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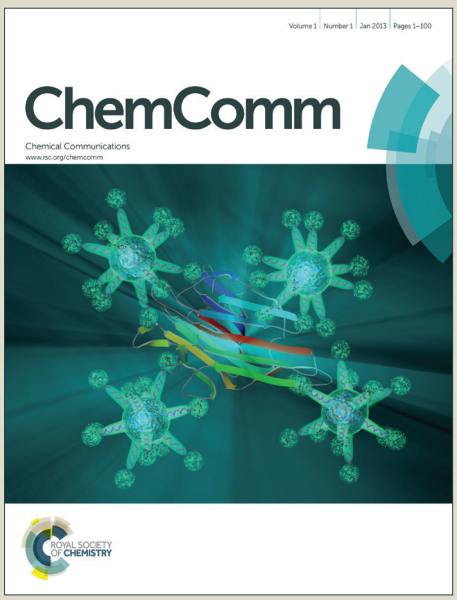

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Stepwise radial complexation from the outer-layer to the inner-layer of the dendritic ligand: Phenylazomethine dendrimer with an inverted coordination sequence

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***Para*-substituted phenylazomethine dendrimer (pG*n*A) coordinates to Lewis acids in a stepwise radial fashion from the inner-layer to the outer-layer. The inversion of this coordination sequence was achieved for the first time by just changing the substitution position of the phenylazomethine group from the *para* position to *meta* position (mG*n*A).**

The energy (potential) level distribution in a molecule or a molecular system is an important factor that controls the electric properties. Especially, some of the geometric potential architectures such as gradients (steps), square well potentials, and p-n junctions are the essence of the photosynthesis system,[1] and some electronic devices, such as laser diodes,[2] light emitting diodes,[3] and solar cells.[4] Therefore, the manipulation of the intra- and inter- molecular potential structure is a promising key technology for next generation materials that are related to electronics and photonics.

Dendrimers[5] are nm to 10nm order objects that have a perfectly branched molecular backbone. Due to the distinctive spherical molecular structure and stable conformation, dendrimers have the ability to locate functional groups in three-dimensional space. This feature is appropriate to build-up spherical potential gradients, such as light harvesting systems with several chromophores,[6] and redox cascades.[7] The para-substituted phenylazomethine dendrimer (**pDPA**, Fig.1)[8] is reported to have an inner-layer electron rich and outer-layer electron poor potential gradient even while its backbone is formed by the repetition of absolutely identical monomers.[9] This spontaneous expression of the potential gradient was an unexpected achievement and is not an extension of the usual method to construct a potential gradient (connecting different molecules). According to this anomalous feature, DPA has a layer by layer gradient of basicity and can coordinate to Lewis acids in a stepwise radial fashion.[8] This can be used to locate precise numbers of Lewis acids, making it useful as a sub-nanometer metal cluster template.[10] It further can be used as a molecular rectifier for electron-transfer,[11] and is expected to be a model for "atom mimicry".[12] The expression

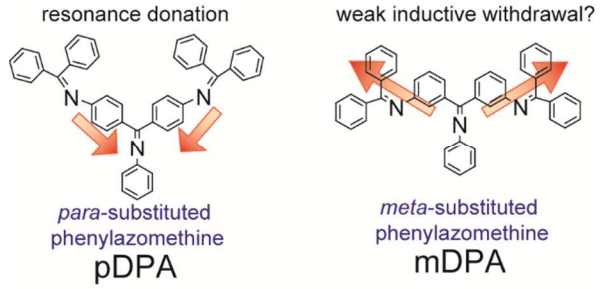

Figure 1. Image of the different substituent effect that leads to inverted potential gradient in *para*- and *meta*- substituted phenylazomethine dendrimers (DPA).

mechanism of the potential gradient is still unclear, but the importance of the rigid π-conjugated backbone and the electron donation from the outer-layer to the inner-layer has been pointed out.[13] Recently, we have tried to control the coordination sequence by installation of an electron withdrawing group in the core.[14] However, this approach only weakened the binding of the innermost layer, and inversion of the potential gradient was not achieved. As mentioned above, the electron donation (substituent effect) from the outer-layer to the inner-layer of phenylazomethine seems to play an important role for the spontaneous expression of the inner-layer electron rich potential gradient. The origin of this donation is ascribable to resonance donation. Therefore, presumably, changing the substitution position from *para* to *meta* will suppress this donation and allow a weak inductive electron withdrawal due to the difference in the electron negativity of the carbon and nitrogen atoms (essentially this should also exist in the *para* substituted DPA, but the withdrawal is masked with the stronger donation). Accordingly, herein we report the synthesis, and an inverted potential gradient

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(coordination sequence) of *meta*-substituted phenylazomethine dendrimer (**mDPA**) together with the expression mechanism.

The synthesis of the *meta*-substituted phenylazomethine dendron is summarized in scheme S1. Traditional *para*-substituted phenylazomethine dendrimer (**pDPA**) is synthesized by a convergent method that repeats the dehydration reaction, and oxidation of the benzyl position to reproduce the ketone.[15] The **mDPA** dendrons were also synthesized according to this method. To measure the basic property and the existence of the potential gradient, the G1 to G4 dendrons were reacted with aniline to give a 1-substituted dendrimer (**mG*n*A** (*n* = generation), Fig. 2, Scheme S2). Additionally, *meta*- and *para*-phenylazomethine substituted phenyl ferrocenes were synthesized (**pFc**, and **mFc**, Fig. 2, Scheme S3) by reacting ferrocene-linked anilines [16] with benzophenone. All the new compounds were identified by ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, and elemental analysis. Additionally, the purity of **mG*n*A** was checked by HPLC analysis (see ESI).

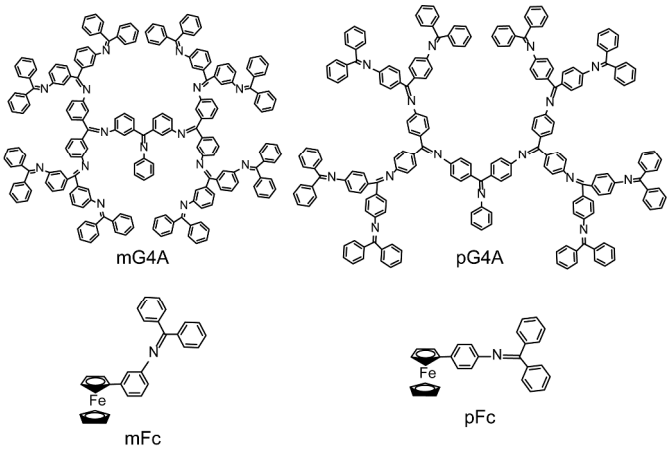

Figure 2. Structure of fourth-generation meta-, and para-substituted phenylazomethine dendrimers, and phenylazomethine substituted ferrocenes.

To compare the conjugation length of **mG*n*A** and **pG*n*A**, the UV-vis absorption spectra were measured (Fig. S24). The peak of **pG*n*A** around 350nm showed a bathochromic shift when the generation increased from **pG2A** to **pG4A** (342, 360, and 367 nm, respectively). On the other hand, the absorption of **mG2A**, **mG3A**, and **mG4A** were consistent (326, 325, and 324nm, respectively). The absorption edge also showed the same trend. This result suggested that the conjugation-induced inner-layer electron rich potential gradient of **pDPA** is suppressed in **mDPA**.

The steric crowding around the binding site may affect the binding property. Therefore, to obtain steric information about the **pDPA** and **mDPA**, the intrinsic viscosity was measured and a Mark-Houwink-Sakurada plot was created (Fig. S25). The intrinsic viscosity of **mDPA** was slightly lower than of **pDPA** and the hydrodynamic radius also decreased. This could also be confirmed by the molecular model (Fig. S26).[17] However, the difference in size and steric hindrance around the binding sites are small, thus it can be assumed that the steric factor does not affect the complexation.

The stepwise complexation of DPA can be observed by careful UV-vis titration with Lewis acids. In the case of **pG4A**, four isosbestic points can be observed during the titration, and the shift occurs when the amount of Lewis acids matches the number of imine sites in each layer of the **pG4A** from the inner-layer (1, 2, 4, and 8 equivalents). One isosbestic point corresponds to one equilibrium state, therefore, this strongly supports the plausible assumption that the complexation of **pG4A** is occurring sequentially from the inner-layer to the outer-layer. Following this method, the UV-vis titration of **mG4A** with $GaCl_3$ in chloroform: acetonitrile = 1: 1 solvent was performed (Figs. 3, S27) ($GaCl_3$ was chosen because it complexes strongly with imines[18] and does not have any absorption beyond 270 nm). During the titration, four isosbestic points were observed, and the amount of $GaCl_3$, that was necessary for the shift, was 8, 4, 2, and 1 equivalents. This corresponds to the number of imine sites from the outer-layer of **mG4A** and indicates the sequential complexation from the outer-layer to the inner-layer. Other generations (**mG3A**, and **mG2A,** Fig. S28) and another Lewis acid ($BF_3O(Et)_2$, Fig. S29)[18] had also shown the absolutely same behaviour that supports the stepwise complexation from the outer-layer. These results are opposite compared to **pG4A** and clearly indicate that the potential gradient in the dendritic structure is inverted by changing the binding position of the phenylazomethines from *para* to *meta* position.

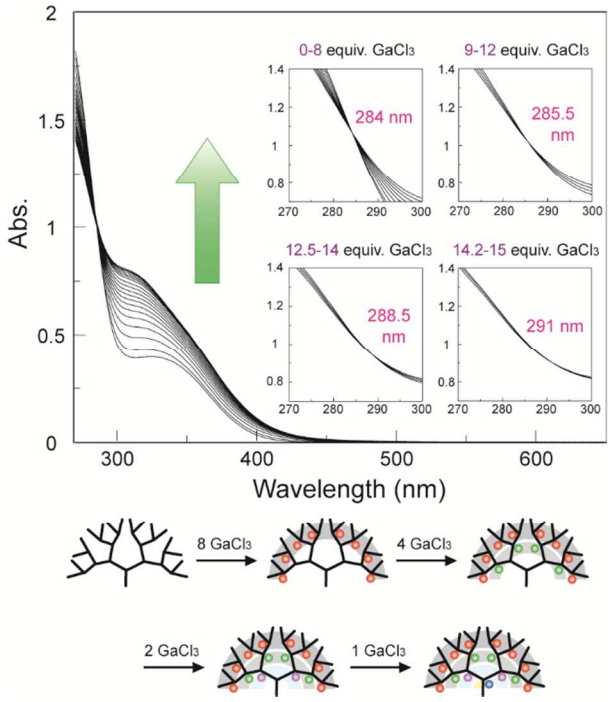

Figure 3. UV–vis spectra of **mG4A** during the addition of GaCl3 (solvent is chloroform: acetonitrile = 1: 1) and the image of the stepwise radial complexation from the outer-layer to the inner-layer of the dendrimer.

To determine the details of the potential gradient in **mG*n*A**, the titration with a weak acid (H^+, trifluoroacetic acid) was performed according to the literature method that was used to

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determine the binding constants of each layer in **pG*n*A** (Fig. S30).[19] The result clearly shows that the outer-layer has a higher binding constant to H^+ and it sequentially decreases toward the inner-layer in all generations of the **mG*n*A**, but the slope is steeper in **pGnA** because, probably, the resonance donation is stronger than inductive withdrawal (Fig. S31).

To understand the potential gradient of **DPA**, the features of the *meta* and *para* substituted phenylazomethines have to be understood. Ether and amino substituents are known to have a significant difference in the *para* and *meta* substituent effect (in some cases, the donating group changes to a withdrawing group)[20] which is explained by the effectivity of the resonant donation from the lone-pair. To determine the substituent effect of the phenylazomethines, the redox potential of the phenylazomethine linked ferrocenes (Fig. 1) were measured (Fig. S32). The redox potential (V vs Fc/Fc^+) of **pFc** and **mFc** was -10mV and +15mV, respectively. This clearly indicates that *para* substitution of the phenylazomethine is electron donating, while *meta*-substitution is electron withdrawing.

For further investigation of the expression mechanism of the potential gradient in the **DPA**, the ^{13}C and ^{15}N NMR spectra were studied (Figs. 4, S33-35). The NMR spectra of the azomethines are complicated and the assignment was difficult because the *cis* and *trans* positions of the C=N bond are nonequivalent. Therefore, the spectra of each compound was compared to the outer-layer ^{13}C=N labelled DPAs and inner-layer C=^{15}N labelled DPAs (prepared by using ^{13}C labelled benzophenone (^{13}C=O) and ^{15}N labelled aniline) for the assignment of the outer-layer ^{13}C NMR spectra and the inner-layer ^{15}N NMR spectra. The ^{13}C NMR spectra of the outermost C=N carbons had the highest chemical shift in both **mG*n*A** and **pG*n*A** (Fig. 6(a)). This indicates that the outermost C=N carbon is de-shielded compared to the other layer carbons. Assignments of other layers are difficult, but it is assumed that the environment around the C=N carbons (NOE from ^1H atom) is similar, therefore, the integration is helpful information. The integration value of **mG4A** is 8, 6(4+2), 1 from the low field, and the peak with the value of 6 has a small peak at the higher field. This means that the ^{13}C=N chemical shift is sequentially shifting from the outer layer to the inner layer. On the other hand, the ^{15}N NMR spectra of **mG2A** showed that the outer layer C=N nitrogen is more shielded than the inner layer, and in the case of **pG2A**, it showed the opposite trend (Fig. 4(a)). The complexation of acids to the imine reflects the electron density of the nitrogen atom, and the outer layer shielding (=higher electron density) of the **mG2A** agrees with the stepwise complexation from the outer-layer. The inner layer shielded (=higher electron density) behaviour of **pG2A** also agrees with the stepwise complexation from the inner-layer. The difference in the chemical shift between the first and second layers is smaller than **pG2A** in **mG2A** which also agrees with the complexation constants that are determined by the titration with TFA. However, even the ^{15}N NMR spectra matches the complexation behaviour, the ^{13}C NMR spectra of **mG*n*A** shows the opposite electron density compared to the ^{15}N NMR spectra (inner-layer shielded). This can be explained by the mechanism of the electron donation or withdrawal (Fig. 4(b)). In **pG*n*A**, the electron donation from the outer layer is a resonance mechanism and the inner-layer carbon and nitrogen are both shielded, but in **mG*n*A**, the electron withdrawal is a π-polarization mechanism[21] in which the C=N bond takes a $^{\delta-}C=N^{\delta+}$ type polarized electronic structure (Fig.4b).

In conclusion, a new *meta*-substituted phenylazomethine dendrimer was synthesized. This dendrimer showed a stepwise radial complexation from the outer-layer to the inner-layer which was opposite compared to the *para*-substituted phenylazomethine dendrimers. The inversion of the potential gradient could be explained by the substituent effect of the repeat unit. Of course, this dendrimer can expand the range of DPA applications. For example, the greater variation in the accumulable numbers and combination of metal atoms (Fig. S36) has an important meaning. However, the inversion of the potential gradient and the discovery of the simple mechanism has a more significant fundamental meaning it is a novel method to design and control the intramolecular potential structure.

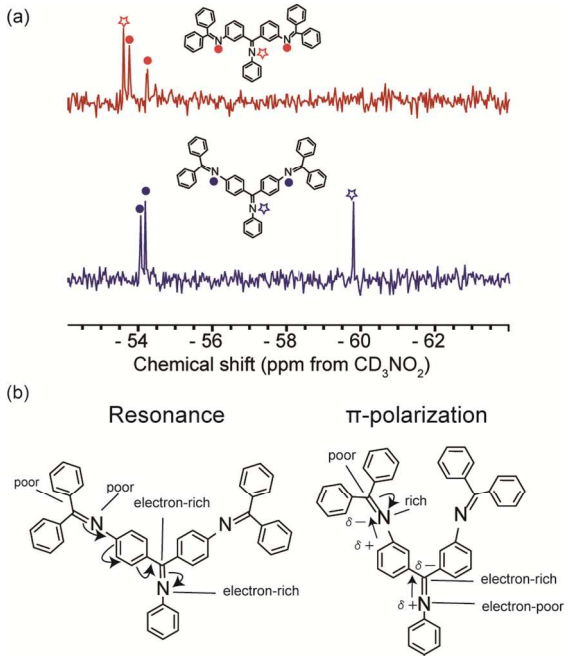

Fig.4 (a) ^{15}N NMR spectra of **mG2A**, and **pG2A** in $CDCl_3$. (b) Proposed expression mechanism of the electron density gradient of the nitrogen atom.

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† Electronic Supplementary Information (ESI) available: [Experimental section, identification data, calculated molecular models, titration, cyclic voltammograms, and NMR spectra]. See DOI: 10.1039/c000000x/

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