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Shuta Iseki, Kohei Nonomura, Sakura Kishida, Daiji Ogata, and Junpei Yuasa

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Zinc Ion-Stabilized Charge-Transfer Interactions Drive Self- or Complementary Molecular Recognition

Shuta Iseki,[†] Kohei Nonomura,[†] Sakura Kishida,[†] Daiji Ogata,[†] and Junpei Yuasa^{*,†}

[†]Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

ABSTRACT: Here, we show that charge-transfer interactions determine whether donor and acceptor ditopic ligands will associate in a complementary or self-complementary fashion upon metal ion clipping. Anthracene- (${}^{9,10}L_D$ and ${}^{1,5}L_D$) and anthraquinone- (${}^{1,5}L_A$) based ditopic ligands containing two imidazole side arms as zinc coordination sites were designed. The ${}^{9,10}L_D$ and ${}^{1,5}L_A$ system associated in a complementary fashion ($L_A/L_D/L_A$) upon clipping by two zinc ions (Zn^{2+}) to form an alternating donor-acceptor assembly [(${}^{9,10}L_D$)(${}^{1,5}L_A$)₂-(Zn^{2+})₂]. However, once the charge-transfer interactions were perturbed by subtle modifications of the imidazole side arms (${}^{9,10}L_D'({}^{(5)})$ and ${}^{1,5}L_A'({}^{(5)})$), self-complementary association ($L_D'/L_D'/L_D'/L_D'/L_D'/L_A'/L_A'/L_A'/L_A')$ between the donor- (${}^{9,10}L_D'({}^{(5)})$) and acceptor- (${}^{1,5}L_A'({}^{(5)})$ ligands predominantly occurred to form homo-assemblies [(${}^{9,10}L_D'({}^{(5)})_{4-}(Zn^{2+})_{2}$] and (${}^{1,5}L_A'({}^{(5)})_{4-}(Zn^{2+})_{2}$]. As in the case of a homochiral pair (${}^{9,10}L_D'({}^{(5)})_{4-}(Zn^{2+})_{2}$) and (${}^{1,5}L_A'({}^{(6)})_{4-}(Zn^{2+})_{2}$]. Narcissistic self-sorting) occurred in the Zn²⁺ assembly with heterochiral combinations of the donor and acceptor ligands (${}^{9,10}L_D'({}^{(5)})_{1,5}L_A'({}^{(6)})_{1,5}L_A'$

• INTRODUCTION

Molecular recognition is a specific interaction that can distinguish one molecule from another by means of noncovalent interactions. Such recognition has an important role in supramolecular chemistry. Hydrogen bonding is the most extensively used type of noncovalent interaction in this context. Hydrogen bonding is highly directional and has high association constants that are effective in either self-complementary or complementary molecular recognition.1 Alternatively, charge-transfer (CT) interactions are another unique motif that drives alternative association between donor (D) and acceptor (A) molecules owing to its intrinsic complementary nature.²⁻⁵ However, association constants of D-A complexes are typically very low (Scheme 1a),²⁵ therefore CT-based molecular recognition requires a third component (M) that combines D and A through other noncovalent interactions such as solvophobic forces, hydrogen bonding, and metal-ligand coordination.6-11 If the binding forces of M with D and with A are greater than the CT interaction between D and A, a statistical mixture of the ternary complexes results (Scheme 1b). It might also be possible to produce a driving bias for alternating D-A association by design of D and A such that their CT interactions are reinforced upon combination with M (Scheme 1c). Conversely, if self-complementary interactions are high enough, complementary D-D and A-A associations will dominate (Scheme 1d). Such weakly attractive CT interactions have not previously been considered to be a core molecular recognition motif that can control self-complementary and complementary molecular recognition in supramolecular systems.

Herein, for the first time, we successful demonstrated that the weak attractive force of CT interactions effectively determines whether D and A molecules associate in a self-complementary or complementary fashion upon self-assembly with zinc ions (Zn^{2+}). We designed D and A ditopic ligands (^{9,10} L_D and ^{1,5} L_A , respectively)



Scheme 1. (a) Relative Gibbs energy changes (ΔG) of a charge transfer complex (D–A), (b-d) mediator (M)-assisted self-complementary (D–M–D and A–M–A) and complementary (D–M–A) molecular recognitions in b) $-\Delta G_{AA} = -\Delta G_{DD} = -\Delta G_{DA}$, (c) $-\Delta G_{AA}$, $-\Delta G_{DD} < -\Delta G_{DA}$, and (d) $-\Delta G_{AA}$, $-\Delta G_{DD} < -\Delta G_{DA}$. (e) Chemical structures of anthracene- ($^{9,10}L_D$, $^{9,10}L_D'^{(R)}$, and $^{9,10}L_D'^{(S)}$) and anthraquinone-based ditopic ligands ($^{1.5}L_A$, $^{1.5}L_A'^{(R)}$, and $^{1.5}L_A'^{(S)}$).

containing two imidazole side arms at 9,10-positions of anthracene and 1,5-positions of anthraquinone through ethynyl spacers (Scheme 1e) so that they could form an alternating A-D-A stack $[({}^{9,10}L_D)({}^{1,5}L_A)_2-(Zn^{2+})_2]$ upon clipping by Zn^{2+} with a tetrahedral coordination preference (*vide infra*, Figure 3a).¹²⁻¹⁴ Notably, once

the CT interactions were perturbed by subtle modifications of the imidazole side arms, D and A ditopic ligands $({}^{9,10}L_{D}'{}^{(S)})$ and ${}^{15}L_{A}'{}^{(S)}$, respectively) began to associate in a self-complementary fashion to form homo-assemblies $[({}^{9,10}L_{D}'{}^{(S)})_4-(Zn^{2+})_2$ and $({}^{1,5}L_{A}'{}^{(S)})_4-(Zn^{2+})_2]$. This finding suggests a potential role of CT interactions as unique molecular recognition motifs in fine-tuning of supramolecular systems. Because CT interactions have an important influence on photophysical properties, the present work will also provide a basis for future design of CT-based functional materials.

• **RESULTS AND DISCUSSION**

Zinc Ion-Stabilized Charge-Transfer Interactions. Figure 1a shows UV-vis absorption spectral changes during titration of a ^{9,10} L_D /¹⁵ L_A mixture ([^{9,10} L_D]₀ = 6.7 × 10⁻⁶ M; [^{1,5} L_A]₀ = 1.3 × 10⁻⁵ M) with $Zn(OTf)_2$ (OTf = OSO₂CF₃) in acetonitrile, where the ^{9,10}L_D/^{1,5}L_A mixture shows successive spectral change with isosbestic points at 281 and 486 nm and a characteristic CT band was clearly visible at $\lambda = 520$ nm. Noteworthy, theoretical UV-vis absorption spectrum calculated by time-dependent density function theory (TD-DFT) indicates that the CT band appeared at $\lambda = 546$ nm (Supporting Information Figure S1-S3). The isosbestic points indicate the quantitative conversion of ${}^{9,10}L_D$ and ${}^{1,5}L_A$ into a single self-assembly (Scheme 2a). A titration plot of the absorbance monitored at $\lambda = 420$ nm has a saturation point at $[Zn^{2+}]/([^{9,10}L_D]_0 +$ $[^{1,5}L_A]_0$ = 0.67 (inset of Figure 1a), indicating that the three ditopic ligands $({}^{1,5}L_A/{}^{9,10}L_D/{}^{1,5}L_A)$ were clipped by the two Zn^{2+} ions (Scheme 2a).

Next, we subtly modified ^{9,10}L_D and ^{1,5}L_A by replacing the methyl groups of the imidazole side arms with branched substituents $({}^{9,10}L_{D}'^{(S)}$ and ${}^{1,5}L_{A}'^{(S)}$, respectively) to reduce solvophobic effects, which should reduce the CT interactions.^{5,15} Unlike the $^{9,10}L_D/^{1.5}L_A$ mixture (Figure 1a), a $^{9,10}L_D'^{(S)/1.5}L_A'^{(S)}$ mixture showed biphasic UV-vis absorption spectral changes (Figure 1d; Supporting Information Figure S4) with individual isosbestic points in response to the molar ratio of $[Zn^{2+}]/([{}^{9,10}L_D'^{(S)}]_0 + [{}^{1,5}L_A'^{(S)}]_0) = 0 -$ 0.25 (first phase: red lines) and 0.25-0.58 (second phase: blue lines). These results are attributed to self-complementary associations of ${}^{15}L_{A'}(S)$ ($L_{A'}L_{A'}L_{A'}L_{A'}$) and of ${}^{9,10}L_{D'}(S)$ ($L_{D'}L_{D'}L_{D'}L_{D'}$) upon assembly with Zn²⁺ (Scheme 2b).^{16–18} The titration plot shows the inflection and saturation points at $[Zn^{2+}]/([^{9,10}Lp'^{(S)}]_0 +$ $[^{1,5}L_{A'}(S)]_{0} = 0.25$ and 0.50, respectively (Figure 1d inset), which illustrates the stoichiometry of the self-complementary associations as $[{}^{9,10}L_D'^{(S)}]$: $[Zn^{2+}] = 2:1$ and as $[{}^{1,5}L_A'^{(S)}]$: $[Zn^{2+}] = 2:1$ corresponding to L₄Zn₂-assemblies. In this context, we have revealed that the imidazole-based ditopic ligands (L) with Zn²⁺ mostly give rise to L₄Zn₂-assemblies.^{14a,d,e}

Next, differential UV–vis absorption spectral changes (Figure 2a and d) were produced from the Zn^{2+} -titration data of the 9,10Lp/15LA mixture and 9,10Lp'(5)/15LA'(5) mixture (Figure 1a and b, respectively) and compared with those obtained with individual titration experiments of the D or A ditopic ligand alone with Zn^{2+} (Figure 2b, c, e and f; Supporting Information Figure S6 and S7). In the Zn^{2+} -titration of the 9,10Lp'(5)/15LA'(5) mixture, the corresponding differential spectra at the first- and second-phase (Figure 2d) appear to be identical to those obtained with the individual spectral titration of $^{15}LA'^{(S)}$ with Zn^{2+} and that of $^{9,10}Lp'^{(S)}$ with Zn^{2+} (Figure 2e and f). Conversely, the differential UV–vis absorption spectra in the Zn^{2+} -titration of the $^{9,10}Lp'^{1,5}L_A$ mixture (Figure 2a) disagreed with those obtained from the individual Zn^{2+} -titration of $^{9,10}L_D$ and that of $^{1.5}L_A$ (Figure 2b and c).



Figure 1. (a and d) UV-vis absorption spectral changes during titration of (a) $^{9,10}L_D/^{1,5}L_A$ mixture ($[^{9,10}L_D]_0 = 6.7 \times 10^{-6}$ M and $[^{1,5}L_A]_0 = 1.3 \times 10^{-5}$ M) with Zn^{2+} [0 (green line)-2.0 × 10⁻⁵ M (orange line)], (d) ${}^{9,10}L_{D'}(S)/1.5L_{A'}(S)$ mixture ([${}^{9,10}L_{D'}(S)$]₀ = 2.0×10^{-5} M and $[^{1,5}L_{A}'^{(S)}]_0 = 2.0 \times 10^{-5}$ M) with Zn^{2+} [0–1.0 × 10⁻⁵ M (red lines)–2.3 \times 10⁻⁵ M (blue lines)] in acetonitrile at 298 K. Insets show plots of absorbance at (a) λ = 420 nm vs $x = [Zn^{2+}]/([^{9,10}L_D]_0 + [^{1,5}L_A]_0), (d) \lambda = 500 nm vs x = [Zn^{2+}]/([^{9,10}L_D'^{(S)}]_0)$ + $[^{1,5}L_A'^{(S)}]_0$. (b and e) UV-vis absorption spectra of (b) blue line: $(^{9,10}L_D)_4$ - $(Zn^{2+})_2$, red line: $({}^{1,5}L_A)_4 - (Zn^{2+})_2$, (e) blue line: $({}^{9,10}L_D'^{(S)})_4 - (Zn^{2+})_2$, red line: $({}^{1,5}L_A'^{(S)})_4 - (Zn^{2+})_2$ (Zn2+)2.19 E values were calculated based on the ligand concentration. (c and f) Orange solid lines show the observed UV-vis absorption spectra of (c) 9,10 Lp/1,5 LA mixture $([^{9,10}L_D]_0 = 6.6 \times 10^{-6} \text{ M and } [^{1,5}L_A]_0 = 1.3 \times 10^{-5} \text{ M})$ in the presence of $Zn^{2+} (2.0 \times 10^{-5} \text{ M})$ ⁵ M), (f) ${}^{9,10}L_D{}'^{(S)/1.5}L_A{}'^{(S)}$ ([${}^{9,10}L_D{}'^{(S)}$] $_0 = 1.0 \times 10^{-5}$ M and [${}^{1.5}L_A{}'^{(S)}$] $_0 = 1.0 \times 10^{-5}$ M) in the presence of Zn^{2+} (1.0 × 10⁻⁵ M) in acetonitrile. Dashed lines in Figure 1c and 1f show calculated UV-vis absorption spectra obtained from the sum of the absorption spectra of the homoligand-assemblies in the ratios: (c) (9,10 Lp)4-(Zn2+)2 (33%) and $(^{1,5}L_A)_4 - (Zn^{2+})_2 (67\%), (f) (^{9,10}L_D (S))_4 - (Zn^{2+})_2 (50\%) and (^{1,5}L_A (S))_4 - (Zn^{2+})_2 (50\%).$



Figure 2. (a–f) Left: differential UV–vis absorption spectra obtained from titration of (a) ${}^{9,10}L_D{}^{I,5}L_A$ mixture ($[{}^{9,10}L_D]_0 = 6.7 \times 10^{-6}$ M and $[{}^{15}L_A]_0 = 1.3 \times 10^{-5}$ M) with Zn^{2+} (0–2.0 × 10⁻⁵ M), (b) ${}^{15}L_A$ (2.0 × 10⁻⁵ M) alone with Zn^{2+} (0–1.2 × 10⁻⁵ M), (c) ${}^{9,10}L_D$ (2.0 × 10⁻⁵ M) alone with Zn^{2+} (0–1.0 × 10⁻⁵ M), (c) ${}^{9,10}L_D$ (${}^{9,10}L_D{}^{I,6}){}^{I,5}L_A$ (3,0 D alone with Zn^{2+} (0–1.2 × 10⁻⁵ M), (c) ${}^{9,10}L_D$ (${}^{9,10}L_D{}^{I,6}){}^{I,5}L_A$ (3,0 D alone with Zn^{2+} (0–1.0 × 10⁻⁵ M), (d) ${}^{9,10}L_D{}^{I,6}{}^{I,5}L_A$ (3,0 D alone with Zn^{2+} (0–1.0 × 10⁻⁵ M), (d) ${}^{9,10}L_D{}^{I,6}{}^{I,5}L_A$ (3,0 D alone with Zn^{2+} (0–1.2 × 10⁻⁵ M) alone alone alone alone alone alone alone alone

In the same manner, a calculated absorption spectrum (Figure 1f black dashed line) obtained from the sum of the absorption spectra of the individual homo-assemblies $[({}^{9,10}L_D'{}^{(S)})_4-(Zn^{2+})_2$ and



Scheme 2. Schematic illustration for Zn^{2+} -driven assembly formation between (a) ^{9,10}L_D and ^{1,5}L_A, (b) ^{9,10}L_D^(S) and ^{1,5}L_A^(S). Photograph shows the colors of acetonitrile solutions of ^{9,10}L_D/^{1,5}L_A (right) mixture and ^{9,10}L_D^{(S)/1,5}L_A^(S) (left) mixture containing Zn^{2+} .

 $({}^{1,5}\mathbf{L}_{A}'{}^{(S)})_{4-}(\mathbb{Z}n^{2+})_{2}$ (Figure 1e)¹⁹ was in complete agreement with the observed absorption spectrum of the ${}^{9,10}\mathbf{L}_{D}'{}^{(S)}/{}^{1,5}\mathbf{L}_{A}'{}^{(S)}$ mixture with $\mathbb{Z}n^{2+}$ (Figure 1f orange solid line), which indicates that $\mathbb{Z}n^{2+}$ -assisted self-complementary associations occurred in the ${}^{9,10}\mathbf{L}_{D}'{}^{1,5}\mathbf{L}_{A}'{}^{(S)}$ system (Scheme 2b). Conversely, the calculated absorption spectrum (Figure 1c dashed line) obtained from the sum of the two absorption spectra [$({}^{9,10}\mathbf{L}_{D})_{4-}(\mathbb{Z}n^{2+})_{2}$ and $({}^{1,5}\mathbf{L}_{A})_{4-}(\mathbb{Z}n^{2+})_{2}$ (Figure 1b)]¹⁹ appeared to disagree with the observed absorption spectrum of the ${}^{9,10}\mathbf{L}_{D}/{}^{1,5}\mathbf{L}_{A}$ mixture with $\mathbb{Z}n^{2+}$ showing the CT band at $\lambda = 520$ nm (Figure 1c orange solid line). The developing CT band produced notable differences in the apparent colors of the ${}^{9,10}\mathbf{L}_{D}/\mathbf{L}_{A}$ and ${}^{9,10}\mathbf{L}_{D}'{}^{(S)}/{}^{1,5}\mathbf{L}_{A}'{}^{(S)}$ upon addition of $\mathbb{Z}n^{2+}$ (Scheme 2 photograph).

We further verified the stoichiometry of the alternating A-D-A assembly by global titration analysis (Figure 2g), where the ratios of the ^{9,10}L_D and ^{1,5}L_A were changed from $[^{9,10}L_D]_0/([^{9,10}L_D]_0 + [^{1,5}L_A]_0) = 0$ to 1.0 while the total concentrations of ^{9,10}L_D and ^{1,5}L_A were kept constant ($[^{9,10}L_D]_0 + [^{1,5}L_A]_0 = 2.0 \times 10^{-5}$ M). The Jobplot analysis based on the absorbance at $\lambda = 520$ nm assigned to the CT band suggests that the stoichiometry of $[^{9,10}L_D]_0/([^{9,10}L_D]_0 + [^{1,5}L_A]_0) = 0.33$ (Figure 2g inset), which clearly indicates an alternating A-D-A assembly ($(^{9,10}L_D)(^{1,5}L_A)_2-(Zn^{2+})_2$). The structure of $(^{9,10}L_D)(^{1,5}L_A)_2-(Zn^{2+})_2$ was optimized at B3LYP/6-31G(d,p) [C, H, N, O]; LANL2DZ (Zn) assuming the most symmetrical structure of the alternating A-D-A association (Figure 3a and b), which seems to be reasonable for situations in which CT interactions were reinforced upon clipping by two Zn²⁺ ions.

Thus, the positive ESI-MS of the ^{9,10}L_D/^{1,5}L_A mixture was measured in acetonitrile containing Zn²⁺ (Figure 3c) and the results compared with those of their homo-assemblies (Figure 3d, e) as well as the ^{9,10}L_D^{r(S)/1,5}L_A^{r(S)} mixture with Zn²⁺ (Supporting Information Figure S8). The ^{9,10}L_D/^{1,5}L_A mixture showed a mass peak corresponding to the alternating A-D-A assembly at m/z = 1794.13and fragment mass signals.²⁰ Conversely, we could not find any mass signal corresponding to the alternating A-D-A assembly in the ^{9,10}L_D^{r(S)/1,5}L_A^{r(S)} mixture with Zn²⁺ (Supporting Information Figure S8).

Furthermore ¹H NMR spectra of the ^{9,10}L_D/¹⁵L_A mixture and ^{9,10}L_D'^{(S)/15}L_A'^(S) mixture with Zn²⁺ (Figure 4a and d) were compared with those of their homo-assemblies (Figure 4b, c and 4e, f).¹⁹ Among the homo-assemblies studied here, NMR-based structure determination of (^{9,10}L_D'^(S))₄–(Zn²⁺)₂ was achieved in our recent report.^{14d} In the other cases, the structures of (^{9,10}L_D)₄–(Zn²⁺)₂ and (¹⁵L_A)₄–(Zn²⁺)₂ were determined with the use of ¹H,¹H-COSY,



Figure 3. (a) Equation and (b) the structure of (^{9,10}L_D)(^{1,5}L_A)₂–(Zn²⁺)₂ optimized at B3LYP/6-31+G(d,p) [C, H, N, O]; LANL2DZ (Zn). Color code, ^{9,10}L_D: blue, ^{1,5}L_A: red, Zn²⁺: yellow. (c–e) Positive ESI-MS spectrometry of (c) ^{9,10}L_D/^{1,5}L_A mixture, (d) ^{1,5}L_A alone, and (e) ^{9,10}L_D alone in acetonitrile with the presence of Zn²⁺. Intensity is normalized by their most intense fragment. Mass spectrum of the whole region is given in Supporting Information Figure S9.

ROESY, and NOESY NMR experiments in this work (see details in the Supporting Information Figure S10-S16). Although $(^{1,5}L_{A}'^{(S)})_4$ -(Zn²⁺)₂ underwent line broadening, likely because of its dissociation and reassociation on the NMR timescale (Figure 4e), we assumed the same L_4Zn_2 structure as $(^{1,5}L_A)_4 - (Zn^{2+})_2$ for $(^{1,5}L_{A'}(S))_4$ -(Zn²⁺)₂ judging from the similarity of their UV-vis titration results (Figure 2b vs e). The homo-assemblies, (9,10LD)4- $(Zn^{2+})_2$ and $(^{1,5}L_A)_4$ - $(Zn^{2+})_2$, exhibited upfield-shifted protons at 5.24 and 6.14 ppm, respectively (Figure 4b and c), which are attributed to shielding of aromatic protons owing to stacking of aromatic rings inside the homo-assemblies (insets of Figure 4b and c).^{14d,21} Conversely, the ${}^{9,10}L_D/{}^{1,5}L_A$ mixture with Zn²⁺ had an NMR spectrum with almost no signal from the homoligand assemblies $[({}^{9,10}L_D)_4 - (Zn^{2+})_2$ and $({}^{1,5}L_A)_4 - (Zn^{2+})_2]$ (Figure 4a). This result clearly indicates the formation of the A-D-A assembly $[(^{9,10}L_D)(^{1,5}L_A)_2 - (Zn^{2+})_2]$. In contrast to the upfield-shifted protons observed for $({}^{9,10}L_D)_4$ -(Zn²⁺)₂ and $({}^{1,5}L_A)_4$ -(Zn²⁺)₂ (Figure 4b and c), no such signals were observed for $({}^{9,10}L_D)({}^{1,5}L_A)_2 - (Zn^{2+})_2$. This



Figure 4. (a–c) ¹H NMR spectra of (a) ^{9,10}L_D^{/1,5}L_A mixture ([^{9,10}L_D]₀ = 1.0 × 10⁻³ M and [1⁵L_A]₀ = 2.0 × 10⁻³ M) with Zn²⁺ (2.0 × 10⁻³ M), (b) ^{9,10}L_D (2.0 × 10⁻³ M) alone with Zn²⁺ (1.0 × 10⁻³ M), and (c) ^{1.5}L_A (2.0 × 10⁻³ M) alone with Zn²⁺ (1.0 × 10⁻³ M), in CD₃CN at 298 K. Insets: Structures of (a) (^{9,10}L_D)(^{1.5}L_A)₂-(Zn²⁺), (b) (^{9,10}L_D)₄-(Zn²⁺)₂ determined by NMR analysis. Color code, ^{9,10}L_D blue, (^{1.5}L_A: red, **Zn²⁺**; yellow, H: white. (d–f) ¹H NMR spectra of (d) ^{9,10}L_D'⁽⁵⁾/L⁵L_A'⁽⁵⁾ mixture (f^{9,10}L_D'⁽⁵⁾)₀ = 2.0 × 10⁻³ M and [^{1.5}L_A'⁽⁵⁾]₀ = 2.0 × 10⁻³ M) with Zn²⁺ (4.0 × 10⁻³ M), (e) ^{1.5}L_A'⁽⁵⁾ (2.0 × 10⁻³ M) alone with Zn²⁺ (1.0 × 10⁻³ M), (f) ^{9,10}L_D'⁽⁵⁾ (2.0 × 10⁻³ M) in CD₃CN at 298 K.

observation suggests that both the anthracene and anthraquinone aromatic protons exist outside of the aromatic rings, which is consistent with an A-D-A stack having three aromatic rings in an almost complete overlapping arrangement (Figure 4a inset). Conversely, the ¹H NMR spectrum of (^{9,10}L_D)(^{1,5}L_A)₂-(Zn²⁺)₂ contained both broadened and well-resolved signals. We used NMR techniques, including ¹H,¹H-COSY, and ROESY, in combination with ligand exchange experiments to determine the structure of $({}^{9,10}L_D)({}^{1,5}L_A)_2 - (Zn^{2+})_2$ (see details in the Supporting Information Figure S18-S24). These results suggested that the broadened and resolved signals likely came from ^{1,5}L_A and ^{9,10}L_D inside the A-D-A assembly, respectively. The broadening of the NMR signals is likely caused by rapid dissociation and reassociation of the ¹⁵L_A ligands on the NMR timescale.^{22,23} Conversely, the central ^{9,10}L_D ligand inside the A-D-A assembly should be fixed by strong polyaromatic CT interactions with the two ¹⁵L_A ligands, and therefore no dissociation and reassociation took place on the NMR timescale. In contrast to the ${}^{9,10}L_D/{}^{1,5}L_A$ mixture with Zn^{2+} , the ${}^{9,10}L_D'{}^{(S)}/{}^{1,5}L_A'{}^{(S)}$ mixture with Zn²⁺ exhibited an NMR spectrum (Figure 4d) that comprised individual donor and acceptor homoligand assemblies

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(blue circles and red triangles, respectively), where the broadened NMR signals of $(^{1,5}L_A'^{(S)})_4$ -(Zn²⁺)₂ were shifted (see Supporting Information S25). This finding also underlines that the ^{9,10}L_D'^{(S)/1,5}L_A'^(S) system favored self-complementary association (D/D/D or A/A/A/A) rather than complementary A-D-A stacking upon Zn²⁺ binding (Scheme 2b).²⁴

Self-Sorting According to Chirality Along with the CT Interactions. Next, we examined whether self-complementary association (narcissistic self-sorting) as observed in the $^{9,10}L_D'^{(S)/15}L_A'^{(S)}$ system (homochiral pair) can be switched to com-10 plementary association (social self-sorting) by altering the combi-11 nation of chirality of the donor and acceptor ligands. To this end, we tested two kinds of heterochiral pairs, ${}^{9,10}L_{D}'^{(S)/1.5}L_{A}'^{(R)}$ and 12 $^{9,10}L_D'^{(S)/1.5}L_A'^{(R)/1.5}L_A'^{(S)}$. These combinations open up the possibil-13 ity of new alternating A-D-A assemblies $[(^{9,10}L_D'^{(S)})(^{1,5}L_A'^{(R)})_2-$ 14 $(Zn^{2+})_2$ and $({}^{9,10}L_D{}'^{(S)})({}^{1,5}L_A{}'^{(R)})({}^{1,5}L_A{}'^{(S)})-(Zn^{2+})_2]$ (Scheme 3). If 15 these heterochiral A-D-A assemblies are markedly lower in energy 16 than the homochiral one $[({}^{9,10}L_{D}'{}^{(S)})({}^{1,5}L_{A}'{}^{(S)})_2 - (Zn^{2+})_2]$, comple-17 mentary association along with heteroligand assembly will take 18 place. The ${}^{9,10}L_{D}'^{(S)/1.5}L_{A}'^{(R)}$ mixture with Zn²⁺ gave a UV-vis ab-19 sorption spectrum (Figure 5a orange solid line) that agreed well 20 with a calculated absorption spectrum obtained from the sum of the 21 absorption spectra of the individual homoligand-assemblies 22 $[({}^{9,10}L_{D}'^{(S)})_4 - (Zn^{2+})_2 \text{ and } ({}^{1,5}L_{A}'^{(R)})_4 - (Zn^{2+})_2]$ (Figure 5a dashed line), 23 whereas no CT band was detected (for the corresponding UV-vis 24 titration analysis, see Supporting Information Figure S27). In the 25 same manner, almost complete agreement was obtained between the UV-vis absorption spectrum of the ${}^{9,10}L_D{}'^{(S)/1,5}L_A{}'^{(R)/1,5}L_A{}'^{(S)}$ 26 27 mixture with Zn2+ and a calculated absorption spectrum obtained from the sum of the absorption spectra of their individual homolig-28 and-assemblies (Figure 5b). Notably, the ¹H NMR spectra of the 29 $^{9,10}L_D'^{(S)/1.5}L_A'^{(R)}$ mixture with Zn^{2+} and that of the 30 $^{9,10}L_D'^{(S)/1.5}L_A'^{(R)/1.5}L_A'^{(S)}$ mixture with Zn²⁺ comprised their individ-31 ual homoligand-assemblies (Supporting Information Figure S28). 32 These results suggest that self-complementary associations also oc-33 in the heterochiral $^{9,10}L_{D}'^{(S)/1.5}L_{A}'^{(R)}$ curred and 34 $^{9,10}L_D'^{(S)/1.5}L_A'^{(R)/1.5}L_A'^{(S)}$ systems (Scheme 3). All possible isomers 35 for the A/D/A-type heteroligand assemblies and A/A/A/A-type 36 homoligand assemblies from the hetero chiral pair 37 $({}^{9,10}L_{D}'^{(S)}/{}^{1,5}L_{A}'^{(R)}/{}^{1,5}L_{A}'^{(S)})$ were optimized by DFT to check the rel-38 ative energy of the isomers (Supporting Information Figure S29). 39 The DFT study indicated that the overall energy gain by the change 40 from a homochiral pair to a hetero chiral pair is at most only 1.00 41 kcal/mol, which is not a sufficient driving bias to change over com-42 plementary association (A-D-A) from self-complementary associ-43 ation (D/D/D/D and A/A/A). Conversely, in the $^{9,10}L_D{}^{\prime(S)/15}L_A{}^{\prime(R)/15}L_A{}^{\prime(S)}$ system, a maximum of nine isomers were 44 envisioned for $({}^{1,5}L_A {}^{\prime (R \text{ or } S)})_4 - (Zn^{2+})_2$ depending on the arrangement 45 of $L_A'^{(R)}$ and $L_A'^{(S)}$. Although we could not determine the major iso-46 mer because of NMR line broadening of $({}^{1,5}L_{A}'^{(R \text{ or } S)})_{4-}(Zn^{2+})_{2}$ 47 (Supporting Information Figure S28), the DFT calculations sug-48 gested a small energy difference ($\Delta E < 8.03$ kcal/mol) between the 49 possible isomers of $({}^{1,5}L_{A}'(R \text{ or } S))_4 - (Zn^{2+})_2$ (Supporting Information 50 Figure S29). Hence, the $({}^{1,5}L_{A'}(R \text{ or } S))_4 - (Zn^{2+})_2$ assembly formation 51 should be statistical in nature. 52

Effects of Substituent Positions in Donor and Acceptor Ligands on Self-Sorting. Finally, we investigated how positions of the imidazole side arms in the donor and acceptor ligands affect Zn2+-assisted self-complementary or complementary association.²⁵⁻³⁰ To this end, we synthesized a 1,5-substituted donor lig



Scheme 3. Summary of Zn^{2+} -driven assembly in (a) ${}^{9,10}Lp^{2}(S)/15LA^{(R)}$ mixture (b) ^{9,10}L_D^{,(S)/1,5}L_A^{,(R)/1,5}L_A^{,(S)} mixture.



Figure 5. Orange solid lines show the observed UV-vis absorption spectra of (a) ${}^{9,10}L_{D}{}^{'(S)/1.5}L_{A}{}^{'(R)}$ mixture ([${}^{9,10}L_{D}{}^{'(S)}$]₀ = 1.0 × 10⁻⁵ M and [${}^{1,5}L_{A}{}^{'(R)}$]₀ = 1.0 × 10⁻⁵ M) in the presence of Zn^{2+} (6.0 × 10⁻⁵ M), (b) ^{9,10}Lp'(⁽⁵⁾/^{1,5}LA'(^(R)/^{1,5}LA'(^(S))</sup> mixture ([^{9,10}Lp'(^(S))]₀ = 1.0×10^{-5} M, $[^{1,5}L_{A}'^{(R)}]_{0} = 5.0 \times 10^{-6}$ M, and $[^{1,5}L_{A}'^{(S)}]_{0} = 5.0 \times 10^{-6}$ M) in the presence of Zn^{2+} (6.0 × 10⁻⁵ M) in acetonitrile. Dashed lines show calculated UV–vis absorption spectra obtained from the sum of the absorption spectra of the homoligand-assemblies in the ratios: (a) $\binom{9,10}{L_D} L_{-}^{(S)}$ (2n²⁺)₂ (50%) and $\binom{1,5}{L_A} L_{-}^{(R)}$ (2n²⁺)₂ (50%), (b) $({}^{9,10}L_{D}{}^{(S)})_{4-}(Zn^{2+})_{2}(50\%), ({}^{1,5}L_{A}{}^{(R)})_{4-}(Zn^{2+})_{2}(25\%), and ({}^{1,5}L_{A}{}^{(S)})_{4-}(Zn^{2+})_{2}(25\%).$

and $({}^{1,5}L_D)$ and used ${}^{1,5}L_D$ as an isomorphous 1,5-substituted acceptor ligand ($^{1,5}L_A$). DFT-based modeling of a ($^{9,10}L_D$)($^{1,5}L_D$)₂-(Zn²⁺)₂ structure indicated that the combination of ^{9,10}L_D and ^{1,5}L_D could have three anthracene rings in an almost complete overlapping position (Scheme 4). To investigate this possibility, we conducted



Scheme 4. Summary of Zn²⁺-driven assembly in ^{9,10}L_D/1.⁵L_D mixture. Optimized structure of (^{9,10}L_D)(^{1.5}L_D)₂-Zn²⁺ calculated by DFT/B3LYP/6-31G(d) [C, H, N, O]; LANL2DZ (Zn).

UV-vis titration and ¹H NMR studies of a ^{9,10}L_D/^{1,5}L_D mixture in the presence of Zn²⁺ (Figure 6a,b and 7d, respectively). Prior to these experiments, we used NMR to determine the homoligand assembly of ^{1,5}L_D in combination with ESI-mass spectrometry and the UV-vis titration of ^{1,5}L_D with Zn²⁺ to confirm the stoichiometry of the self-complementary associations as $[^{1,5}L_D]$: $[Zn^{2+}] = 2:1$ (see details in the Supporting Information Figure S30-34). On the basis of these results we conclude that ${}^{1,5}L_{\rm D}$ also formed an open-type Zn₂L₄ assembly $[(^{1,5}L_D)_4 - (Zn^{2+})_2]$ as in the case of $^{1,5}L_A$. Figure 6a shows the UV-vis absorption spectral changes during titration of the $^{9,10}L_D/^{1,5}L_D$ mixture with Zn^{2+} in acetonitrile, where essentially two sets of spectral characteristics were observed in response to the molar ratio of $[Zn^{2+}]/([{}^{9,10}L_D]_0 + [{}^{1,5}L_D]_0) = 0.00-0.25$ (first phase: right blue lines) and 0.25-0.50 (second phase: dark blue lines). Quantitative analysis of the differential absorption spectra obtained from the titration experiments indicates that the observed spectral changes at the first and second phase mainly arose from homoligand assembly formation of ^{1,5}L_D and ^{9,10}L_D, respectively (Supporting Information Figure S34). The resulting UV-vis absorption spectrum of the ${}^{9,10}L_D/{}^{1,5}L_D$ mixture with Zn^{2+} (Figure 6b blue solid line) agreed well with a calculated absorption spectrum (Figure 6b black dashed line) obtained from the sum of the absorption spectra of the individual homo-assemblies $[(^{9,10}L_D)_4 - (Zn^{2+})_2]$ and $(^{1,5}L_D)_4 - (Zn^{2+})_2$ (Zn²⁺)₂], thus suggesting self-complementary association (narcissistic self-sorting) occurred in the ${}^{9,10}L_D/{}^{1,5}L_D$ system (Scheme 4). Further conclusive evidence for narcissistic self-sorting was obtained from ¹H NMR spectroscopy. The ^{9,10}L_D/^{1,5}L_D mixture with Zn²⁺ had a NMR spectrum (Figure 7d; Supporting Information Figure S35) that comprised individual homoligand assemblies (blue closed and open circles), which was apparent when the spectrum was compared with that of $({}^{9,10}L_D)_4 - (Zn^{2+})_2$ and $({}^{1,5}L_D)_4 - (Zn^{2+})_2$ (Figure 7f and e, respectively). The negative results obtained with ^{1,5}L_D (isomorphous of ^{1,5}L_A) underlines the importance of CT interactions for complementary association (social self-sorting) between the donor $({}^{9,10}L_D)$ and acceptor $({}^{1,5}L_A)$ ligands with Zn^{2+} .



Figure 6. (a,c) UV–vis absorption spectral changes during titration of (a) ${}^{9,10}L_D/{}^{1,5}L_D$ mixture ([${}^{9,10}L_D$]₀ = 2.0 × 10⁻⁵ M and [${}^{1,5}L_D$]₀ = 2.0 × 10⁻⁵ M) with Zn^{2+} [0–1.0 × 10⁻⁵ M (right blue lines)–6.0 × 10⁻⁵ M (dark blue lines)], (c) ${}^{1,5}L_D/{}^{1,5}L_A$ mixture ([${}^{1,5}L_D$]₀ = 2.0 × 10⁻⁵ M and [${}^{1,5}L_A$]₀ = 2.0 × 10⁻⁵ M) with Zn^{2+} (0—6.0 × 10⁻⁵ M) in acetonitrile at 298 K. Insets show plots of absorbance at (a) λ = 500 nm vs [Zn^{2+}]/([${}^{9,10}L_D$]₀ + [${}^{1,5}L_D$]₀), (c) λ = 460 nm vs [Zn^{2+}]/([${}^{1,5}L_D$]₀ + [${}^{1,5}L_D$]₀). (b,d) Solid lines show the observed UV–vis absorption spectra of (b) ${}^{9,10}L_D/{}^{1,5}L_D$ mixture ([${}^{9,10}L_D$]₀ = 2.0 × 10⁻⁵ M) with Zn^{2+} (2.0 × 10⁻⁵ M), (d) ${}^{1,5}L_D$ ${}^{1,5}L_A$ mixture ([${}^{1,5}L_D$]₀ = 2.0 × 10⁻⁵ M) with Zn^{2+} (2.0 × 10⁻⁵ M), in acetonitrile. Dashed lines show calculated UV–vis absorption spectra obtained from the sum of the absorption spectra of the homoligand-assemblies in the ratios: (b) (${}^{9,10}L_D$)₄–(Zn^{2+})₂ (50%), (d) (${}^{1,5}L_D$)₄–(Zn^{2+})₂ (50%) and (${}^{1,5}L_A$)₄–(Zn^{2+})₂ (50%).

As a further comparative experiment, we also examined the possibility of complementary association (social self-sorting) between ^{1,5}L_D and ^{1,5}L_A (isomorphous pair) by the same procedure as that used for the ^{9,10}L_D/^{1,5}L_D system. Prior to the experiments, we performed DFT-based modeling of a A-D-A stack $[(^{1,5}L_D)(^{1,5}L_A)_{2-}(Zn^{2+})_2]$ and a D-A-D stack $[(^{1,5}L_D)_2(^{1,5}L_A)-(Zn^{2+})_2]$. Hence, we predicted three aromatic rings in a partial overlapping fashion for both A-D-A and D-A-D stacking (Scheme 5). The ^{1,5}L_D/^{1,5}L_A mixture underwent UV–vis absorption spectral changes during the titration with Zn²⁺ (Figure 6c). The spectral changes were completed when 0.5 eq of Zn²⁺ was added relative to the total concentration of ^{1,5}L_D and ^{1,5}L_A (Figure 6c inset), whereas no clear isosbestic point was observed. On the basis of the obtained stoichiometry of

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Scheme 5. Summary of Zn^{2+} -driven assembly in ${}^{1,5}L_D/{}^{1,5}L_A$ mixture. Optimized structures of $({}^{1,5}L_D)({}^{1,5}L_A)_2 - Zn^{2+}$ and $({}^{1,5}L_D)_2({}^{1,5}L_A) - Zn^{2+}$ calculated by DFT/B3LYP/6-31G(d) [C, H, N, O]; LANL2DZ (Zn). Color code, ${}^{1,5}L_D$: blue, ${}^{1,5}L_A$: red, Zn^{2+} : yellow.

 $[Zn^{2+}]/([^{1,5}L_D]_0 + [^{1,5}L_A]_0) = 0.50, Zn_2L_4$ assemblies were envisioned for the ^{1,5}L_D/^{1,5}L_A system with Zn²⁺. The resulting UV-vis absorption spectrum of the $^{1,5}L_D/^{1,5}L_A$ mixture with Zn^{2+} (Figure 6d orange solid line) showed no CT band and a subtle difference from that of a calculated absorption spectrum (Figure 6d black dashed line) of the sum of the absorption spectra of the individual homo-assemblies [($^{1,5}L_D$)₄–(Zn²⁺)₂ and ($^{1,5}L_A$)₄–(Zn²⁺)₂]. A ¹H NMR spectrum of the ${}^{1,5}L_D/{}^{1,5}L_A$ mixture with Zn^{2+} (Figure 7c) had a large number of weak signals over a wide chemical shift range. The resulting featureless NMR spectrum (Figure 7c) likely arises from statistical association of ^{1,5}L_D and ^{1,5}L_A in the Zn₂L₄ assemblies owing to their structural similarity (Scheme 5). There are nine possible isomers depending on the arrangement of ¹⁵L_D and ^{1,5}L_A in Zn₂L₄. DFTbased structures of the homoligand Zn₂L₄ assemblies are geometrically similar to their homoligand assemblies (Figure 7a). ESI-mass (positive) spectrum of the ${}^{15}L_{D}/{}^{15}L_{A}$ mixture with Zn²⁺ (Figure 7b) provided the signals due to Zn₂L₄ assemblies containing ^{1,5}L_D and ^{1,5}L_A ligands ([(^{1,5}L_D)_n(^{1,5}L_A)(4 - n)Zn₂(OSO₂CF₃)₂]²⁺ (n = 1-4)), whose relative intensity ratio was essentially statistical in nature. These results suggest that the substitution position of the imidazole side arms in donor and acceptor ligands also determines whether donor/acceptor systems follow self-complementary association (narcissistic self-sorting) or complementary association (social self-sorting). In addition to these experimental results, we



Figure 7. (a) Possible Zn₂L₄ isomers obtained from ^{1.5}L_D/^{1.5}L_A mixture. The structures were optimized by DFT/B3LYP/6-31G(d) [C, H, N, O]; LANL2DZ (Zn), which were modeled considering quasi symmetry and the vacant sites of Zn²⁺ were occupied by acetonitrile molecules. (b) Positive ESI-MS spectrometry of ^{1.5}L_D/^{1.5}L_A mixture in acetonitrile with the presence of Zn²⁺. Simulated ESI-MS spectra of [(^{1.5}L_D)/_n(^{1.5}L_A)/₄- _n/Zn₂(OSO₂CF₃)₂]²⁺ (n = 1-4). Mass spectrum of the whole region is given in Supporting Information Figure S37. (c-f) ¹H NMR spectra of (c) ^{1.5}L_D/^{1.5}L_A mixture [1^{1.5}L_D]₀ = 2.0×10^{-3} M and [1^{.5}L_A]₀ = 2.0×10^{-3} M) with Zn²⁺ (4.0 $\times 10^{-3}$ M), (d) ^{9.10}L_D/^{1.5}L_D mixture (1^{9.10}L_D)₀ = 2.0×10^{-3} M and [1^{.6}L_D]₀ = 2.0×10^{-3} M) with Zn²⁺ (4.0 $\times 10^{-3}$ M), (c) (1^{.5}L_D)₄-(Zn²⁺)₂, and (f) (^{9.10}L_D)₄-(Zn²⁺)₂ (D₃C₃) Cl₃C₃)² and (1^{.5}L_D)₄-(Zn²⁺)₂, respectively. Inset: (e) Structure of (1^{.6}L_D)₄-(Zn²⁺)₂ determined by NMR analysis. Color code, ^{9.10}L_D; blue, ^{1.5}L_A: red, Zn²⁺: yellow, H: white.

conducted systematic structural modeling of A-D-A and D-A-D stacking structures of donor and acceptor ligands with different substitution positions through the use of DFT methods, where only the combination of ${}^{9,10}L_D$ and ${}^{1.5}L_A$ leads to three aromatic rings in an almost complete overlapping position (Supporting Information Figure S36). Thus, these data further verified the proposed A-D-A assembly between ${}^{9,10}L_D$ and ${}^{1.5}L_A$ and their CT interactions.

SUMMARY AND CONCLUSIONS

In conclusion, we have successfully demonstrated that CT interactions effectively determine whether a combination of D and A ditopic ligands will associate in self-complementary (D/D/D/D and A/A/A/A) or complementary (A/D/A) fashion upon metal-ion clipping. The D and A ditopic ligands (^{9,10}L_D and ^{1,5}L_A, respectively) consisted of two imidazole side arms through ethynyl spacers, which were pre-designed to form an alternating A-D-A stack upon clipping by two Zn²⁺ ions. Hence, ^{9,10}L_D and ^{1,5}L_A favor the formation of an alternating A-D-A assembly $[(^{9,10}L_D)(^{1.5}L_A)_2-(Zn^{2+})_2]$ with Zn²⁺. However, once the CT interactions were weakened by

subtle modifications of the imidazole side arms, the corresponding reference ligands 9,10 Lp'(S) and 1,5 LA'(S) associated into self-complementary structures (D/D/D/D or A/A/A/A), giving rise to their homoligand-assemblies $[({}^{9,10}L_D{}'{}^{(S)})_4 - (Zn^{2+})_2$ and $({}^{1,5}L_A{}'{}^{(S)})_4 - (Zn^{2+})_2$ $(Zn^{2+})_2$]. Self-complementary association (narcissistic self-sorting) observed between $^{9,10}L_{D'}^{(S)}$ and $^{1,5}L_{A'}^{(S)}$ (homochiral pair) was preserved even in heterochiral pairs $({}^{9,10}L_{D}'^{(S)}/{}^{1,5}L_{A}'^{(R)}$ and $^{9,10}L_{D'}(S)/^{1,5}L_{A'}(R)/^{1,5}L_{A'}(R)$. In the same manner, narcissistic selfsorting, assisted by Zn²⁺-binding, took place between the positional isomer of the donor ligands $({}^{9,10}L_D$ and ${}^{1,5}L_D$), giving rise to their homoligand assemblies, $({}^{9,10}L_D)_4 - (Zn^{2+})_2$ and $({}^{1,5}L_D)_4 - (Zn^{2+})_2$. Conversely, an isomorphous pair of the donor and acceptor ligands $(^{1,5}L_{D} \text{ and } ^{1,5}L_{A})$ with Zn^{2+} resulted in statistical formation of $Zn_{2}L_{4}$ assemblies. Thus, the present work reveals that the weak attractive forces of CT interactions have considerable potential as a useful molecular recognition motif that can control self-complementary and complementary molecular associations in supramolecular systems, which will be informative for CT-based functional materials.³¹⁻³³

ASSOCIATED CONTENT

Supporting Information. Experimental details, TD DFT of A-D-A assembly, titration analysis, ESI mass spectra, NMR assignment of the assemblies using ¹H,¹H COSY and 2D-ROESY NMR spectra, optimized structures of the assemblies and association constant of A-D-A assembly. This material is available free of charge via the Internet at <u>http://pubs.acs.org</u>.

• AUTHOR INFORMATION

Corresponding Author

yuasaj@rs.tus.ac.jp

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 - (17) ${}^{1,5}L_{A'}{}^{(S)}$ first formed the assembly with Zn^{2+} prior to forming the Zn^{2+} -assembly with ${}^{9,10}L_{D'}{}^{(S)}$ (Scheme 2b). The higher affinity of ${}^{1.5}L_{A'}{}^{(S)}$ than that of ${}^{9,10}L_{D'}{}^{(S)}$ for Zn^{2+} might be attributed to the positions of the imidazole side arm in ${}^{1.5}L_{A'}{}^{(S)}$, which provides appropriate coordination vectors for building the L₄Zn₂-assembly in a tetrahedral coordination.

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- (20) The mass peak at m/z = 1794.13 corresponds to $\{({}^{9,10}L_D)({}^{1.5}L_A)_2(Zn)_2(OSO_2CF_3)_3 + H\}^+$, where one of the two the anthraquinone molecules could undergo one-electron reduction $({}^{1.5}L_A + e^- \rightarrow {}^{1.5}L_A^+)$ during the ionization process.
- (21) Closed-type complexes might offer another possible geometry for the L_4Zn_2 structure; however, such a coordination geometry causes strain in the ditopic ligands. A DFT study indicated that the proposed open-type L_4Zn_2 structures (insets of Figure 4b and c) are 91.8 and 59.9 kcal/mol lower in energy than those of the closed-type complexes (Supporting Information Figure S17).
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- (33) For future applications of the A-D-A system, we confirmed the stability of the one-electron reduced species of the acceptor ligand by reversible cyclic voltammetry of the ^{1,5}L_A⁻⁻ /^{1,5}L_A redox system and direct detection of ^{1,5}L_A⁻⁻ by electron spin resonance (ESR) spectroscopy (Supporting Information Figure S39). Conversely, the ^{9,10}L_D/^{9,10}L_D⁻⁺ redox system is irreversible, suggesting that the one electron oxidized species of the donor ligand is unstable. Further synthetic modification of the donor ligand should be necessary to use the present A-D-A system as a CT-based material.