ESI for a manuscript:

Anti-parallel Dimer and Tetramer Formation of Cyclic and Open Structure Tertiary Amides, *N*-methyl-2-pyrrolidone and *N*,*N*-dimethylacetamide, in Solution of a Non-polar Solvent, Benzene

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^{1}H-NMR Spectra: Figure ESI-1 shows typical ^{1}H-NMR spectra (signal intensities, I_{NMR}, vs chemical shift, δ) at several concentrations, c, for a NMP/(d)Bz system. The spectrum data for (5)CH_2 and (4)CH_2 protons demonstrated remarkable chemical shift changes more than 0.5 ppm with increasing the concentration, c. However, chemical shift changes observed in (N)CH_3 and (3)CH_2 protons were not so profound, but less than 0.1 ppm. Although the dependencies of chemical shift data for (5)CH_2 and (N)CH_3 protons on the c value were fully discussed in the main manuscript using the evaluated two equilibrium constants, K_d^{NMR} = 1.2 M^{-1} and K_t^{NMR} = 0.2 M^{-1}, that for (3)CH_2 and (4)CH_2 protons were not included.

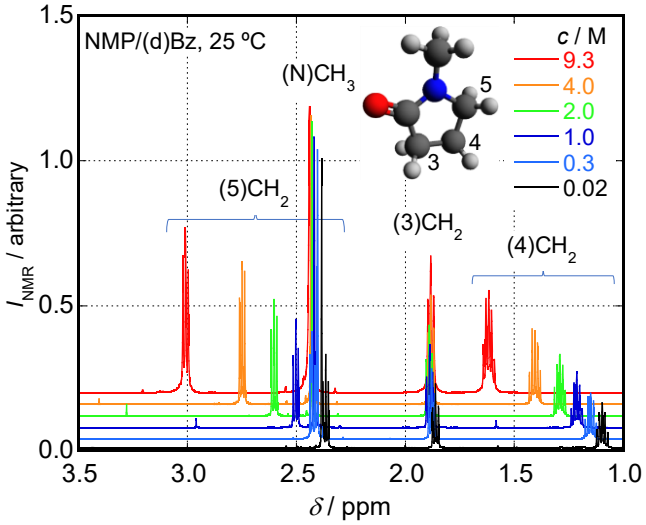

Figure ESI-1. ^{1}H-NMR spectra for the NMP/(d)Bz system at several concentrations from 0.02 to 9.3 M. Assignment for each proton is presented in the figure.

The concentration, c, dependencies of chemical shift data, δ, for (4)CH_2 and (3)CH_2 protons are shown in Figure ESI-2. A solid blue line represents calculated δ value based on the three-state model using the K_d^{NMR} = 1.2 M^{-1} and K_t^{NMR} = 0.2 M^{-1} evaluated in the main manuscript assuming chemical shifts for (4)CH_2 protons at the monomer, dimer and tetramer state, δ_m = 1.09, δ_d = 1.23 and δ_t = 2.25 ppm, respectively. On the other hand, a solid red line represents calculated δ using the same K_d^{NMR} and K_t^{NMR} assuming chemical shifts for (3)CH_2 protons for each state, δ_m = 1.86, δ_d = 1.917 and δ_t = 1.847 ppm, respectively. Perfect agreement between δ data and calculated lines for both the protons seen in Figure ESI-2 reveals that the equilibrium constants evaluated in the main manuscript are not far from the real values.

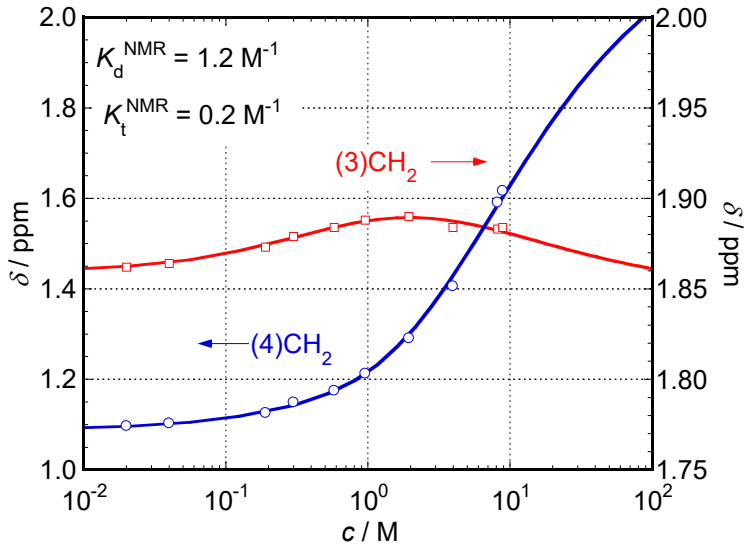

Figure ESI-2. The dependencies of chemical shifts, δ, for (4)CH_2 and (3)CH_2 protons for the NMP/(d)Bz system. Solid blue and red lines represent the calculated δ values using the equilibrium constants, K_d^{NMR} = 1.2 M^{-1} and K_t^{NMR} = 0.2 M^{-1}, based on the three-state model (see the main manuscript).

Figure ESI-3 shows typical ^{1}H-NMR spectra at several c for a DMAc/(d)Bz system. The spectrum data for (N_β)CH_3 protons demonstrated a profound chemical shift change more than 0.6 ppm with increasing the concentration, c. (C)CH_3 protons demonstrate a moderate chemical shit change of ca 0.1 ppm, and (N_α)CH_3 protons only a small chemical shit charge less than 0.1 ppm as observed in Figure ESI-3. Although the dependencies of chemical shift data for (N_β)CH_3 and (N_α)CH_3 protons on the c value were discussed in the main manuscript using the evaluated two equilibrium constants, K_d^{NMR} = 0.35 M^{-1} and K_t^{NMR} = 0.25 M^{-1}, that for (C)CH_3 protons was not included.

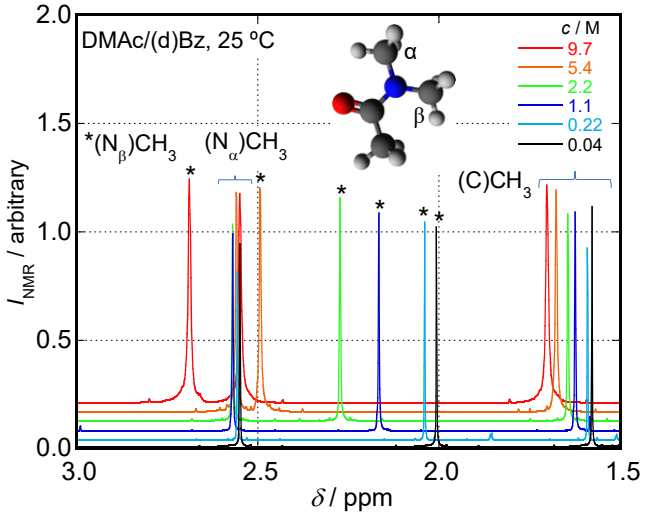

Figure ESI-3. ^{1}H-NMR spectra for the DMAc/(d)Bz system at several concentrations from 0.04 to 9.7 M. Assignment for each proton is presented in the figure.

The c dependence of the δ value for $(C)CH_3$ protons is shown in Figure ESI-4. A solid blue line represents calculated δ value based on the three-state model using the same $K_d^{NMR} = 0.35\ M^{-1}$ and $K_t^{NMR} = 0.25\ M^{-1}$ values assuming chemical shifts for $(C)CH_2$ protons at the monomer, dimer and tetramer state, $\delta_m = 1.58$, $\delta_d = 1.72$ and $\delta_t = 1.76$ ppm, respectively. The calculated line agrees well with δ data for the $(C)CH_3$ protons as seen in Figure ESI-4. This agreement strongly proposes that the equilibrium constants evaluated in the main manuscript are close to the real values.

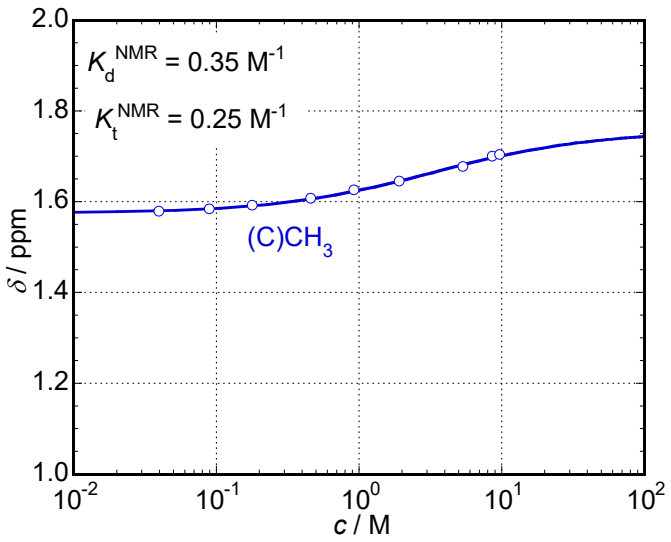

Figure ESI-4. The dependencies of chemical shifts, δ, for $(C)CH_3$ protons for the DMAc/(d)Bz system. Solid blue line represents the calculated δ values using the equilibrium constants, $K_d^{NMR} = 0.35\ M^{-1}$ and $K_t^{NMR} = 0.25\ M^{-1}$, based on the three-state model (see the main manuscript).