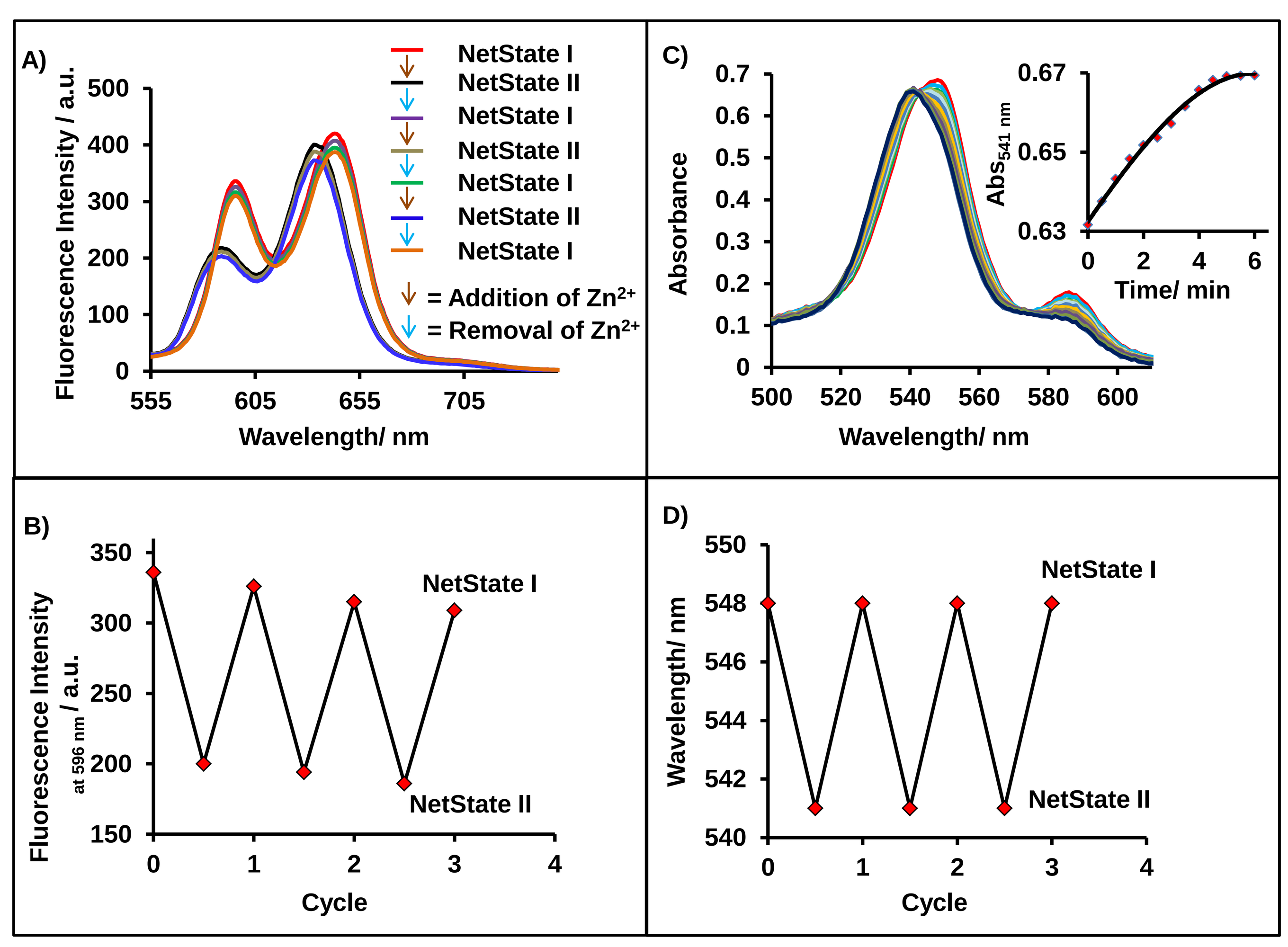
Nanorotor	k_{298} (kHz)	$\Delta G^‡_{298}$ (kJ mol⁻¹)	$\Delta H^‡$ (kJ mol⁻¹)	$\Delta S^‡$ (J mol⁻¹ K⁻¹)
$[Cu(S)(R2)]^+$	38.0 [a]	47.1	50.0 ± 0.4	11.5 ± 0.8
$[Zn(S)(R2)]^{2+}$	62.0 [b]	45.8	48.4 ± 0.6	10.9 ± 2.1
$[Cu(S)(R1)]^+$	620 [a]	40.1	43.4 ± 0.3	11.9 ± 0.7
$[Zn(S)(R1)]^{2+}$	980 [b]	39.0	42.6 ± 0.5	12.4 ± 1.7

[a] In DCM. [b] In DCM/CD_3CN=5:1.

Reversible switching between NetState I and NetState II







➢ In conclusion, we have fabricated a new class of multifunctional network of twelve components that reversibly controls not only the self-assembly of nanorotors or architectures but also two different catalytic reactions in an alternative ON/OFF manner. This is the first example for reversible shuffling of components (metal ions, ligands) within the network that requires a four-bit information transfer on the molecular level. The functions of this system can only be realized in presence of all components used for networking.

Acknowledgements:

We are thankful to the DFG (Deutsche Forschungs-gemeinschaft, Schm 647/20-1), and the University of Siegen for financial support.

References :

(a) A. Goswami, I. Paul and M. Schmittel, *Chem. Commun.*, 2017, **53**, 5186.
(b) A. Goswami, S. Pramanik, M. Schmittel, *Chem. Commun.* 2018, **54**, 3955.