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Magnetic exchange coupling tunable by means of selective cation binding into poly(radical-armed) azacrowns†

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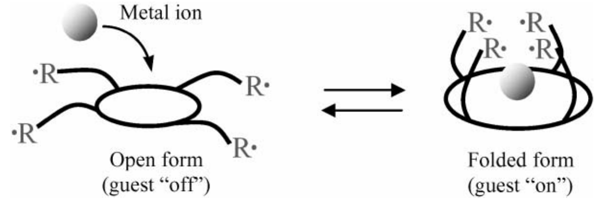
Host–guest complexes of tris(NN–CH_2)-substituted 1,4,7-triazacyclononane and tetrakis(NN–CH_2)-substituted 1,4,7,10-tetraazacyclododecane afforded the folded structures of the hosts where the NN radical oxygen atoms were coordinated to the guest metal ion, leading to enhanced antiferromagnetic couplings in the solid state and an ESR line broadening in the solution phase (NN = 4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide).

Supramolecular techniques such as host–guest complex formation have been applied to tune molecule-based magnetic materials[1–7] toward the development of information storage and molecular computing devices. We have proposed transition-metal-based paramagnetic host compounds possessing a polyether group as a side-arm, and reported that the guest-binding into the polyether cavity affected the magnetic properties of the host.[8] We now designed a straightforward way in which the paramagnetic centers such as nitroxide (>N–O$^\bullet$) directly coordinated to the metal ion (M^{n+}) as a guest, thus affording an O$^\bullet$–M^{n+}–O$^\bullet$ superexchange pathway. The nitronyl nitroxide radical group (abbreviated as NN; 4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide)[9] has been well investigated for metal–radical hybrid solids,[10] and we planned that the NN–CH_2– group could be introduced as an arm into azacrown ethers using a precursory NN–CH_2Cl reagent.[11] As Scheme 1 shows, the magnetic exchange coupling can be changed depending on the "off" and "on" states of the guest ions.

1,4,7-Tris- and 1,4,7,10-tetrakis(NN–CH_2)-substituted 1,4,7-triazacyclononane (tacn) and 1,4,7,10-tetraazacyclododecane (cyclen) are good candidates for this purpose (abbreviated as tacnNN_3 and cyclenNN_4, respectively). They could be prepared according to the method reported by Ulrich,[12] though details or characterization have not reported yet.‡,§ It is well known that the host–guest complex formation using (aza)crown ethers and metal ions is dominantly controlled by size-matching.[13,14] We prepared host–guest complexes of [Li^+·tacnNN_3] and [K^+·cyclenNN_4] simply by crystallization from ethanol or methanol solutions with appropriate salts.



Scheme 1 Open and folded forms of poly(radical-armed) azacrowns.

As Fig. 1 shows, the folded structures of tacnNN_3 and cyclenNN_4 are unequivocally characterized by means of crystallographic analysis for [Li^+·tacnNN_3]ClO_4^- (**1**) and [K^+·cyclenNN_4]SCN^-·3EtOH (**2a**).§ The Li ion in **1** has an octahedral structure coordinated by three tacn nitrogen atoms with the bond lengths of 2.179(7)–2.212(6) Å and by three NN oxygen atoms with those of 2.011(7)–2.119(6) Å. Interatomic O$^\bullet$···O$^\bullet$ distances (2.904(3)–3.043(3) Å) are very close to, or shorter than, the sum of the van der Waals radii (3.04 Å).[15]

Similarly, the K^+ ion in **2a** is octa-coordinated by four cyclen nitrogen atoms with the bond lengths of 2.943(2)–3.031(2) Å and by four NN oxygen atoms with those of 2.715(2)–2.803(2) Å. The coordination structure is a square antiprism. Interatomic O···O

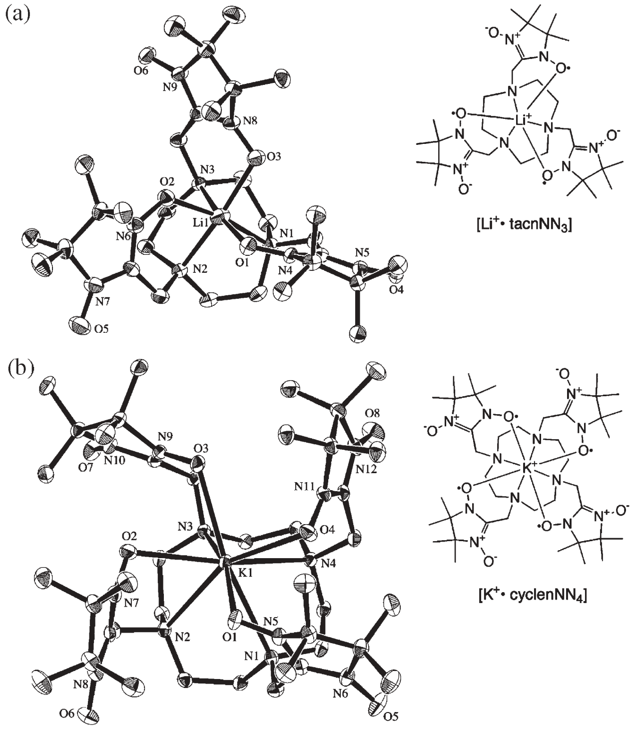


Fig. 1 (a) ORTEP drawings of [Li^+·tacnNN_3] in **1** and [K^+·cyclenNN_4] in **2a** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

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distances are 3.139(2)–3.739(2) Å, which are longer than those of **1** because of the larger ion radius of K^+. The crystal packing including the solvent molecules brings about a lower symmetry. Preliminary crystallographic analysis on a non-solvated form showed an exact square array of the radicals due to a genuine four-fold axis in a tetragonal *P*4/*ncc* space group. Fig. 1(b) shows the crystal structure of **2a** instead of the non-solvated form because of the better refinement in the crystallographic analysis. The molecules of **1** and **2a** have an approximate helical symmetry, but the whole crystals consisted of racemates owing to the crystallographic inversion symmetry.

Tsukube and co-workers reported that the remarkably stable encapsulation of Na^+ in various armed tacn derivatives, such as 1,4,7,10-tetrakis(alkoxycarbonylmethyl)tacn.[16,17] In the present study, however, we could not observe stable complexation between Na^+ and cyclenNN$_4$, because of the different size of a side-arm chelate; the O–N chelate has a five-membered ring in that case, while a six-membered ring in our case.

We measured magnetic properties of the solids of various complexes [M^{n+}·tacnNN$_3$] and [M^{n+}·cyclenNN$_4$] typically prepared using metal perchlorate salts. The magnetic susceptibility data of tacnNN$_3$ and cyclenNN$_4$ showed weak antiferromagnetic interaction (Fig. 2). As for tacnNN$_3$, remarkably enhanced antiferromagnetic interaction was observed after the host–guest complexation (**1**); the decrease of the $\chi_{\mathrm{mol}}T$ value and a plateau at *ca.* 0.38 cm^3 K mol^{-1} on cooling (Fig. 2(a)) indicate the ground doublet state of **1**. A triangular spin–spin exchange interaction can be expected around the Li ion. In addition to the through-space interaction across the relatively short $O^{\bullet}\cdots O^{\bullet}$ distances, the through-bond superexchange mechanism along the $O^{\bullet}$–Li^+–$O^{\bullet}$ bonds also seems possible. Theoretical fit to the van Vleck equation derived from the spin–spin Hamiltonian $H = -2J(S_1{\cdot}S_2 + S_2{\cdot}S_3 + S_3{\cdot}S_1)$ gave the following optimized parameters: $J/k_B = -24.5(8)$ K and $g = 2.02(1)$. The calculated curve satisfactorily reproduced the experimental data. The final drop of the $\chi_{\mathrm{mol}}T$ value is attributed to intermolecular antiferromagnetic coupling among the residual $S = 1/2$ species. No meaningful solids were prepared using Na^+ or K^+ perchlorates.

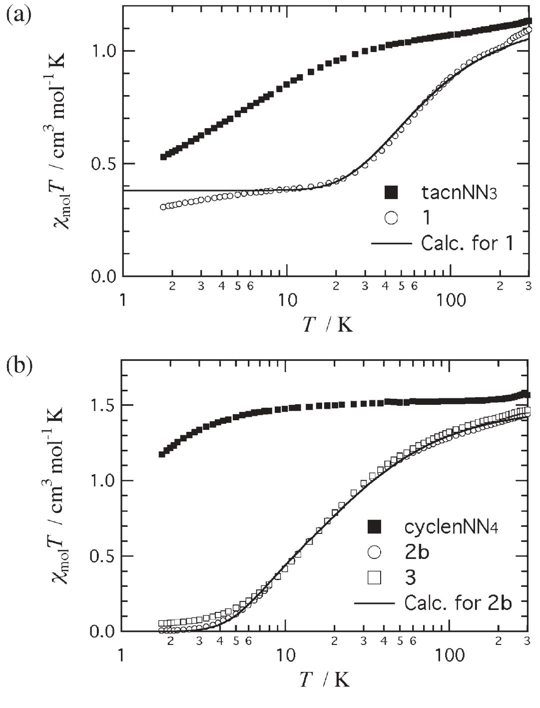

Fig. 2 Temperature dependence of $\chi_{\mathrm{mol}}T$ for (a) tacnNN$_3$ and [Li^+·tacnNN$_3$]ClO_4^- (**1**) and (b) cyclenNN$_4$, [K^+·cyclenNN$_4$]ClO_4^-·2CH$_3$OH (**2b**) and [Ca^{2+}·cyclenNN$_4$]$(ClO_4^-)_2$ (**3**) with an applied field of 5000 Oe. The solid lines are drawn from the theoretical fit for **1** (a) and **2b** (b). See the text for the models and parameters.

Similarly, considerably large antiferromagnetic interactions were observed after the host–guest complexation using cyclenNN$_4$ with K^+ and Ca^{2+} ions (**2b** and **3** in Fig. 2(b)). Based on the crystal structure of **2a**, we applied the spin–spin Hamiltonian $H = -2J(S_1{\cdot}S_2 + S_1{\cdot}S_3 + S_1{\cdot}S_4 + S_2{\cdot}S_3 + S_2{\cdot}S_4 + S_3{\cdot}S_4)$ for **2b**, assuming that superexchange couplings through $O^{\bullet}$–K^+–$O^{\bullet}$ are dominant. The best fit calculated curve well reproduced the experimental one with $J/k_B = -9.05(6)$ K and $g = 1.99(1)$.[18] Though the structure of **3** could not be solved, a similar treatment on **3** gave $J/k_B = -8.5(2)$ K and $g = 1.99(1)$, indicating the Ca^{2+} encapsulation.

The solids from cyclenNN$_4$ with Li^+ and Na^+ ions have a 1 : 1 M^{n+} : cyclenNN$_4$ molar ratio as clarified from elemental analysis. The molecular structures are speculated in which some radical arms are coordinated to the metal center while the other arms are not, owing to the size-mismatching.[14] Such compounds showed moderately weak antiferromagnetic coupling as the $\chi_{\mathrm{mol}}T$ data fell between those of cyclenNN$_4$ and **2** (and **3**). For example, the $\chi_{\mathrm{mol}}T$ *vs.* T plot of [Na^+·cyclenNN$_4$]ClO_4^- showed a shoulder at *ca.* 0.75 cm^3 K mol^{-1} around 10 K, suggesting two NN groups out of four would be antiferromagnetically correlated as partially folded conformation of cyclenNN$_4$.

Solution ESR spectra give an information of the population of open and folded conformation structures. We measured X-band (9.4 GHz) ESR of tacnNN$_3$ in methanol. The spectra of tacnNN$_3$ (4.0×10^{-4} mol L^{-1}) in the absence and presence of 2.0×10^{-2} mol L^{-1} of LiClO$_4$ are shown in Fig. 3(a) and (b),

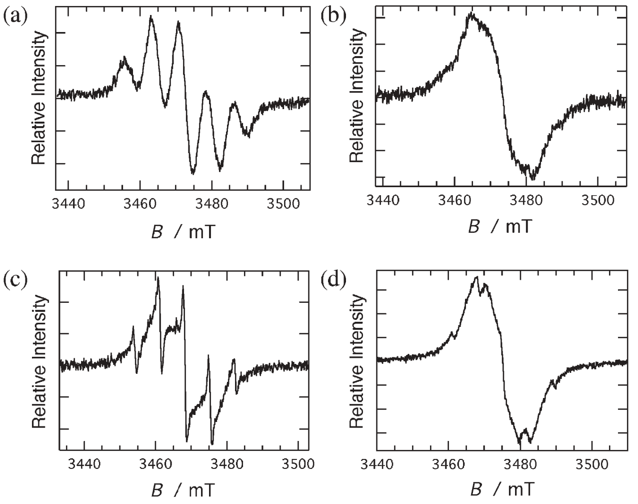

Fig. 3 X-Band ESR spectra of (a) tacnNN$_3$ (4.0×10^{-4} mol L^{-1}) in methanol, (b) tacnNN$_3$ (4.0×10^{-4} mol L^{-1}) and LiClO$_4$ (2.0×10^{-2} mol L^{-1}) in methanol, (c) cyclenNN$_4$ (4.0×10^{-4} mol L^{-1}) in 1 : 1 dichloromethane–toluene and (d) cyclenNN$_4$ (4.0×10^{-4} mol L^{-1}) and KClO$_4$ (4.0×10^{-4} mol L^{-1}) in 1 : 1 dichloromethane–toluene. The spectra were recorded at room temperature.

respectively. Fig. 3(a) shows five lines with a relative intensity of 1 : 2 : 3 : 2 : 1 due to two nitrogen atoms (a_N = 7.37 G; g = 2.0064), indicating that the intramolecular exchange interactions are negligible compared to the hyperfine (a_N) interaction. On the other hand, Fig. 3(b) shows only one broad signal owing to dipolar coupling and/or relatively strong intramolecular exchange interaction, suggesting that most of tacnNN$_3$ have a folded conformation even in a polar methanol solution. This change could not be observed in the presence of Na$^+$, K$^+$, or other ions. Thus, tacnNN$_3$ might be utilized as a specific ESR sensing reagent for Li$^+$.

The ESR spectrum of cyclenNN$_4$ (4.0×10^{-4} mol L^{-1}) in a 1 : 1 mixed solvent of dichloromethane and toluene (Fig. 3(c)) is interpreted as the superposition of open and folded conformers which are related to five lines (a_N = 7.21 G; g = 2.0067) and a broad single signal, respectively. In the presence of equimolar amount of KClO$_4$, the lines turned to a practically single one (Fig. 3(d)), suggesting the dominant population of the folded conformer in the solution. We attempted a similar experiment in methanol, but the resolved five lines were relatively ambiguous even without guest ions. This finding implies the presence of equilibrium between the open and folded forms which depends on the solvent used.

The ESR study of a biradical derived from the 18-N$_2$O$_4$ "kryptofix" in the presence of alkali metal ions has been reported.[12] That work demonstrated less drastic change of the line shapes after the alkali-metal ion binding (furthermore, negative results on tacnNN$_3$ and cyclenNN$_4$ were commented). We clarified the advantage of *polyradicals* such as tacnNN$_3$ and cyclenNN$_4$; *i.e.*, line-broadening due to dipolar and/or exchange effects is more remarkable because of increasing pathways of the radical–radical contact. The present work is regarded as practically the first example of radical-armed azacrowns showing drastic magnetic changes on guest-inclusion.

In conclusion, we have demonstrated that the significant enhance of magnetic coupling of tacnNN$_3$ and cyclenNN$_4$ using diamagnetic alkali metal ions. In addition to the technique of supramolecular magnetic control of organic magnetic materials, tacnNN$_3$ and cyclenNN$_4$ may provide sensing agents for Li$^+$ and K$^+$(and Ca^{2+}), respectively, in both solid and solution phases, which can be detected on highly sensitive magnetic apparatuses such as SQUID and ESR.

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Notes and references

‡ tacnNN$_3$: Mp 108–110 °C (from diethyl ether–hexane). IR (KBr disc): 540, 1140, 1371, 1411, 1452, 2929, 2987 cm^{-1}. MS (ESI): *m/z* 637.4 (100%, M + H$^+$) (calc. 637.4 for C$_{30}$H$_{54}$N$_9$O$_6$ + H), 659.4 (46%, M + Na$^+$) (calc. 659.4 for C$_{30}$H$_{54}$N$_9$O$_6$ + Na). UV/Vis (methanol): λ_{max} 319, 534 nm. Anal. Found: C, 56.12; H, 8.40; N, 19.24. Calc. for C$_{30}$H$_{54}$N$_9$O$_6$: C, 56.58; H, 8.55; N, 19.80%. cyclenNN$_4$: A solvated form cyclenNN$_4$·2CH$_3$CN was determined by means of elemental analysis and crystallographic analysis (Fig. S1, ESI†). Mp 135–138 °C (from acetonitrile). IR (KBr disc): 542, 1140, 1373, 1417, 1452, 2937, 2991 cm^{-1}. MS (ESI): *m/z* 871.6 (100%, M + Na$^+$) (calc. 871.5 for C$_{40}$H$_{72}$N$_{12}$O$_8$ + Na). UV/Vis (methanol): λ_{max} 310, 321, 531 nm. Anal. Found: C, 56.84; H, 8.58; N, 21.18. Calc. for C$_{44}$H$_{78}$N$_{14}$O$_8$: C, 56.75; H, 8.44; N, 21.06%.

§ Diffraction data of single crystals of cyclenNN$_4$·2CH$_3$CN, **1**, and **2a** were collected on a Rigaku R-axis RAPID diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Selected data for cyclenNN$_4$·2CH$_3$CN: C$_{44}$H$_{78}$N$_{14}$O$_8$, triclinic, space group $P\bar{1}$, a = 10.395(4), b = 10.988(4), c = 11.511(5) Å, α = 73.43(3), β = 78.50(3), γ = 82.51(3)°, V = 1231.1(8) Å^3, Z = 1, D_c = 1.256 g cm^{-3}, μ(Mo-Kα) = 0.088 mm^{-1}, T = 100 K, R_{int} = 0.035, $R(F)$ ($I > 2\sigma(I)$) = 0.0530 and $R_w(F^2)$ (all data) = 0.0937 for 5569 unique reflections. Selected data for **1**: C$_{30}$H$_{54}$ClLiN$_9$O$_{10}$, monoclinic, space group $P2_1/c$, a = 13.93(1), b = 18.12(2), c = 15.60(1) Å, β = 101.47(7)°, V = 3857(5) Å^3, Z = 4, D_c = 1.280 g cm^{-3}, μ(Mo-Kα) = 0.162 mm^{-1}, T = 90 K, R_{int} = 0.103, $R(F)$ ($I > 2\sigma(I)$) = 0.0534 and $R_w(F^2)$ (all data) = 0.0588 for 8246 unique reflections. Selected data for **2a**: C$_{47}$H$_{90}$KN$_{13}$O$_{11}$S, monoclinic, space group $P2_1/n$, a = 20.0470(8), b = 13.5737(5), c = 22.9917(8) Å, β = 109.223(2)°, V = 5907.5(4) Å^3, Z = 4, D_c = 1.219 g cm^{-3}, μ(Mo-Kα) = 0.189 mm^{-1}, T = 100 K, R_{int} = 0.134, $R(F)$ ($I > 2\sigma(I)$) = 0.0535, and $R_w(F^2)$ (all data) = 0.0774 for 13347 unique reflections. CCDC 618910–618912. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b613637k

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18 Anion dependence was observed by a slightly larger J ($-12.3(2)$ K) with g = 2.02(1) for **2a**, but a similar molecular structure is rationally assumed to **2b** (Fig. S2, ESI†). Unfortunately, **2b** did not gave a single crystal suitable for the X-ray crystallographic analysis so far.