Doctoral Dissertation

Development of Chirality-Organized Redox-Active Conjugates with Oligoanilines

Satoshi Ohmura

January 2013

Department of Applied Chemistry

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（不斉組織化されたレドックス活性なオリゴアニリン共役系の開発）

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Preface

The studies presented in this dissertation were performed under the guidance of Prof. Toshikazu Hirao, Department of Applied Chemistry, Graduate School of Engineering, Osaka University during 2007-2013.

The objects of this dissertation are studies on chiral regulation and their redox properties of oligoanilines through intramolecular hydrogen bondings by the introduction of amino acid moieties.

The author hopes that this basic work described in this dissertation contributes to the further development of chirality-organized polymeric anilines, macromolecular complex, organic luminescence materials, and so on.

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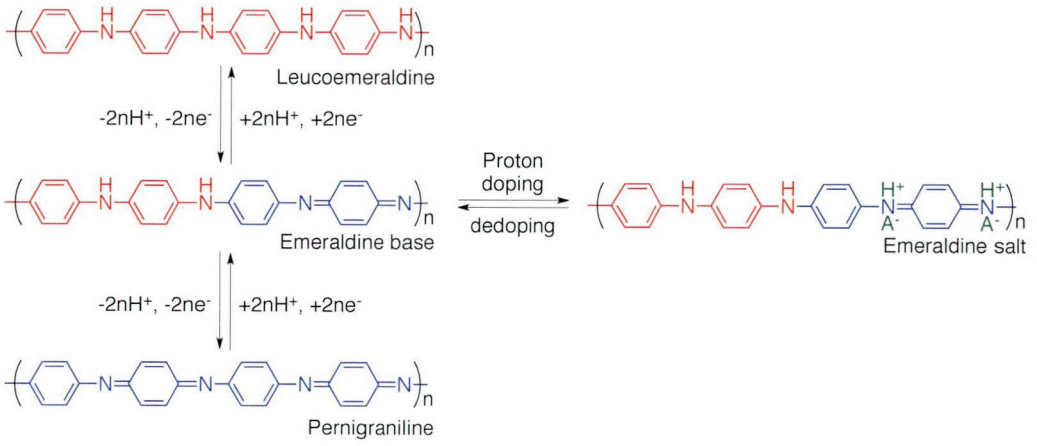
Contents

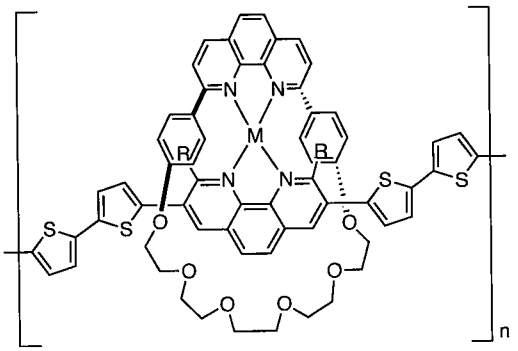
General Introduction

Polymers and oligomers containing π-conjugated functional groups have increasingly attracted attention because of their potential applications in electronic materials due to their electrical properties.[1] In 2000, Heeger, MacDiarmid and Shirakawa received the Nobel Prize in Chemistry for the discovery and subsequent development of these materials.[1c] The conformations and redox properties of π-conjugated backbones can also be controlled for further functionalization.[2] Polyanilines are one of the most important π-conjugated polymers with chemical stability and straightforward to synthesize.[3] Polyaniline is a phynylene-based polymer having amino group on either side of phenylene ring. The oxidation and reduction take place on the polymer chain. Aniline basically undergoes oxidative polymerization in the presence of a protonic acid. The product formed is a simple 1,4-coupling of the monomer. Protonation induces an insulator-to-conductor transition, while the number of π-electrons in the chain remains constant. Polyanilines are also unique among conducting polymers in that they have a reversible and relatively simple acid-base doping-dedoping pathway, useful for tuning its electrical and optical properties.[4] Polyaniline possesses three different discrete redox forms, which are the fully oxidized pernigranilne base, the half oxidized emeraldine base, and the fully reduced leucoemeraldine (Scheme 1).[1]



Scheme 1.

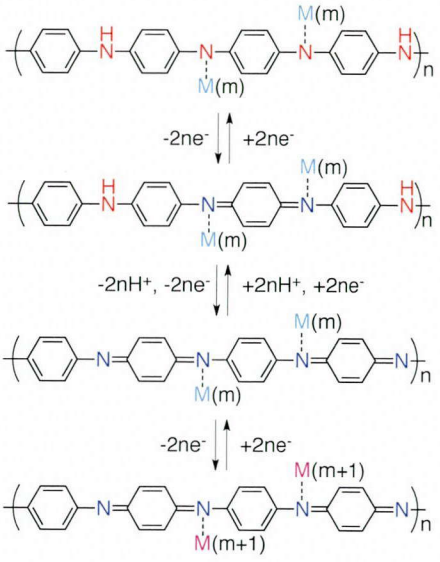
Coupling transition metal complexes to π-conjugated polymers and oligomers gives hybrid materials in which the properties of the metal complex may be coupled to those of the conjugated backbone.[5] In this approach, the polymer or oligomer acts as a ligand to the metal. There exists a diverse collection of systems that incorporate transition metals into conducting polymer structures. For example, Kern, Sauvage and their coworkers have published extensively on entwined conducting metallopolymers (Figure 1),[6] and Wolf and his coworkers have classified metal-containing polythiophenes according to the location of the metal moieties.[7]



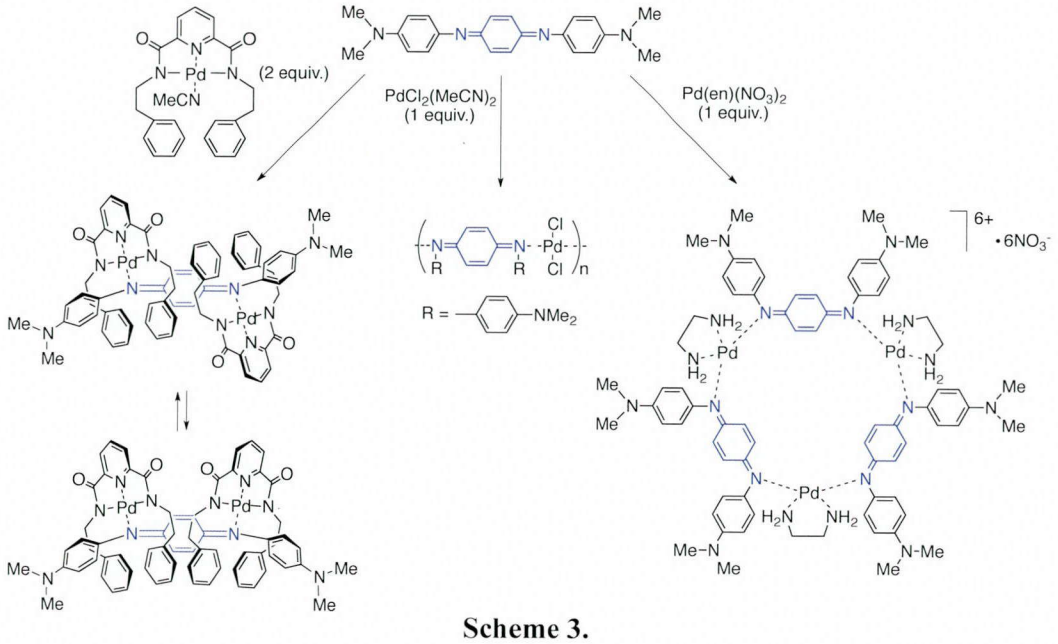
M = none, Cu, Zn, Co
R = H, Me

Figure 1. Examples of entwined metallopolymers.

One of the interesting properties of polyanilines is the coordination ability of the two nitrogen atoms on the quinonediimine moiety. The quinonediimine moiety has been found to be capable of complexation to afford d,π-conjugated polymer complexes.[8] This type of polymer complex permits the construction of the redox systems with electronic communication between metals (Scheme 2). Hirao's group has achieved the synthesis of d,π-conjugated complexes of polyanilines and derivatives with various metal salts, and investigated their redox properties and catalytic activities.[9] Also, controlled complexation with redox-active quinonediimine derivatives has been demonstrated to create conjugated polymeric, trimetallic, or bimetallic complexes, depending on the coordination modes (Scheme 3).[10]



Scheme 2.



Scheme 3.

Helical chirality is common in important biopolymers such as proteins, nucleic acids and DNA, and it often contributes to the exceptional specificity of metabolic processes in animals and plants where the active sites to enzymes bind almost exclusively to only one hand of an enantiomeric pair of substrates. As a consequence, there has been intense research interest for several decades in the design and synthetic chiral polymers that may mimic the exceptional behavior of biological polymers. A wide range of such organic polymers have been synthesized and applied in areas as diverse as chiral sensors, chiral catalysts, and chromatographic separations of enantiomeric drugs.[11] Conducting organic polymers that possess chirality show some unique opportunities when they used as chiral substrates or as chiral electrode materials. In 1985, Baughman's group proposed that optical activity could be induced in the π-conjugation moieties by either the presence of enantiopure substituents or the incorporation of a chiral dopant anion onto the polymer chains.[12] The former approach has been subsequently found to be efficacious for the synthesis of a wide range of chiral polypyrroles and polytiophenes (Figure 2), while the latter route has proven widely successful for generating chiral polyanilines.[13]

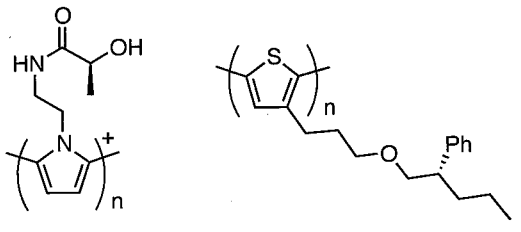


Figure 2. Examples of chiral polypyrrole and polythiophene.

Chiral polyanilines have been focused on because of their potential applications to molecular recognition, chiral separation, and so on.[14] In pioneering studies, Kaner's group has shown from electronic spectral changes and flow-injection quartz microbalance studies that chiral polyaniline films exhibit chiral discrimination between the enantiomeric amino acids.[15] Chiral polyanilines have been synthesized by doping with a chiral acid,[16] polymerization of anilines in the presence of a chiral acid dopant (Figure 3a),[17] or templated polymerization of anilines in the presence of a chiral molecular template.[18] The induction of chirality in π-conjugated polyanilines through chiral complexation with chiral palladium(II) complex has been achieved to afford chiral conjugated polymer complexes (Figure 3b).[19] However, polyanilines bearing chiral substituents in order to induce chirality have only been reported in a few cases to date.[20]

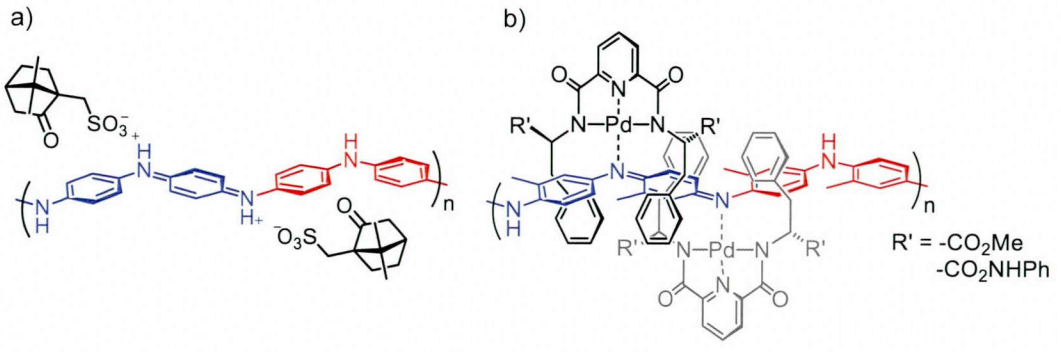


Figure 3. a) Chiral induced polyaniline with chiral acid dopant. b) Chiral induced polyaniline through chiral complexation.

In contrast, control of hydrogen bonding is regarded as a potential strategy to design various molecular assemblies by virtue of directionality and specificity.[21] The utilization of amino acid moieties, which possess chiral centers and hydrogen bonding sites, is considered to be a convenient approach to a highly ordered system. In this system, inter/intramolecular hydrogen bonding plays an important role in enforcing well-defined assembly structures. Hirao's group has demonstrated chirality organization through the intramolecular and/or intermolecular hydrogen bondings by the introduction of amino acids or dipeptide chains into molecular scaffolds such as ferrocene,[21c, 22a] pyridine,[22b] or urea.[22c] Meanwhile, chiral π-conjugated polymers or oligomers with amino acid moieties were reported (Figure 4).[23] However, to the best of my knowledge, there are no report about structural and physical properties of polyanilines which are perturbed from intramolecular hydrogen bonding. From this point of view, the introduction of the amino acid moieties into oligoanilines to induce chirality-organized structures and modify the redox species by intramolecular hydrogen bonding interactions is studied (Figure 5).

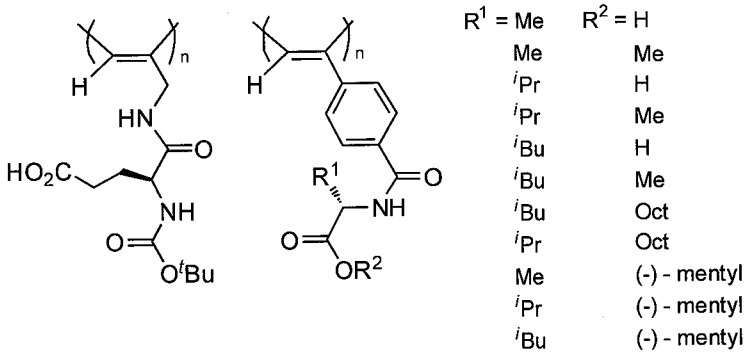


Figure 4. Examples of chiral π-conjugated polymers bearing amino acid moieties.

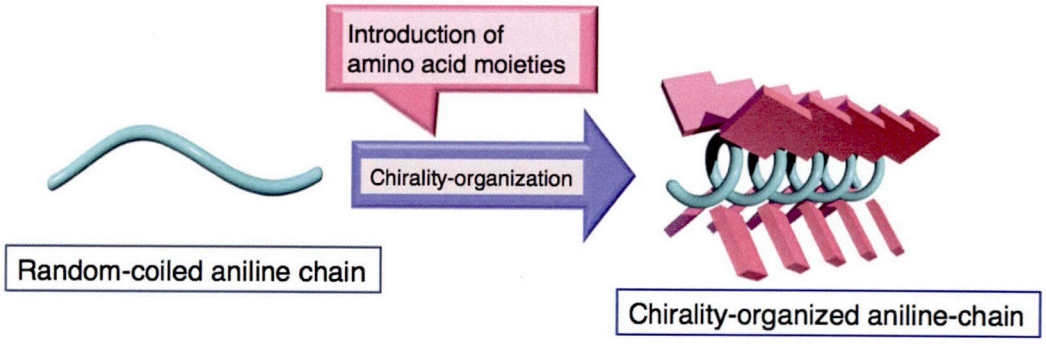


Figure 5. Concept of this work.

This dissertation deals with the studies on structural and redox properties of chirality-organized polyaniline derivatives and its oligomers through intramolecular hydrogen bondings based on the introduction of amino acid moieties.

Chapter 1 describes the syntheses and their chiral structural properties of polyanilines and oligoanilines bearing amino acid moieties. Chapter 2 describes the synthesis of phenylenediamines and quinonediimines bearing amino acid moieties and their structural and redox properties through intramolecular hydrogen bonding or complexation with palladium(II) atoms. Chapter 3 describes the luminescence-switching properties of phenylenediamine derivatives based on their redox states.

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Chapter 1. Chirality organized polyanilines and oligoanilines bearing amino acid moieties

1-1. Introduction

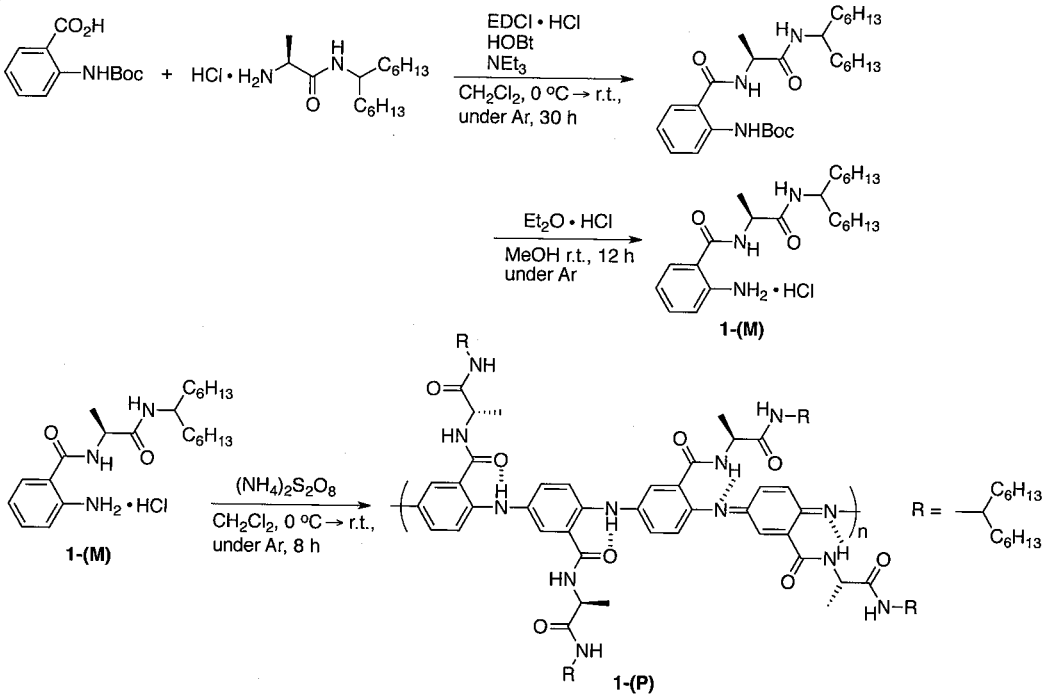
The synthesis of chiral conjugated polymers in particular has remained one of the most intriguing issues in polymer science. The methods proposed for preparing chiral conjugated polymers include the polymerization of monomers bearing chiral center,[1] asymmetric selective polymerization,[2] the introduction of a chiral group into an achiral polymer by the polymer reaction,[3] polymerization in a cholesteric liquid crystal field,[4] and electrochemical polymerization using a chiral nematic electrolyte.[5] A chiral polyaniline complex has been recently synthesized by various methods, however, there have been few reports on polyanilie bearing chiral center via covalent bonds.[6] From this point of view, the structural and optical properties of chirality-organized polyaniline bearing amino acid moieties were investigated.

On the other hand, oligomers not only provide the opportunity to design and produce synthetically well-defined and well-characterized species with defined functionality and properties, but are also used as model compounds to elucidate the structural and physical properties of polymers.[7] The oligomer approach using tetra(aniline) derivatives bearing amino acid moieties were also synthesized and studied.

1-2. Result and Discussion

1-2-1. Synthesis and structural property of polyaniline bearing amino acid moieties

The chiral amino acid moiety was introduced into Boc-protected anthranilic acid via condensation reaction using by the carbodiimide. Then, the monomer unit **1-(M)** was obtained by Boc-deprotection under acidic condition. The thus-obtained chiral aniline derivative was fully characterized spectroscopically. The chiral polymer **1-(P)** was prepared by polymerization with $(NH_4)_2S_2O_8$ in a H_2O/CH_2Cl_2 system (Scheme 1).



Scheme 1.

The obtained compound **1-(P)** through oxidative polymerization was investigated by the MALDI-TOF mass spectrum. The peak positions were consistent with the molecular weight of monomer-unit and the maximum observed number of polymerized monomer was octamer in the measuring condition ($[M]^+ = 3114.4$, n = 2) (Figure 1).

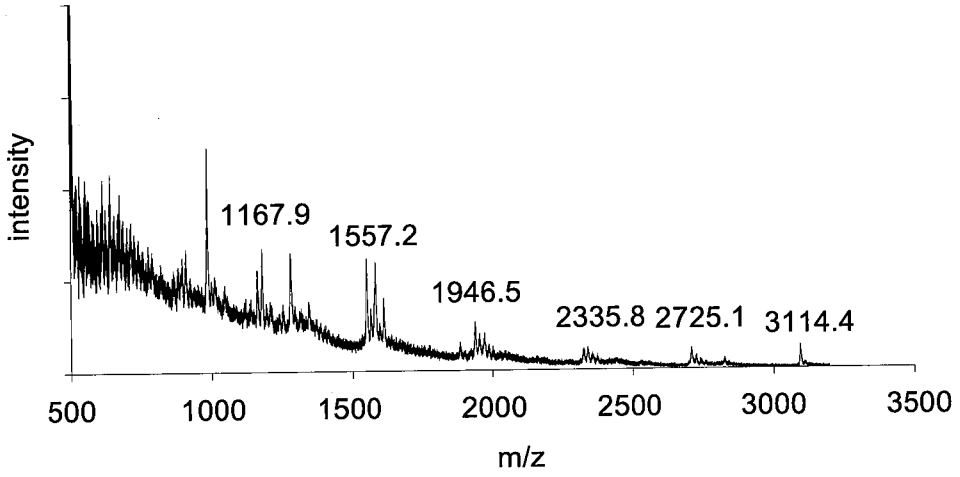


Figure 1. MALDI-TOF mass spectrum of **1-(P)**.

The electronic spectrum of **1-(P)** in dichloromethane exhibited a broad absorption at around 450-900 nm, which is probably due to a low-energy charge-transfer transition of the π-conjugated moiety (Figure 2a). It should be noted that **1-(P)** exhibits an induced circular dichroism (ICD) at the absorbance region of the π-conjugated moiety shown in Figure 2b. This result might indicate that the chirality induction of a π-conjugated backbone aniline polymer is achieved by the chirality organization through the intramolecular hydrogen bonding.

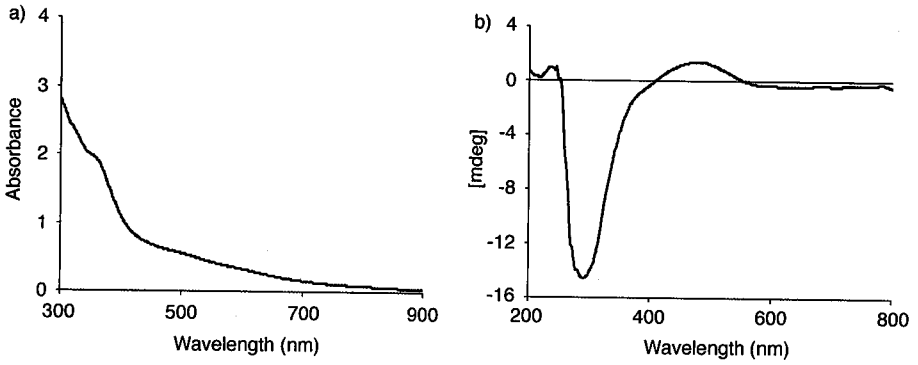


Figure 2. a) The electronic spectrum and b) CD spectrum of **1-(P)** in dichloromethane at 25 °C under a nitrogen atmosphere.

1-2-2. Synthesis, structural and redox properties of oligoanilines bearing amino acid moieties

In the preceding section, a chiral aniline polymer was obtained by polymerization of chiral aniline monomer. To gain insight into the chirality organization of polyaniline through intramolecular hydrogen bonding, oligoanilines bearing hydrogen bonding sites were synthesized and investigated. Two types of oligomers, **2** and **4**, bearing alanine moieties as an amino acid group, are designed to investigate the chirality-organized structures (Figure 3). Oligomers **2** and **4** were synthesized from L/D-alanine methyl ester hydrochloride salt and the carboxylic acids, which were prepared from the ethyl esters **3** and **5**. The thus-obtained aniline oligomers were fully characterized by spectral data and elemental analyses.

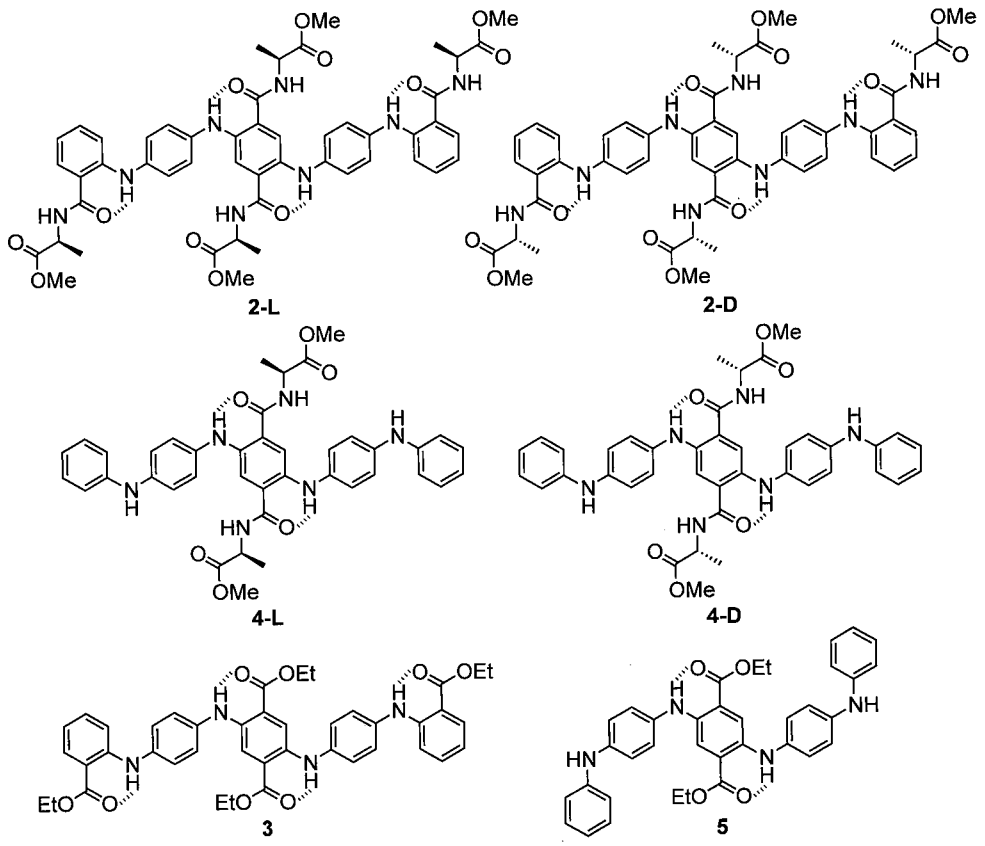


Figure 3. Structures of aniline tetramer derivatives.

In the ^{1}H NMR spectra of **2-L** in CD_2Cl_2 (5.0 x 10^{-3} M), the central-amino NHs of the aniline moieties were hardly perturbed by the addition of an aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: δ = 9.26, CD_2Cl_2- DMSO-d_6 (9:1): δ = 9.28) although the terminal-amino NHs showed a slight downfield shift (CD_2Cl_2: δ = 8.02, CD_2Cl_2-DMSO-d_6(9:1): δ = 8.27). The FT-IR spectrum of **2-L** in dichloromethane (5.0 x 10^{-3} M) showed the hydrogen-bonded NHs stretching bands at 3293 and 3333 cm^{-1}. The central-amino NHs are indicated to be locked in strong intramolecular hydrogen bondings and the terminal-amino NHs might participate in weak intramolecular

hydrogen bondings in a solution state. The ^{1}H NMR spectra of **4-L** in CD_2Cl_2 (5.0 x 10^{-3} M) indicate that the central-amino NHs of the aniline chain were hardly perturbed by the addition of an aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: δ = 7.94, CD_2Cl_2-DMSO-d_6(9:1): δ = 8.17), although the terminal-amino NHs were perturbed decidedly (CD_2Cl_2: δ = 5.70, CD_2Cl_2- DMSO-d_6(9:1): δ = 6.48). The FT-IR spectrum of **4-L** in CH_2Cl_2 (5.0 x 10^{-3} M) showed the hydrogen-bonded NHs and no hydrogen-bonded NHs stretching bands at 3342 and 3423 cm^{-1} in a solution state, respectively. These results indicate that the central-amino NHs form the intramolecular hydrogen bonding although the terminal-amino NHs do not participate in hydrogen bonding (Table 1 and 2).

Table 1. Selected ^{1}H NMR data for compounds **2-5**.

		^{1}H NMR N-H (ppm) (5.0 x 10^{-3} M)		
		CD_2Cl_2	CD_2Cl_2/DMSO-d_6 (9:1)	CD_2Cl_2/DMSO-d_6 (1:1)
2-L	amide (central)	6.74	8.19	8.90
	amide (terminal)	6.69	7.73	8.65
	amine (central)	9.26	9.28	9.42
	amine (terminal)	8.02	8.27	8.53
4-L	amide (central)	6.85	8.17	8.85
	amine (central)	7.94	8.04	8.40
	amine (terminal)	5.70	6.48	7.63
3	amine (central)	9.40	9.41	
	amine (terminal)	8.75	8.75	
5	amine (central)	8.63	8.60	
	amine (terminal)	5.73	7.04	

Table 2. Selected FT-IR data for compounds **2-5**.

compound	$\nu_{N\text{-}H}$ (cm^{-1}) [a]
2	3441, 3418, 3375, 3340
4	3411, 3337
3	3424, 3342
5	3416, 3360

[a] 5.0×10^{-3} M in CH_2Cl_2

The electronic spectrum of **2-L** in CH_2Cl_2 exhibited a broad absorption at around 450 nm, which is probably due to a low-energy charge-transfer transition of the π-conjugated moiety (Figure 4a). It should be noted that **2-L** exhibits an induced circular dichroism (ICD) at the absorbance region of the π-conjugated moiety. This result indicates that the chirality induction of a π-conjugated backbone aniline oligomer is achieved by the chirality organization based on the intramolecular hydrogen bonding. The mirror image of the CD signals observed with **2-L** was obtained in the CD spectrum of **2-D** as shown in Figure 4b, indicating that a chiral molecular arrangement based on the regulated structures via intramolecular hydrogen bonding is formed. ICD and the mirror-imaged CD signals were also observed in the case of **4**. The CD signals of **2-L** were changed at around 360 nm by the addition of DMSO (Figure 4c). On the contrary, only a little change of the CD signals was observed in the case of **4-L**. The shape of the CD signal of **2** in CH_2Cl_2-DMSO (1:1) is similar to that of **4** in CH_2Cl_2-DMSO (1:1). From the above-mentioned results of the ^1H NMR and FT-IR experiments, the chirality-organized structure is considered to be preserved through the

intramolecular hydrogen bonding of the center-amino NHs in CH_2Cl_2-DMSO (1:1).

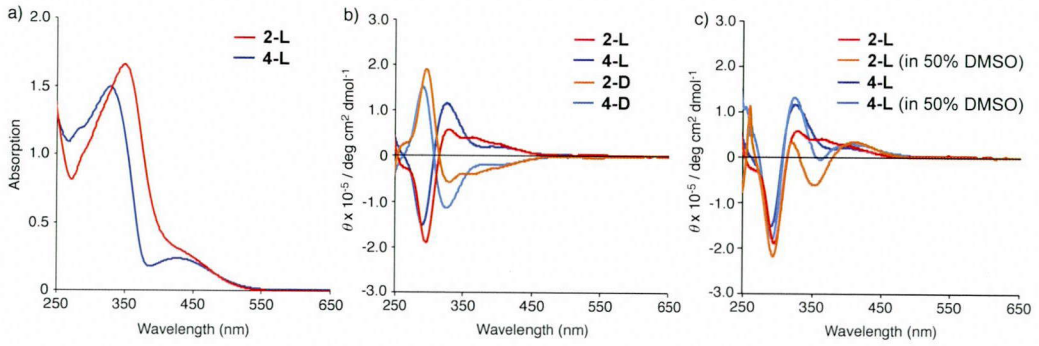


Figure 4. a) Absorption spectra of **2-L** and **4-L**. b) CD spectra of **2** and **4** in dichloromethane (5.0 x 10^{-5} M) under a nitrogen atmosphere. c) CD spectra of **2-L** and **4-L** in dichloromethane-DMSO (1:1) (5.0 x 10^{-5} M) at 25 °C under a nitrogen atmosphere.

On the basis of these observations, the structural elucidation of **2** and **4** was investigated by crystal structural analysis of the ethyl ester **3** and **5**. The crystal structure of the tetraethyl ester **3** revealed the formation of the intramolecular hydrogen bondings between the amino NH and carbonyl CO, resulting in an *anti-anti-anti*-conformation of the π-conjugated moiety. The orientation of the benzene rings has the dihedral angles of 149.5(2)° (central) and 125.4(1)° (terminal) as shown in Figure 5a. A similar structure is considered to be formed with **2** to permit chirality-organization of the aniline oligomer through intramolecular hydrogen bondings of the amino acid moieties. The packing structure of the tetraethyl ester **3** exhibited the ordered-layer structure through π-π stacking (Figure 5b). Contrary to the molecular structure of **4**, a *syn-anti-syn*-conformation of the π-conjugated moieties based on intramolecular

hydrogen bonding was observed in the crystal structure of the diethyl ester **5** (Figure 6a). This difference might arise from the existence of the hydrogen bondings. While all NHs of **3** participated in the intramolecular hydrogen bondings to regulate the conformation of the π-conjugated moieties, the terminal moieties of **5** were not regulated because of the absence of the hydrogen bondings in the terminal amino NHs. The formation of the intramolecular hydrogen bondings was found to play an important role in the structural regulation of the π-conjugated moieties. The orientation of the benzene rings of **5** has the dihedral angles of 98.15(4)° (central) and 62.52(6)° (terminal). Contrary to the packing structure of **3**, the diethyl ester **5** exhibited the sheet-like self-assembly through the intermolecular hydrogen bonding networks, wherein each molecule is bonded to two neighboring molecules by an 18-membered hydrogen-bonded ring (Figure 6b).

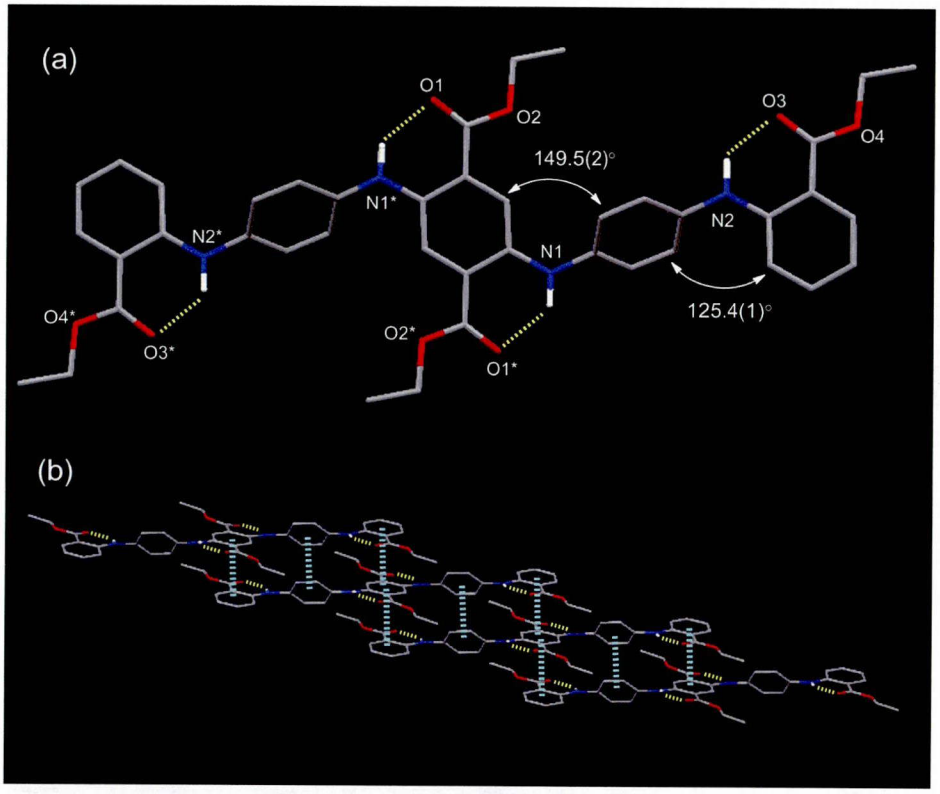


Figure 5. a) Crystal structure of **3**. b) Portion of a layer containing the ordered-layer structure through π-π stacking in the crystal packing of **3**.

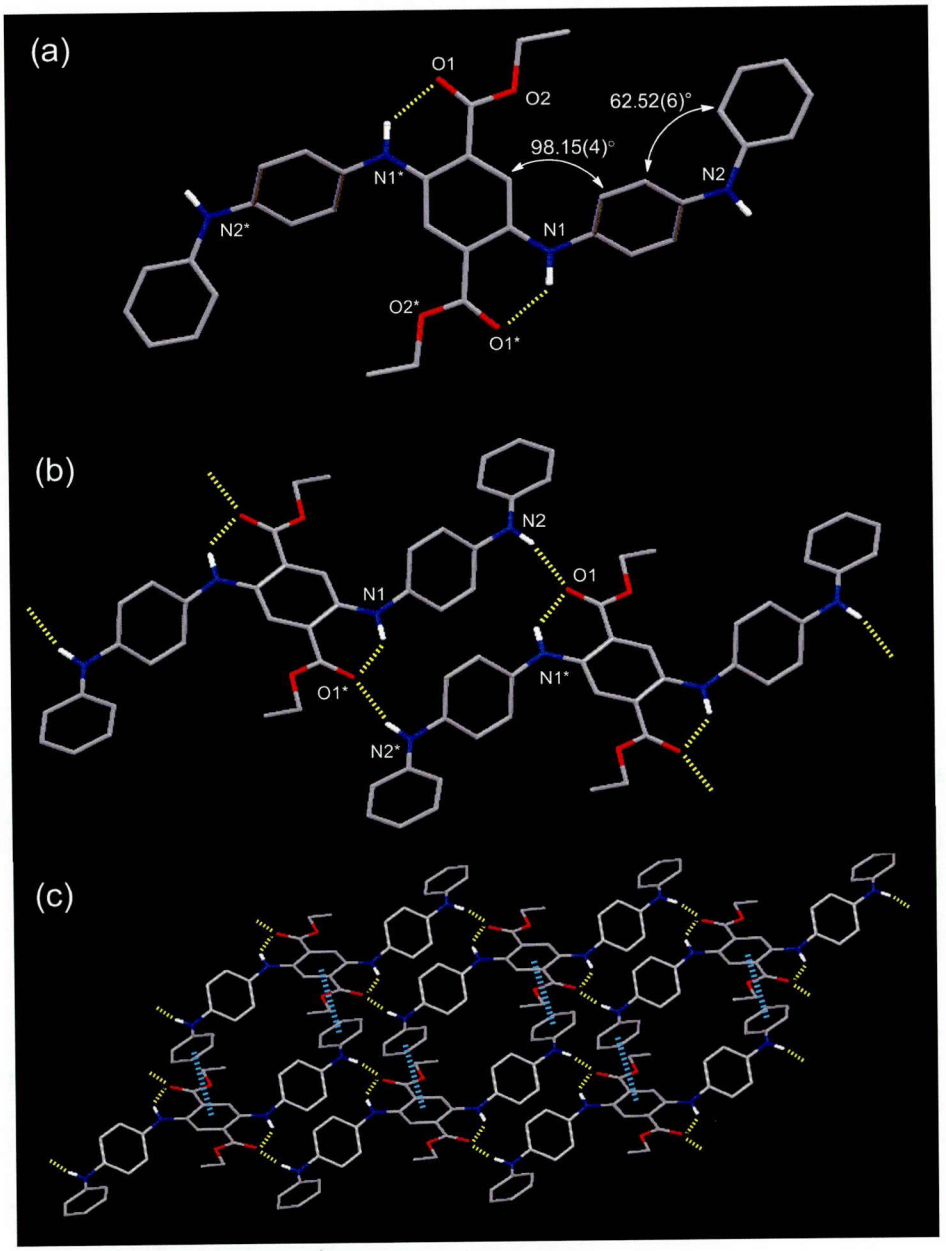


Figure 6. a) Crystal structure of **5**. b) Portion of a layer containing the sheet-like self-assembly through intermolecular hydrogen bonding networks. c) Portion of the π-π stacking in the crystal packing of **5**.

The redox properties of **2-5** were disclosed by cyclic voltammetry (Figure 7). Tetraalanyl oligomer **2-L** in dichloromethane showed three consecutive redox waves ($E_{1/2}$ = 0.24, 0.44, and 0.76 V vs. Fc/Fc^+) as depicted in Figure 8a. The waves at 0.24 and 0.44 V were assigned to consecutive one-electron oxidation of the phenylenediamine moieties to give the corresponding oxidized species. The most positive anodic peak with twice height ($E_{1/2}$ = 0.76 V) is attractive to successive one-electron oxidation processes of the two terminal phenylenediamine moieties. The three successive redox waves ($E_{1/2}$ = -0.06, 0.09, and 0.48 V vs. Fc/Fc^+) were also observed in the cyclic voltammogram of dialanyl oligomer **4-L**. All of the redox waves were more cathodic that those of **2-L**. The shift is probably due to the absence of the electron-withdrawing substituent at the terminal benzene rings.

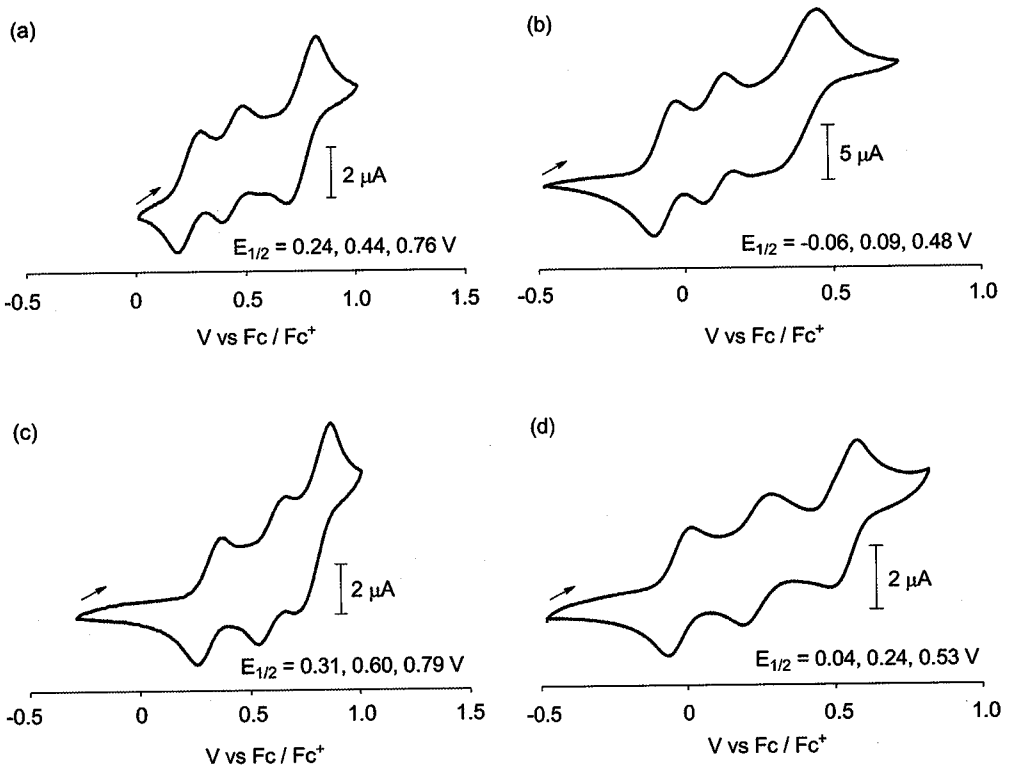


Figure 7. Cyclic voltammograms of (a) **2-L**, (b) **4-L**, (c) **3**, and (d) **5** in dichloromethane (5.0 x 10^{-4} M) containing 0.1 M Bu_4NClO_4 at a platinum working electrode with a scan rate 100 mV s^{-1} under an argon atmosphere.

1-3. Summary

In conclusion, polyaniline and oligoaniline derivatives bearing amino acid moieties were synthesized. Chiralty organization of the π-conjugated moiety has been achieved by the introduction of amino acid moiety. In the investigation of oligoanilines bearing intramolecular hydrogen bonding sites, the formation of the intramolecular hydrogen bondings was found to play an important role in the conformational regulation of the π-conjugated aniline backbone. The chirality organization of oligoanilines was obtained by the introduction of amino acid moieties through intramolecular hydrogen bonding.

1-4. Experimental Section

General Methods

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were obtained with a JASCO FT/IR-480 Plus spectrometer. ^{1}H NMR spectra were recorded on a JEOL JNM-ECP 400 or a JNM-ECS 400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS DX-303 spectrometer. MALDI-TOF mass spectra was measured on a Bruker AUTOFLEX III using 1,8-dihydroxy-9(10H)-anthracenone as a matrix. UV/vis spectra were recorded using a HITACHI U-3500 spectrophotometer monitoring under an argon atmosphere at 25 °C. Circular dichroism spectra were recorded using a JASCO J-820 spectropolalimeter. UV/vis and circular dichroism measurements were conducted using 1-cm pathlength quartz cuvettes. Cyclic voltammograms were recorded on a BAS CV-50W voltammetry analyzer under an argon atmosphere at 25 °C.

Syntheses of Aniline derivative 1-(M)

Anhydrous dichloromethane (40 mL) was added to a mixture of Boc-protected anthranilic acid[8] (237 mg, 1.0 mmol), 1-hydroxybenzotriazole (162 mg, 1.2 mmol), (*S*)-2-amino-*N*-(tridecan-7-yl)propanamide hydrochloride[9] (307 mg, 1.0 mmol), and triethylamine (diluted, 2.5 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (230 mg, 1.2 mmol) in

anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. the mixture was stirred at ambient temperature for 30 h. The resulting mixture was diluted with dichloromethane (20 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 3:1) to give the expected Boc-protected aniline derivative as a white solid. Hydrogen chloride solution in diethyl ether (20 mL) was added to a mixture of thus-obtained compound and anhydrous tetrahydrofuran (10 mL), and stirred at ambient temperature for 12 h under an argon atmosphere. After evaporation of the solvent, a residue was washed with anhydrous diethyl ether to give **1-(M)** as an colorless oil (260 mg, 0.6 mmol).

1-(M): Isolated yield 60%; ^{1}H NMR (400 MHz, $CDCl_3$, 1.0 x 10^{-2} M) δ 10.22 (s, 2H), 8.31 (d, 1H, J = 7.8 Hz), 7.47 (dd, 1 H, J = 7.8, 1.4 Hz), 7.38 (d, 1H, J = 6.6 Hz), 7.43 (dd, 1 H, J = 8.0, 1 5 Hz), 6.96 (t, 1H, J = 8.0 Hz), 6.63 (s, 1H), 4.56 (quant., 1H, J = 6.9 Hz), 3.87-3.82 (m, 1H), 1.45 (d, 3H, J = 6.9 Hz), 1.31-1.13 (m, 20 H), 0.83 (t, 3H, J = 7.3 Hz), 0.77 (t, 3H, J = 7.3 Hz)

Polymerization Procedure for Synthesis of 1-(P).

1-(M) (260 mg, 0.6 mmol) was dissolved in 5 mL of dichloromethane at 0 °C. Subsequently, a solution of $(NH_4)_2S_2O_8$ (164 mg, 0.7 mmol) in 1 mL of water was added, and the mixture was stirred for 8 h. The mixture was poured into a large volume of

methanol. The precipitate was collected by filtration and dried in vacuo to give **1-(P)** (116.8 mg, 50% yield) as a dark-purple solid.

Synthesis of Ethyl 2-(4-Aminophenylamino)benzoate.

To a mixture of cesium carbonate (3.10 g, 9.5 mmol), palladium(II) acetate (89.8 mg, 0.40 mmol), (±)-BINAP (218 mg, 0.35 mmol), ethyl 2-bromobenzoate (454 mg, 2.0 mmol), and *p*-phenylenediamine (865 mg, 8.0 mmol) was added anhydrous toluene (40 mL). The mixture was stirred at 100 °C for 48 h under an argon atmosphere. After cooling to ambient temperature, dichloromethane (30 mL) was added to the brown suspension and filtered. After evaporation of the solvent, a residue was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 4:1) to give the expected compound (62.0 mg, 0.24 mmol) as a brown-yellow solid, R_f = 0.64 (hexane/ethyl acetate = 5:2).

Ethyl 2-(4-Aminophenylamino)benzoate: Isolated yield 66%; mp 73 °C (uncorrected.); IR (KBr) 3289, 3253, 3033, 2992, 2975, 1681, 1583, 1522, 1478, 1449 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 9.17 (s, 1H), 7.93 (dd, 1H, J = 7.8, 1.8 Hz), 7.23 (dt, 1H, J = 7.8, 1.8 Hz), 7.02 (dd, 2H, J = 6.4, 1.8 Hz), 6.89 (dd, 1H, J = 7.8, 0.9 Hz), 6.69 (dd, 2H, J = 6.4, 1.8 Hz), 6.62 (dt, 1H, J = 7.8, 0.9 Hz), 4.33 (q, 2H, J = 7.3 Hz), 3.69 (s, 2H), 1.38 (t, 3H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 168.9, 150.5, 144.5, 134.3, 131.8, 131.6, 126.7, 116.1, 116.0, 113.6, 111.2, 60.9, 14.6 ppm; HRMS (FAB) *m/z*: $[M]^+$ 256.1220, $C_{15}H_{16}N_2O_2$ (calc. 256.1212); Anal. Calcd. for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93; O, 15.82. Found: C, 71.15; H, 5.91; N, 6.87.

General Procedure for Synthesis of Tetraalanyl Oligoaniline Derivative 2.

A mixture of **3** (73.0 mg 0.1 mmol) and sodium hydroxide (c.a. 180 mg) in tetrahydrofuran (10 mL) was refluxed for 27 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1N HCl aqueous solution. The dark brown precipitate was isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture of the thus-obtained dark brown solid, 1-hydroxybenzotriazole (108 mg, 0.8 mmol), L/D-alanine methyl ester hydrochloride (112 mg, 0.8 mmol), and triethylamine (diluted, 0.5 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (154 mg, 0.8 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 25 h. The resulting mixture was diluted with dichloromethane (10 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from dichloromethane to dichloromethane/ethyl acetate = 3:1) to give **2** as a yellow solid (**2-L**: 162 mg; **2-D**: 87.6 mg), R_f = 0.25 (dichloromethane/ethyl acetate = 3:1).

2-L: Isolated yield 61%; mp 167-168 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3316, 1696, 1578, 1522, 1443, 1414, 1313, 1237, 1211 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 9.26 (s, 2H), 8.02 (s, 2H), 7.53 (s, 2H), 7.50 (d, 2H, J = 7.9 Hz),

7.27 (t, 2H, J = 7.9 Hz), 7.19 (d, 2H, 7.9 Hz), 7.15 (d, 4H, J = 6.7 Hz), 7.06 (d, 4H, J = 6.7 Hz), 7.00 (d, 2H, J = 7.3 Hz), 6.74 (t, 2H, J = 7.9 Hz), 6.69 (d, 2H, J = 6.9 Hz), 4.71 (quint., 2H, J = 7.3 Hz), 4.64 (quint., 2H, J = 7.3 Hz), 3.77 (s, 6H), 3.72 (s, 6H), 1.50 (d, 6H, J = 7.3 Hz), 1.42 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.9, 173.4, 169.3, 167.6, 147.3, 139.0, 137.3, 136.0, 132.9, 128.2, 125.0, 123.9, 120.7, 118.4, 117.5, 116.8, 115.0, 52.9, 52.8, 48.9, 48.8, 18.6, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 958.3864, $C_{50}H_{54}N_8O_{12}$ (calc. 958.3861) Anal. Calcd. for $C_{50}H_{54}N_8O_{12}$: C, 62.62; H, 5.68; N, 11.68; O, 20.02. Found: C, 62.48; H, 5.41; N, 11.54.

2-D: Isolated yield 33%; mp 166-168 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3316, 1696, 1578, 1522, 1443, 1414, 1313, 1237, 1211 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 9.26 (s, 2H), 8.02 (s, 2H), 7.53 (s, 2H), 7.50 (d, 2H, J = 7.9 Hz), 7.27 (t, 2H, J = 7.9 Hz), 7.19 (d, 2H, 7.9 Hz), 7.15 (d, 4H, J = 6.7 Hz), 7.06 (d, 4H, J = 6.7 Hz), 7.00 (d, 2H, J = 7.3 Hz), 6.74 (t, 2H, J = 7.9 Hz), 6.69 (d, 2H, J = 6.9 Hz), 4.71 (quint., 2H, J = 7.3 Hz), 4.64 (quint., 2H, J = 7.3 Hz), 3.77 (s, 6H), 3.72 (s, 6H), 1.50 (d, 6H, J = 7.3 Hz), 1.42 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.9, 173.4, 169.3, 167.6, 147.3, 139.0, 137.3, 136.0, 132.9, 128.2, 125.0, 123.9, 120.7, 118.4, 117.5, 116.8, 115.0, 52.9, 52.8, 48.9, 48.8, 18.6, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 958.3858, $C_{50}H_{54}N_8O_{12}$ (calc. 958.3861).

General Procedure for Synthesis of Dialanyl Oligoaniline Derivative 4.

A mixture of **5** (58.6 mg, 0.1 mmol) and sodium hydroxide (c.a. 100 mg) in tetrahydrofuran (10 mL) was refluxed for 20 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1N HCl aqueous solution. The dark brown precipitate was isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture of the thus-obtained black solid, 1-hydroxybenzotriazole (27.0 mg, 0.20 mmol), L/D-alanine methyl ester hydrochloride (27.9 mg, 0.20 mmol), and triethylamine (diluted, 0.5 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (38.3 mg, 0.2 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 45 h. The resulting mixture was diluted with dichloromethane (10 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from dichloromethane to dichloromethane/methanol = 10:1) to give **4** as a yellow solid (**4-L**: 29.2 mg; **4-D**: 18.9 mg), R_f = 0.63 (dichloromethane/methanol = 10:1).

4-L: Isolated yield 42%; mp 178-180 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3424, 3342, 2848, 1738, 1651, 1594, 1508, 1211, 1162, 1063 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 7.94 (s, 2H), 7.48 (s, 2H), 7.22 (t, 4H, J = 7.3 Hz), 7.08 (d, 4H,

J = 9.2 Hz), 7.03 (d, 4H, J = 9.2 Hz), 6.99 (d, 4H, J = 7.3 Hz), 6.85 (t, 4H, J = 7.3 Hz), 5.70 (s, 2H), 4.64 (quant., 2H, J = 7.3 Hz), 3.71 (s, 6H), 1.41 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.6, 167.6, 144.8, 137.9, 137.7, 137.6, 129.7, 124.7, 121.2, 121.0, 120.3, 118.2, 116.6, 52.9, 48.9, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 700.2998, $C_{40}H_{40}N_6O_6$ (calc. 700.3009)

4-D: Isolated yield 27%; mp 179-181 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3424, 3342, 2848, 1738, 1651, 1594, 1508, 1211, 1162, 1063 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 7.94 (s, 2H), 7.48 (s, 2H), 7.22 (t, 4H, J = 7.3 Hz), 7.08 (d, 4H, J = 9.2 Hz), 7.03 (d, 4H, J = 9.2 Hz), 6.99 (d, 4H, J = 7.3 Hz), 6.85 (t, 4H, J = 7.3 Hz), 5.70 (s, 2H), 4.64 (quant., 2H, J = 7.3 Hz), 3.71 (s, 6H), 1.41 (d, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 173.6, 167.6, 144.8, 137.9, 137.7, 137.6, 129.7, 124.7, 121.2, 121.0, 120.3, 118.2, 116.6, 52.9, 48.9, 18.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 700.3022, $C_{40}H_{40}N_6O_6$ (calc. 700.3009)

Synthesis of Tetraethyl Oligoaniline Derivative 3.

A solution of *p*-toluenesulfonate monohydrate (28.5 mg, 0.15 mmol) in ethanol (15 mL) was added to a mixture of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (51.3 mg, 0.20 mmol) and ethyl 2-(4-aminophenylamino)benzoate (154 mg, 0.60 mmol). The mixture was stirred at reflux for 12 h under an argon atmosphere. Once cooling to ambient temperature, the mixture was stirred at reflux for 32 h under oxygen atmosphere. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with ethanol, and dried in vacuo. Aniline tetramer **3** (157 mg) was obtained as a red crystal by recrystallization from dichloromethane.

3: Isolated yield 98%; mp 195-197 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3412, 3337, 3268, 3181, 3161, 1684, 1581, 1515, 1382, 1370, 1314 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 9.38 (s, 2H), 7.99 (s, 2H), 7.97 (d, 2H, J = 8.0 Hz), 7.30 (t, 2H, J = 8.0 Hz), 7.23-7.19 (m, 10H), 7.13 (d, 2H, J = 8.0 Hz), 6.70 (t, 2H, J = 8.0 Hz), 4.35 (q, 4H, J = 7.3 Hz), 4.33 (q, 4H, J = 7.3 Hz), 1.40 (t, 6H, J = 7.3 Hz), 1.34 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 167.7, 166.7, 148.1, 133.2, 130.8, 123.9, 123.8, 120.9, 120.3, 118.3, 117.4, 115.8, 115.7, 112.8, 110.9, 60.5, 59.9, 13.4, 13.2 ppm; HRMS (FAB) *m/z*: $[M]^+$ 730.2989, $C_{42}H_{42}N_4O_8$ (calc. 730.3003)

Synthesis of Diethyl Oligoaniline Derivative 5.

A mixture of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (256 mg, 1.0 mmol) and *p*-aminodiphenylamine (369 mg, 2.0 mmol) in acetic acid (15 mL) was stirred at 100 °C for 18 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with ethanol, and dried in vacuo. Chloroform (15 mL) was added to the pink solid, which was refluxed for 10 h under oxygen atmosphere. After evaporation of the solvent, **5** (498 mg) was obtained as a red crystal by recrystallization from toluene.

5: Isolated yield 85%; mp 211-213 °C (uncorrected); IR (CH_2Cl_2, 5.0 x 10^{-3} M) 3416, 3361, 2926, 1686, 1599, 1513, 1103, 1020 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) δ 8.63 (s, 2H), 7.89 (s, 2H), 7.24 (t, 4H, J = 7.8 Hz), 7.14 (d, 4H, J = 8.7 Hz), 7.10 (d, 4H, J = 8.7 Hz), 7.01 (d, 2H, J = 7.8 Hz), 6.86 (t, 2H, J = 7.8 Hz), 5.73 (s, 2H), 4.31 (q, 4H, J = 7.3 Hz), 1.33 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 5.0 x 10^{-3} M) 167.9, 144.8, 138.9, 138.2, 136.7, 129.7, 122.4, 120.8, 120.4, 119.0, 118.1, 116.7, 61.6, 14.4 ppm; HRMS (FAB) *m/z*: $[M]^+$ 586.2582, $C_{36}H_{34}N_4O_4$ (calc. 586.2580)

General Procedures of UV/vis and CD Measurements

UV/vis spectrum of **1-(P)** was measured in a deaerated dichloromethane solution with the concentration 5.0 x 10^{-4} M under an argon atmosphere at 25 °C. UV/vis spectra of **2** and **4** were measured in a deaerated dichloromethane solution with the concentration 5.0 x 10^{-5} M under an argon atmosphere at 25 °C. CD spectrum of **1-(P)** was measured in a deaerated dichloromethane solution with the concentration 5.0 x 10^{-4} M under an argon atmosphere at 25 °C. CD spectra of **2** and **4** were measured in a deaerated dichloromethane solution with the concentration 5.0 x 10^{-5} M under an argon atmosphere at 25 °C.

General Procedures of Electrochemical Experiments

The cyclic voltammetry was performed in a deaerated dichloromethane solution (5.0 x 10^{-4} M) containing 0.1 M Bu_4NClO_4 as a supporting electrolyte at 25 °C with a three-electrode system consisting of a platinum working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/Ag^+ (0.01 M) reference electrode (BAS) at 100 mVs^{-1} scan rate. Redox potentials are given vs Fc/Fc^+.

X-ray Structure Analysis

Measurements for **3** and **5** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Kα radiation. The structures of **3** and **5** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 3. Hydrogen bonds are listed in

Table 4. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-772855 for **3**, CCDC-772856 for **5**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data for **3** and **5**.

	3	**5**
formula	$C_{44}H_{46}N_4O_8Cl_4$	$C_{36}H_{34}N_4O_4$
formula weight	900.68	586.69
crystal system	triclinic	triclinic
space group	*P*-1 (No. 2)	*P*-1 (No. 2)
a, Å	10.03528(18)	8.03011(17)
b, Å	10.64666(19)	10.2142(2)
c, Å	10.76910(19)	11.2028(2)
α, deg	101.5160(7)	62.5560(10)
β, deg	102.3520(7)	71.5440(12)
γ, deg	101.8180(7)	68.5560(11)
V, Å^3	1063.88(3)	748.25(3)
Z	1	1
D_{calcd}, g cm^{-3}	1.406	1.302
μ(Cu Kα), cm^{-1}	30.157	6.915
T, °C	-150	-150
λ(Cu Kα), Å	1.54187	1.54187
*R*1 [a]	0.0512	0.0378
*wR*2 [b]	0.2205	0.1106

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 4. Intramolecular hydrogen bondings for **3** and **5**.

crystal	donor	acceptor	D • • • A (Å)	D–H • • • A (°)
3 [a]	N(1)	O(1*)	2.715(3)	130(3)
	N(1*)	O(1)	2.715(3)	130(3)
	N(2)	O(3)	2.697(3)	130(3)
	N(2*)	O(3*)	2.697(3)	130(3)
5 [a]	N(1)	O(1*)	2.7026(14)	155.9(18)
	N(1)	O(1)	2.7026(14)	155.9(18)

[a] The moleculars sits on an inversion center.

1-5. Reference

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8. T. Vilaivan, *Tetrahedron Lett.* **2006**, *47*, 6739-6742.
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Chapter 2. Structural and redox properties of chirality organized phenylenediamines and quinonediimines

2-1. Introduction

Oligomeric polyaniline analogues have been synthesized with a variety of well-defined conjugational lengths for the past decade, mostly because of their good solubility in common solvents, ease of crystallization, and chemical manipulation. The studies of structural and physical properties of the unit molecules of polyanilines allow the nature of π-conjugated polymers to be predicted. Thereby, structural and physical properties of aniline oligomers have been discussed in the recent literatures.[1] They are usually assumed to be dimers to tetramers but higher oligomers are produced under suitable conditions. For example, Janssen et al. synthesized and studied the doping and redox behavior of a series of *meta-para* aniline oligomers.[2] Phenylenediamines and quinonediimines, which are trimeric aniline derivatives, having redox center and two nitrogen atoms. In this chapter, chirality-organized phenylenediamines and quinonediimines bearing amino acid moieties are synthesized and investigated the structural and redox properties. In this chapter, redox-active trimeric aniline derivatives including two amino nitrogen atoms were studied.

2-2. Result and Discussion

2-2-1. Structural and redox properties of 2,5-substututed phenylenediamines and quinonediimines

The phenylenediamine derivatives **6red-L** and **6red-D**, which contain amino acid moieties L-Ala-OMe and D-Ala-OMe, respectively, and derivative **7red**, which contains the moieties L-Pro-OMe, were synthesized from the corresponding carboxylic acid form of the phenylenediamine derivative and L/D-amino acid methyl ester hydrochloride salt (Figure 1). Phenylenediamine derivatives **6red-L** and **7red** were oxidized into quinonediimine derivatives **6ox-L** and **7ox**, respectively, by treatment with iodosobenzene or lead(IV) acetate as an oxidant (Figure 1). The oxidized forms, **6ox-L** and **7ox**, could be reduced again to **6red-L** and **7red** with hydrazine monohydrate. The thus-obtained phenylenediamine and quinonediimine derivatives were fully characterized by spectroscopic and elemental analysis.

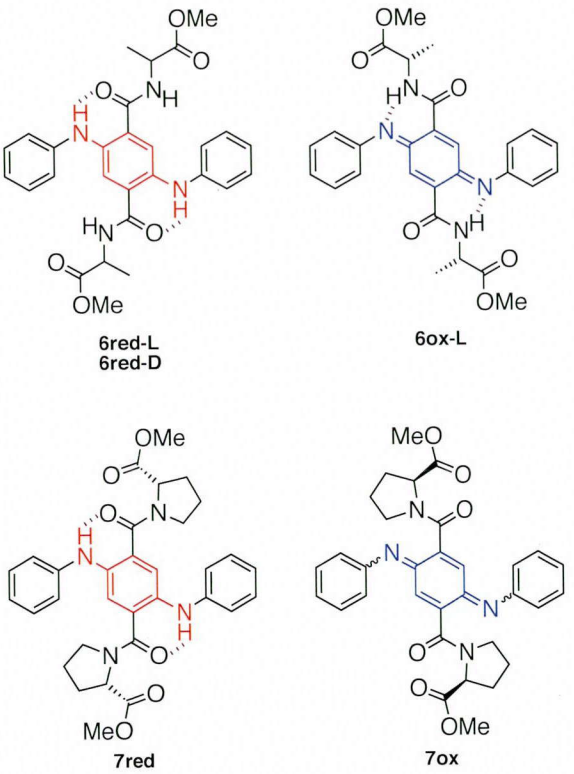


Figure 1. Phenylenediamines and quinonediimines bearing amino acid moieties.

In the ^{1}H NMR spectra of **6red-L** in CD_2Cl_2 (1.0×10^{-2} M), the NH signals for the phenylenediamine moiety were hardly perturbed by the addition of an aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: 8.05 ppm, CD_2Cl_2/DMSO-d_6 (9:1): 8.01 ppm) although the alanine amido NH signals showed a slight downfield shift (CD_2Cl_2: 7.02 ppm, CD_2Cl_2/DMSO-d_6 (9:1): 7.22 ppm). The FT-IR spectrum of **6red-L** in dichloromethane (1.0×10^{-2} M) showed stretching bands for the hydrogen bonded and non-hydrogen-bonded NH protons in solution at 3343 and 3426 cm^{-1}, respectively. The NH protons of the phenylenediamine moiety are shown to be conformationally locked by strong intramolecular hydrogen bonds and the alanine amido NH protons might

participate in weak hydrogen bonding in solution. The alanine amido NH protons were hardly perturbed by the addition of an aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: 10.35 ppm, CD_2Cl_2/DMSO-d_6 (9:1): 10.34 ppm) in the ^1H NMR spectra of **6ox-L** in CD_2Cl_2 (1.0×10^{-2} M). The quinonediimine moiety of **6ox-L** was also indicated to be regulated by intramolecular hydrogen bondings. The FT-IR spectrum of **6ox-L** in dichloromethane (1.0×10^{-2} M) showed a NH stretch at 3207 cm^{-1}, which confirms the hydrogen bonding in **6ox-L**. The ^1H NMR spectra of **7red** in CD_2Cl_2 (1.0×10^{-2} M) show that the NH protons of the phenylenediamine moiety were hardly perturbed by the addition of an aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: 7.13 ppm, CD_2Cl_2/DMSO-d_6 (9:1): 7.13 ppm). The FT-IR spectrum of **7red** in dichloromethane (1.0×10^{-2} M) showed a NH stretch bands at 3360 cm^{-1} in the solution state. These results indicate that the NH protons of the phenylenediamine moiety form intramolecular hydrogen bonds.

The electronic spectrum of the phenylenediamine **6red-L** in dichloromethane exhibited a broad absorption at around 400 nm, which is probably due to a low-energy charge-transfer transition of the π-conjugated moiety (Figure 2a). It should be noted that **6red-L** exhibited an induced circular dichroism (ICD) at the absorbance region of the π-conjugated moiety in the CD spectrum (Figure 2c). This result indicates that the chirality induction of the π-conjugated backbone aniline oligomer is achieved by chirality organization through the intramolecular hydrogen bonding. The mirror image of the CD signals observed with **6red-L** was obtained in the CD spectrum of **6red-D** (Figure 2c), thus indicating that a chiral molecular arrangement based on the regulated structures held together by intramolecular hydrogen bonding is formed. ICD at the

absorbance region of the π-conjugated moiety based on the chirality-organized structure through the intramolecular hydrogen bonding was also observed in the CD spectrum of the quinonediimine derivative **6ox-L** (Figure 2e). The chirality organization of **7red** through intramolecular hydrogen bonding was supported by the appearance of ICD in the absorbance region of the π-conjugated moiety in the CD spectrum (Figure 2f).

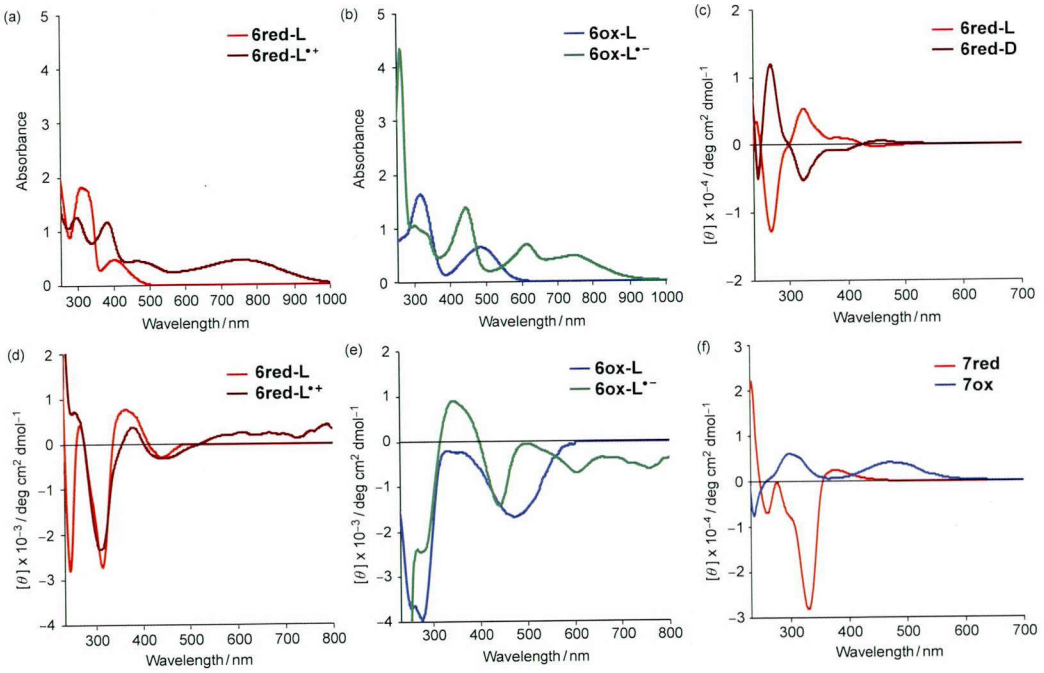


Figure 2. The electronic spectra of a) **6red-L** and **6red-L**$^{\cdot+}$. b) **6ox-L** and **6ox-L**$^{\cdot-}$ in acetonitrile (1.0 x 10^{-4} M). The CD spectra of c) **6red-L** and **6red-D**, f) **7red** in dichloromethane (1.0 x 10^{-4} M), and d) **6red-L** and **6red-L**$^{\cdot+}$. e) **6ox-L** and **6ox-L**$^{\cdot-}$ in acetonitrile (2.5 x 10^{-4} M) at 25 °C under a nitrogen atmosphere.

On the basis of these observations, the structural elucidation of **6red-L** was investigated by single-crystal X-ray spectroscopy. The crystal structure of **6red-L**

revealed the formation of intramolecular hydrogen bondings between the amino NH proton of the phenylenediamine moiety and the carbonyl oxygen atom, which resulted in an *anti*-conformation of the π-conjugated moiety (Figure 3a). Owing to π-conjugation of **6red-L**, the orientation of each terminal benzene ring should be within a limited range of locations parallel to the central benzene ring. However, the steric interaction between the hydrogen atom at C(3) (C(23)) and the hydrogen atom at C(25) (C(5)) causes the terminal benzene ring of **6red-L** to rotate away from this orientation, thereby resulting in a conformation with a dihedral angle of 138.3(2)° and 138.1(2)° between the terminal benzene and central benzene rings; this rotation results in a propeller twist between the planes of the two terminal benzene rings (Figure 3a). The chirality of the alanine moieties is considered to induce a propeller twist in the π-conjugated moiety. The molecular structure of **6red-D** composed of the corresponding D-amino acid (-D-Ala-OMe) is a mirror image of **6red-L**, which indicates that is a conformational isomer (Figure 3c). As a result, the introduction of amino acid moieties into the phenylenediamine moiety was found to induce the chirality organization through the intramolecular hydrogen bondings. The phenylenediamine derivative **6red-L** exhibited the sheet-like self-assembly through the intermolecular hydrogen bonding networks, wherein each molecule is bound to two neighboring molecules in an 18-menbered hydrogen-bonded ring (O(1)···N(3*), 2.832(5) Å; O(11*)···N(13), 2.842(5) Å; Figure 3b). The mirror-image sheet-like molecular arrangement was observed in the crystal packing of **6red-D** (Figure 3d).

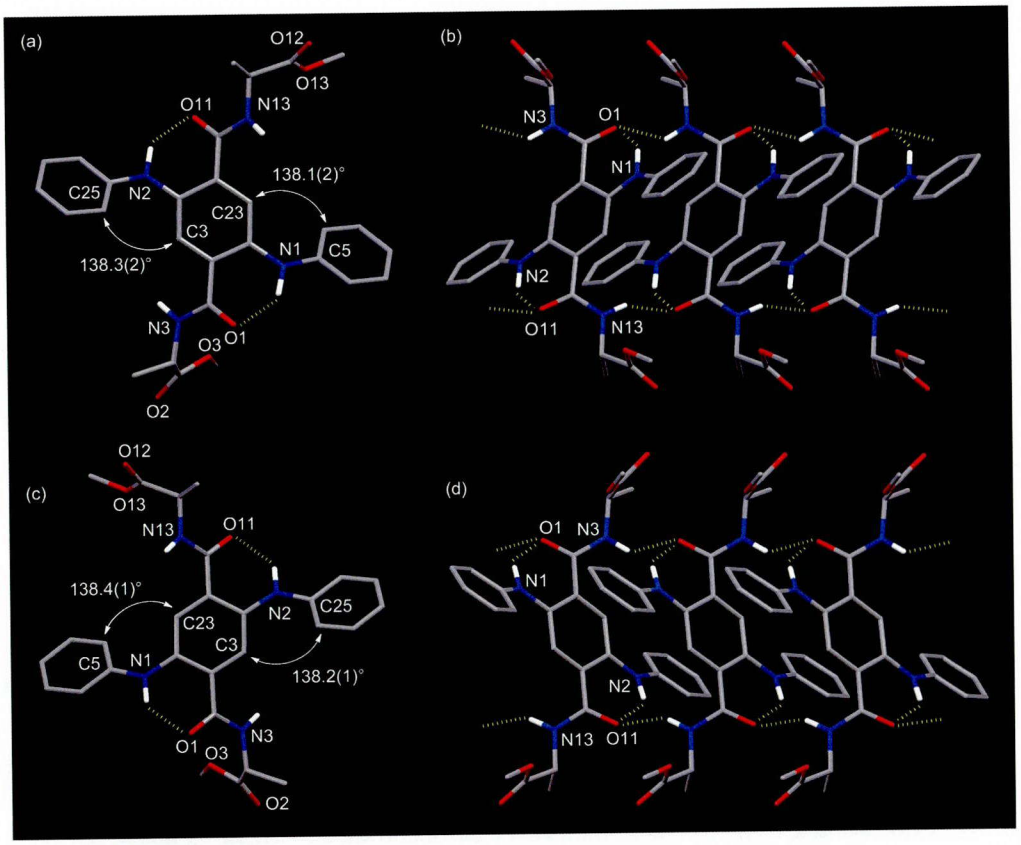


Figure 3. Molecular structures of a) **6red-L** and c) **6red-D**. A portion of a layer containing a sheet-like molecular arrangement through the intermolecular hydrogen bonding networks in the crystal packing of b) **6red-L** and d) **6red-D**.

The redox processes of **6** and **7** were investigated by cyclic voltammetry. The phenylenediamine derivative **6red-L** in dichloromethane showed two one-electron redox waves ($E_{1/2}$ = 0.19 and 0.55 V vs. Fc/Fc^{+}) as shown in Figure 4a, which can be assigned to successive one-electron-oxidation processes of the phenylenediamine moiety to give the corresponding oxidized species. The two one-electron redox waves ($E_{1/2}$ = 0.21 and 0.58 V vs. Fc/Fc^{+}) based the successive one-electron-oxidation

processes of the phenylenediamine moiety were also observed in the cyclic voltammogram of the phenylenediamine derivative **6red-L** (Figure 4c). Interestingly, the quinonediimine derivative **6ox-L** exhibited two one-electron redox waves ($E_{1/2}$ = -1.25 and -1.03 V vs. Fc/Fc^{+}), which can be assigned to the successive one-electron-reduction processes of the quinonediimine moiety to give the corresponding reduced species (Figure 4b). Generally, the generated radical anion appears to be unstable, although this depends on the availability of a proton source. In the case of **6ox-L**, the formation of intramolecular hydrogen bonding is thought to stabilize the corresponding reduced species. On the contrary, the reduction waves (E_{pc} = -1.80 and -1.34 V vs. Fc/Fc^{+}) of the quinonediimine derivative **7ox** shifted cathodically compared with **6ox-L** (Figure 4d). Compared with the non-hydrogen-bonded quinonediimine, the hydrogen-bonded analogue becomes stabilized as an electron sink. Accordingly, the redox properties of the quinonediimine moiety are considered to be modulated by the formation of hydrogen bonding.

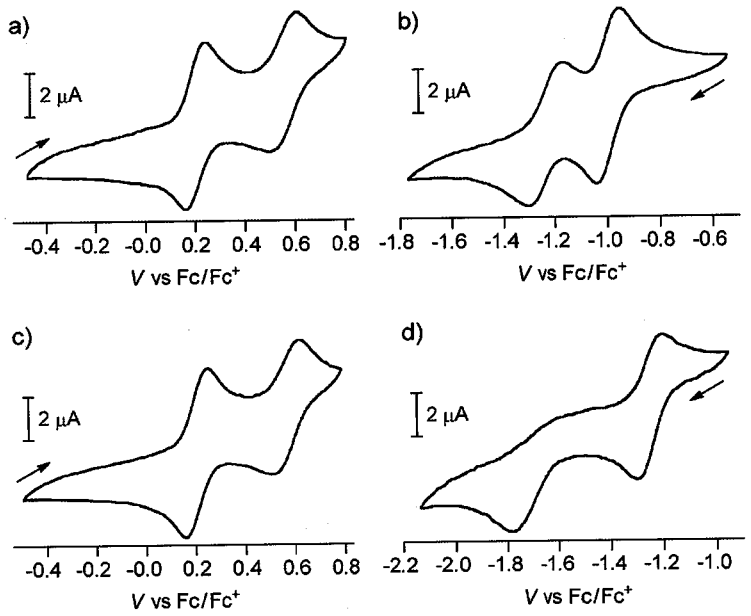


Figure 4. Cyclic voltammograms of a) **6red-L**, b) **6ox-L**, c) **7red**, d) **7ox** in dichloromethane (5.0×10^{-4} M) containing 0.1 M Bu_4NClO_4 at a platinum working electrode with scan rate 100 mVs^{-1} at 25 °C under an argon atmosphere.

To gain insight into the chirality-organized redox species of **6red-L** and **6ox-L**, the redox behavior was investigated spectroscopically. The chemical oxidation of **6red-L** in acetonitrile with an equimolar amount of $NOBF_4$ resulted in the formation of the phenylenediamine radical cation **6red-L**$^{\cdot +}$, which showed a broad absorption at around 750 nm in the electronic spectrum (Figure 2a). It is noteworthy that **6red-L**$^{\cdot +}$ exhibited an ICD at around 750 nm, based on the phenylenediamine radical cation in the CD spectrum (Figure 2d). This result indicates the preservation of the chirality-organized structure through intramolecular hydrogen bonding. The ESR spectrum of **6red-L**$^{\cdot +}$ showed the signals centered around g = 2.0036, with hyperfine coupling as shown in

Figure 5a; this result indicates that the unpaired electron is located mostly on the phenylenediamine moiety. The ESR signal could be approximately simulated by assuming the following parameters: A_N = 5.60 G; A_H = 6.18 G; A_H = 2.17 G; A_H = 1.12 G; A_H = 0.97 G; A_H = 0.50 G (Figure 5a). The semiquinonediimine radical anion **6ox-L**$^{\cdot -}$ could be obtained by the chemical reduction of **6ox-L** in dichloromethane with an equimolar amount of cobaltocene. The generated semiquinonediimine radical anion **6ox-L**$^{\cdot -}$ was characterized by broad bands at around 610 and 750 nm in its electronic spectrum (Figure 2b). An ICD at around 550-800 nm based on the semiquinonediimine radical anion in the CD spectrum (Figure 2e) suggests the formation of the chirality-organized structure through intramolecular hydrogen bonding. The formation of intramolecular hydrogen bondings in the semiquinonediimine radical anion was also confirmed by the observation of hyperfine coupling in the ESR spectrum (A_N = 5.38 G; A_H = 2.63 G; A_H = 1.02 G; A_H = 0.65 G; A_H = 0.57 G), and superhyperfine splitting owing to two equivalent nitrogen and two equivalent proton nuclei (A_N = 1.03 G; A_H = 0.72 G) (Figure 4b); this splitting indicates a stabilization of the semiquinonediimine radical anion by the formation of intramolecular hydrogen bondings.

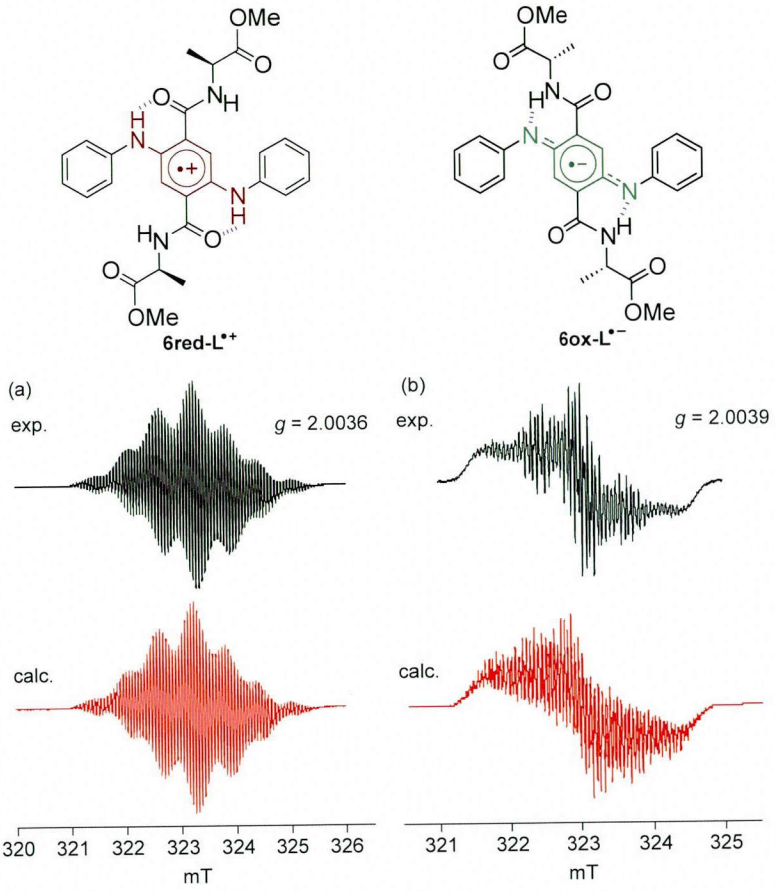
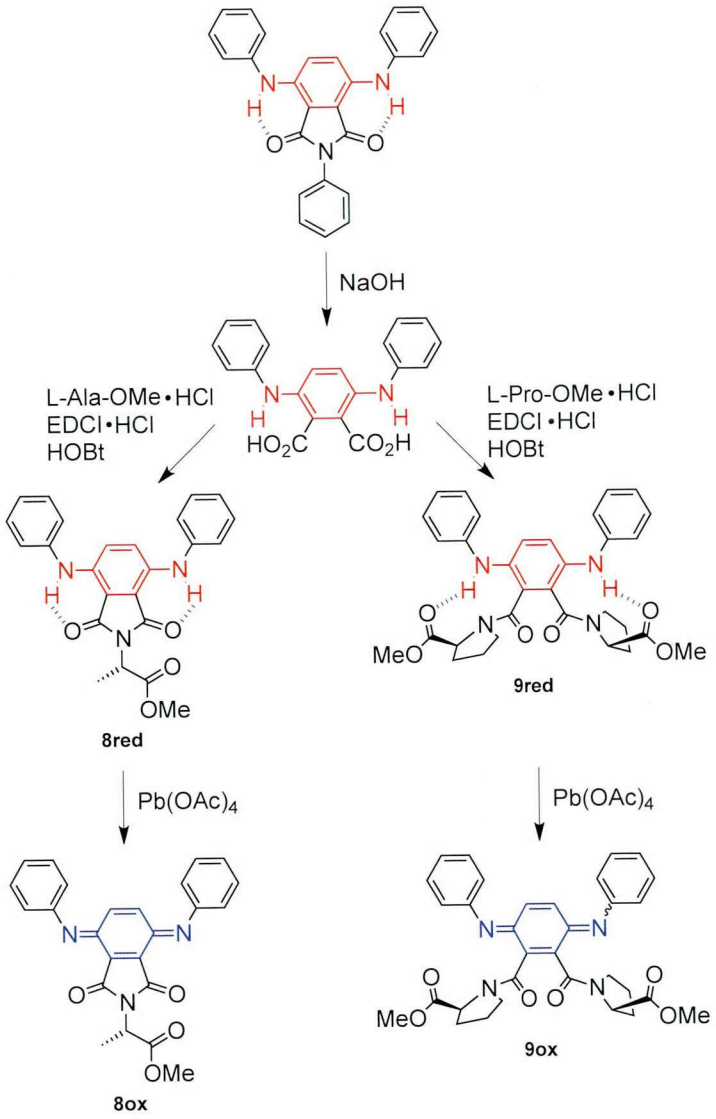


Figure 5. ESR spectra of a) **6red-L**$^{\cdot +}$ in acetonitrile (1.0 x 10^{-3} M) and b) **6ox-L**$^{\cdot -}$ in dichloromethane (1.0 x 10^{-3} M) at 25 ^{o}C under a nitrogen atmosphere (black), and the simulated spectra (red).

2-2-2. Structural and redox properties of 2,3-substututed phenylenediamines and quinonediimines

Conformational changing of π-conjugated moieties was expected by the substituent position of amino acid moieties. Thereby, 2,3-substituted phenylenediamine derivatives were synthesized. The synthetic route of phenylenediamine derivatives bearing the chiral amino acid moieties is outlined in Scheme 1. The phenylenediamine derivative **8red** containing only one amino acid moiety (-L-Ala-OMe), was synthesized by the reaction of the corresponding carboxylic acid, which was obtained by hydrolysis of the corresponding phtalimide derivative, with L-alanine methyl ester hydrochloride. In contrast, the reaction with L-proline methyl ester hydrochloride led to the formation of phenylenediamine derivative **9red**, which containing two amino acid moieties (-L-Pro-OMe), probably because the amino of the prolyl moiety is a secondary amine. The phenylenediamine **8red** and **9red** were easily oxidized to the quinonediimine derivatives **8ox** and **9ox**, respectively, by treatment with lead(IV) acetate as an oxidant. The thus obtained phenylenediamine and quinonediimine derivatives were fully characterized by spectroscopy and elemental analyses.



Scheme 1.

In the ^{1}H NMR spectra of **8red** in CD_2Cl_2 (1.0×10^{-2} M), the signals from the NH groups of the phenylenediamine moiety were not significantly perturbed by the addition of an aliquot of DMSO-d_6 to the CD_2Cl_2 (CD_2Cl_2: δ = 7.82 ppm, CD_2Cl_2-DMSO-d_6 (9:1): δ = 7.82 ppm). The FT-IR spectrum of **8red** in dichloromethane (1.0×10^{-2} M)

showed the hydrogen-bonded NH stretching band at 3372 cm^{-1} in solution. The NH groups of the phenylenediamine moiety are indicated to be locked in intramolecular hydrogen bondings in solution. The ^1H NMR spectra of **9red** in CD_2Cl_2 (1.0×10^{-2} M) indicates that the NH protons of the phenylenediamine moiety were also not significantly perturbed by the addition of an aliquot of DMSO-d_6 to the CD_2Cl_2 (CD_2Cl_2: δ = 6.81 ppm, CD_2Cl_2- DMSO-d_6 (9:1): δ = 6.79 ppm). The FT-IR spectrum of **9red** in dichloromethane (1.0×10^{-2} M) showed the hydrogen-bonded NH stretching bands at 3353 cm^{-1} in solution. These results also indicate that the NH groups of the phenylenediamine moiety of **9red** form intramolecular hydrogen bondings.

The structural elucidation of **9red** was investigated by single-crystal X-ray diffraction. The crystal structure of **9red** (Figure 6) revealed the chirality-organized structure based on the formation of the intramolecular hydrogen bonding between the NH group of the phenylenediamine moiety and the carbonyl oxygen of proline to form a nonpeptidic, reverse-turn, nine-membered, hydrogen-bonded ring, which results in a *syn*-conformation of the π-conjugated moiety. The results of nuclear Overhauser effect (NOE) experiments with **9red** in CD_2Cl_2 at 25 °C suggest that the *syn*-conformation might be preserved in solution (Figure 7). The dihedral angles of 129.9(1) and 40.8(1)° between the terminal benzene and central benzene rings form a propeller twist between the planes of the two terminal benzene rings.

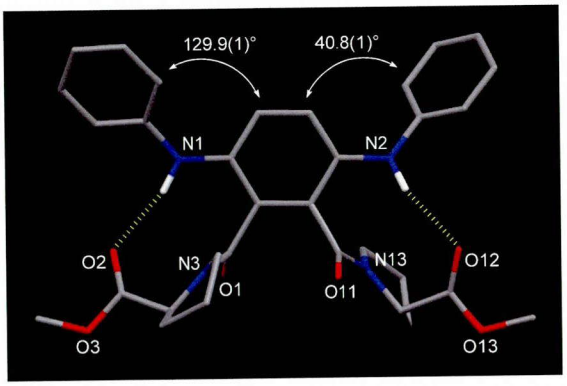


Figure 6. The structure of **9red** as determined by X-ray crystallography.

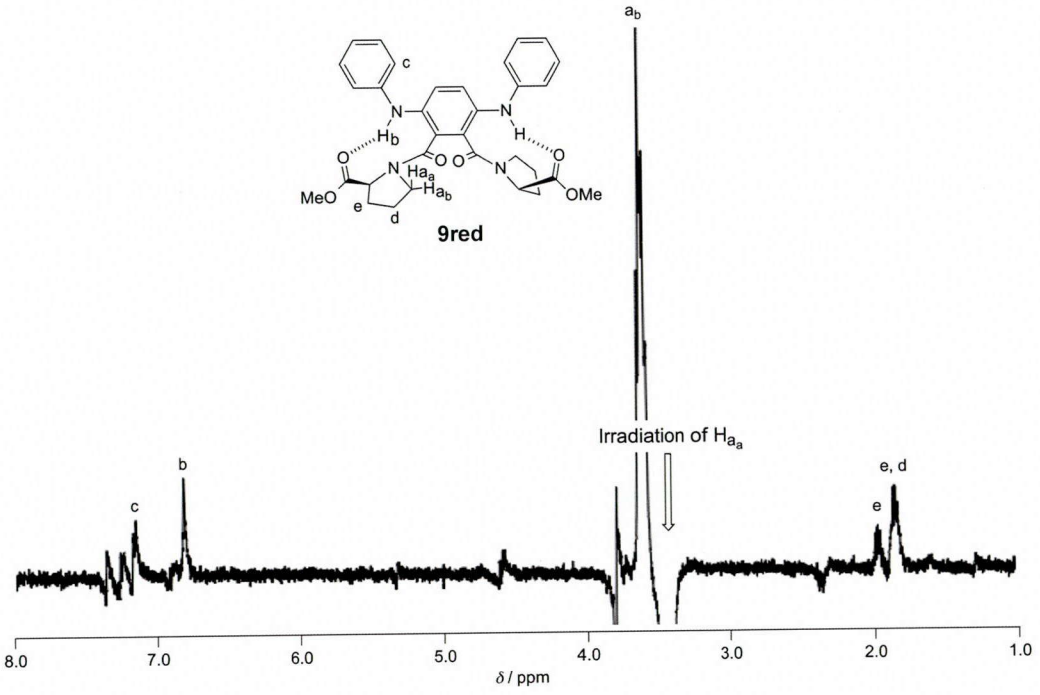


Figure 7. 400 MHz ^{1}H NMR difference NOE experiment performed at 25 °C with 1 second irradiation of a freeze-pump-thaw degassed solution of **9red** in CD_2Cl_2.

The electronic spectrum of **8red** in dichloromethane has a broad band at around 500 nm, which is probably a result of a low-energy charge-transfer transition in the π-conjugation moiety (Figure 8a). It should be noted that **8red** has ICD in the absorbance region of the π-conjugated moiety in the CD spectrum (Figure 8b). This result indicates that the chiral induction of the π-conjugated aniline oligomer is achieved by chirality organization through the intramolecular hydrogen bonding even in solution. ICD in the absorbance region of the π-conjugated moiety based on the chirality-organized structure was also detected in the CD spectrum of **8ox**, probably because of the steric effect of the alanyl moiety (Figure 8b). The chirality organization **9red** and **9ox** was supported by the appearance of ICD in the absorbance region of the π-conjugated moiety in the CD spectra (Figure 8c and 8d). This result is consistent with the chirality-organized structure of **9red** in the solid state.

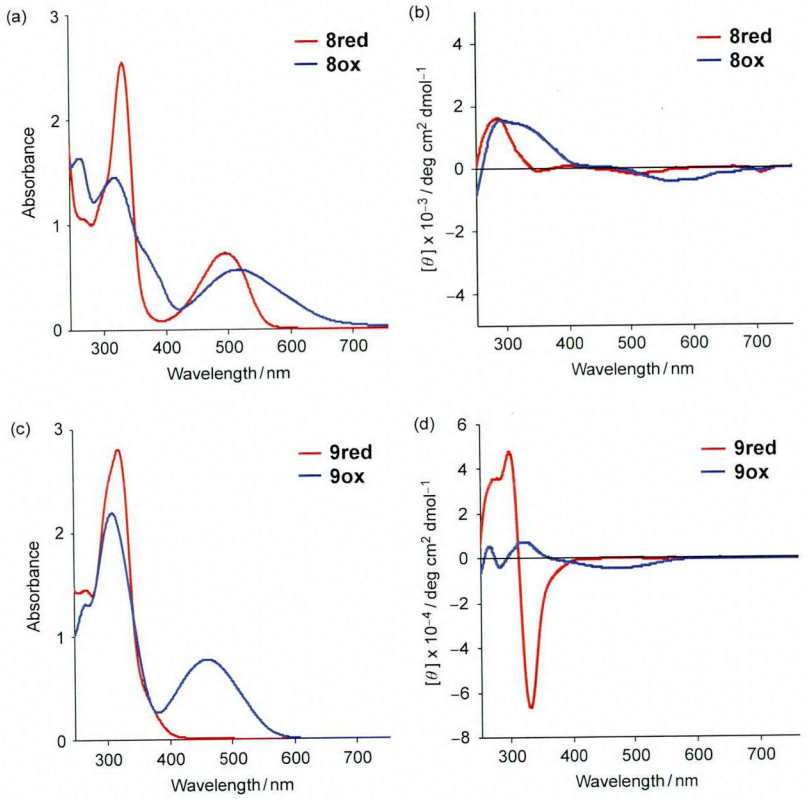


Figure 8. a) The electronic spectra of **8red** and **8ox**. b) The CD spectra of **8red** and **8ox**. c) The electronic spectra of **9red** and **9ox**. d) The CD spectra of **9red** and **9ox**. All these spectra measured in acetonitrile (1.0×10^{-4} M) at 25 °C under a nitrogen atmosphere.

The redox properties of **8red** and **9red** were investigated by cyclic voltammetry. The phenylenediamine derivative **8red** in dichloromethane has two one-electron redox waves ($E_{1/2}$ = 0.45 and 0.72 V vs. Fc/Fc^+), which are assigned to successive one-electron oxidation processes of the phenylenediamine moiety to give the corresponding oxidized species (Figure 9a). The phenylenediamine derivative **9red** also shows two one-electron redox waves ($E_{1/2}$ = 0.19 and 0.63 V vs. Fc/Fc^+), which are

assigned to successive one-electron oxidation processes of the phenylenediamine moiety (Figure 9b).

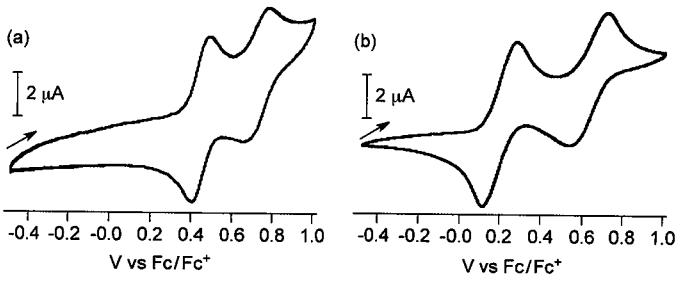


Figure 9. Cyclic voltammograms of a) **8red** and b) **9red** in dichloromethane (5.0×10^{-4} M) containing 0.1 M Bu_4NClO_4 at a platinum working electrode with scan rate 100 mVs^{-1} at 25 °C under an argon atmosphere.

Accordingly, the redox properties of the quinonediimine moiety are modulated by the formation of hydrogen bonding. To gain insight into the chirality-organized redox species of **8red** and **9red**, the phenylenediamine radical cations were investigated spectroscopically. The chemical oxidation of **8red** in acetonitrile with an equimolar amount of nitrosonium fluoroborate resulted in the formation of the phenylenediamine radical cation **8red**$^{\cdot +}$, which has a broad absorption at around 800 nm in the electronic spectrum (Figure 10a). It is noteworthy that **8red**$^{\cdot +}$ has ICD at around the absorbance region of the phenylenediamine radical cation in the CD spectrum (Figure 10b). The ESR spectrum of **8red**$^{\cdot +}$ has signals that are centered around $g = 2.0036$ with hyperfine coupling, as shown in Figure 11a, which indicates that the unpaired electron is located mostly on the phenylenediamine moiety. The ESR signal could be approximately

simulated by assuming the following parameters: A_N= 5.96 G; A_H= 4.91 G; A_H= 1.39 G; A_H= 0.96 G; A_H= 0.05 G; A_H= 0.54 G; A_N= 1.06 G. The chemical oxidation of **9red** in acetonitrile with an equimolar amount of nitrosonium fluoroborate gave a broad absorption at around 750 nm in the electronic spectrum (Figure 10c). **9red**$^{\cdot +}$ has ICD in the absorbance region of the radical species in the CD spectrum (Figure 10d). The ESR spectrum of **8red**$^{\cdot +}$ has signals centered at around g = 2.0037 with hyperfine coupling (Figure 11b), which indicates that the unpaired electron is located mostly on the phenylenediamine moiety. The ESR signal could be approximately simulated by assuming the following parameters: A_N= 6.08 G; A_H= 5.09 G; A_H= 1.55 G; A_H= 1.08 G; A_H = 0.95 G; A_H = 0.52 G. These results indicate the preservation of the chirality-organized structure through intramolecular hydrogen bonding in the phenylenediamine radical cation.

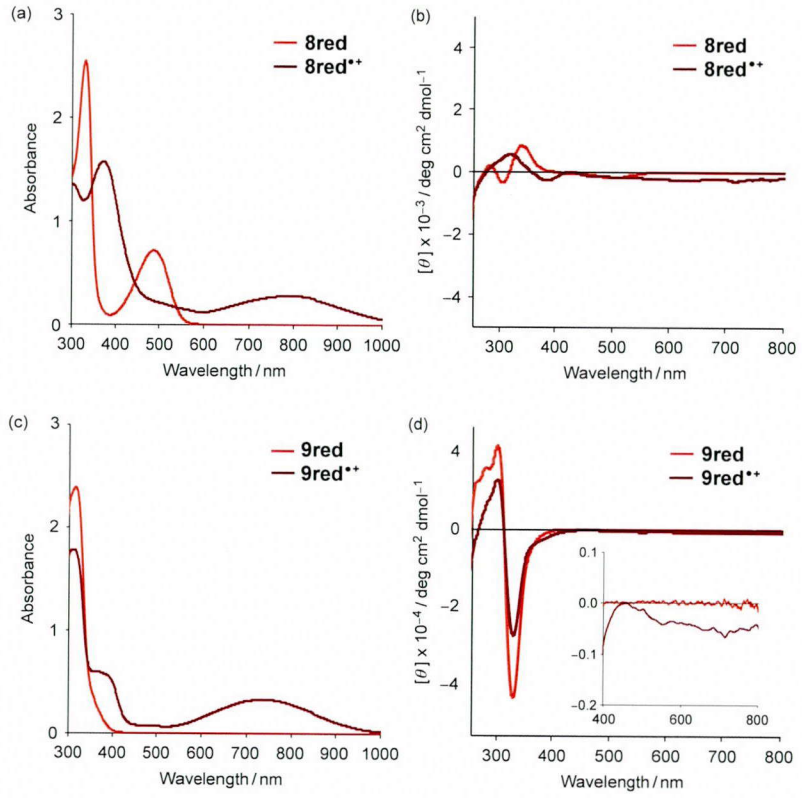


Figure 10. The electronic spectra of a) **8red** and **8red**$^{\cdot +}$. b) The CD spectra of **8red** and **8red**$^{\cdot +}$. c) The electronic spectra of **9red** and **9red**$^{\cdot +}$. d) The CD spectra of **9red** and **9red**$^{\cdot +}$. All these spectra measured in acetonitrile (1.0 x 10^{-4} M) at 25 ^{o}C under a nitrogen atmosphere.

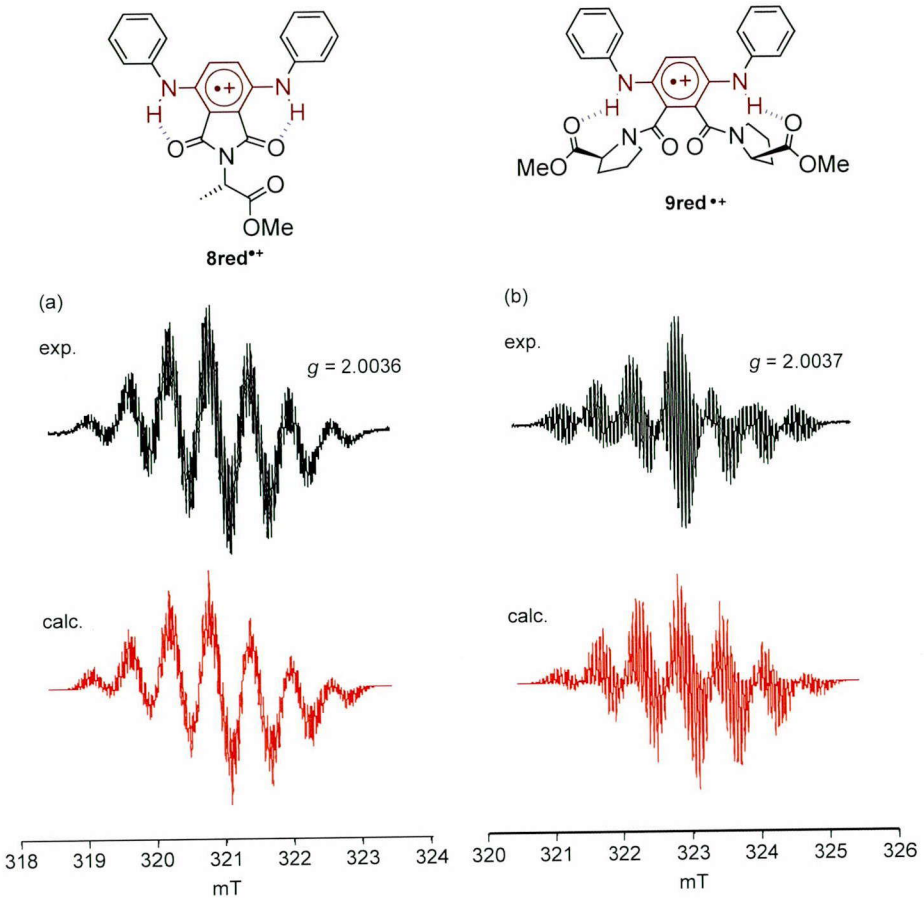
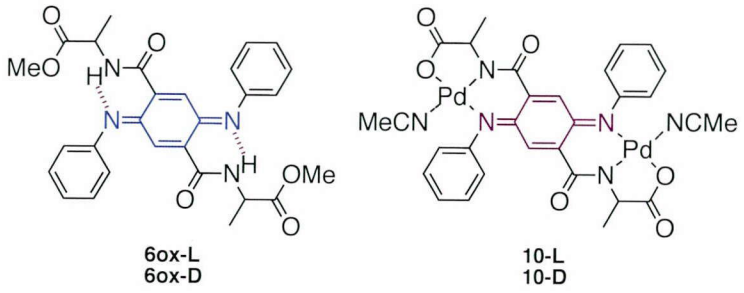


Figure 11. ESR spectra of a) **8red**$^{\cdot +}$ in acetonitrile (1.0 x 10^{-3} M) and b) **9red**$^{\cdot +}$ in dichloromethane (1.0 x 10^{-3} M) at 25 °C under a nitrogen atmosphere (black), and the simulated spectra (red).

2-2-3. Palladium(II) complex composed of chirality-organized quinonediimine moiety

The quinonediimine, which is an oxidized molecular unit of polyanilines, possesses binding sites to metals.[3] Furthermore, chirality induction of π-conjugated polyanilines through chiral complexation with the chiral palladium(II) has been demonstrated to afford conjugated polymer complexes. In this section, d,π-conjugated palladium(II) complexes composed of chirality-organized quinonediimine derivatives as bridging conjugated ligands were synthesized.

The quinonediimine derivatives **6ox-L** and **6ox-D** bearing amino acid moieties L-Ala-OMe and D-Ala-OMe were prepared, respectively. The complexation of the chirality-organized quinonediimine derivative **6ox-L** with 2 molar equiv. of $Pd(OAc)_2$ in acetonitrile led to the formation of the 1:2 conjugated chiral homobimetallic palladium(II) complex **10-L** (Figure 12). The absence of the amide protons in ^1H NMR confirmed that the amide nitrogen atoms coordinate in a deprotonated form.



6ox-L
6ox-D

10-L
10-D

Figure 12.

The single-crystal X-ray structure determination of **10-L** revealed that two palladium(II) atoms with a little distorted square planer geometry are bridged by the quinonediimine moiety, resulting in an anti-conformation of the π-conjugated moiety as shown in Figures 13a and 13c. The quinonediimine and deprotonated amide nitrogen atoms are coplanar to form a six-membered chelate rings with extended conjugation. The carboxylate oxygen, which might be obtained by hydrolysis of the methyl ester in the C-terminal alanyl moiety, arranges in a *trans* position to the quinonediimine nitrogen. The open coordination site is occupied by an ancillary acetonitrile. Owing to π-conjugation of **10-L**, the orientation of each terminal benzene ring should be within a limited range of locations parallel to the central benzene ring. However, the steric interaction between the hydrogen atom ac C(3) (C(23)) and the hydrogen atom at C(25) (C(5)) causes the terminal benzene ring of **10-L** to rotate away from this orientation, thereby resulting in a conformation with a dihedral angle of 74.4(3) and 74.2(3)° between the terminal and central benzene rings in a solid state (Figures 13a and 13c). This conformation results in a propeller twist between the planes of the two terminal benzene rings as shown in Figures 13a and 13c. The chirality of the alanine moieties is considered to induce chirality around the π-conjugated moiety. The molecular structure of **10-D** composed of the corresponding D-amino acid is in a mirror image relationship with **10-L**, indicating conformational isomer (Figures 13b and 13d). As a result, the chirality-organized quinonediimine derivatives through intramolecular hydrogen bondings of the amino acid moieties were found to induce the chirality organization through the complexation with palladium salts.

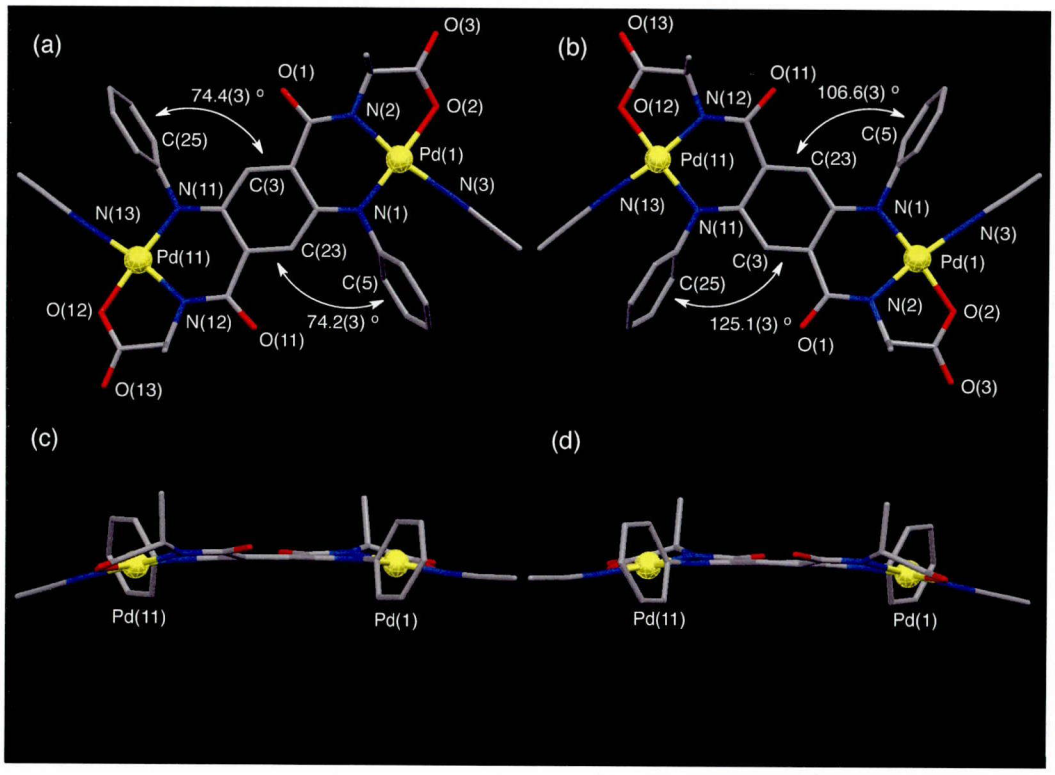


Figure 13. a) Top view and c) side view of molecular structure of **10-L**. b) Top view and d) side view of molecular structure of **10-D** (hydrogen atoms are omitted for clarity).

The electronic spectrum of the complex **10-L** in acetonitrile showed a broad absorption around 450 nm, which is probably due to a low-energy charge-transfer transition of the π-conjugated moiety with contribution from palladium (Figure 14a). It should be noted that **10-L** exhibited an ICD at the absorbance region of the π-conjugated moiety in the CD spectrum as shown in Figure 14b. The mirror image of the CD signals obtained with **10-L** was observed in the CD spectrum of **10-D** (Figure 14c). This result indicates the preservation of the chirality-organized structure of the π-conjugated quinonediimine nitrogen atoms to palladium atoms even in a solution.

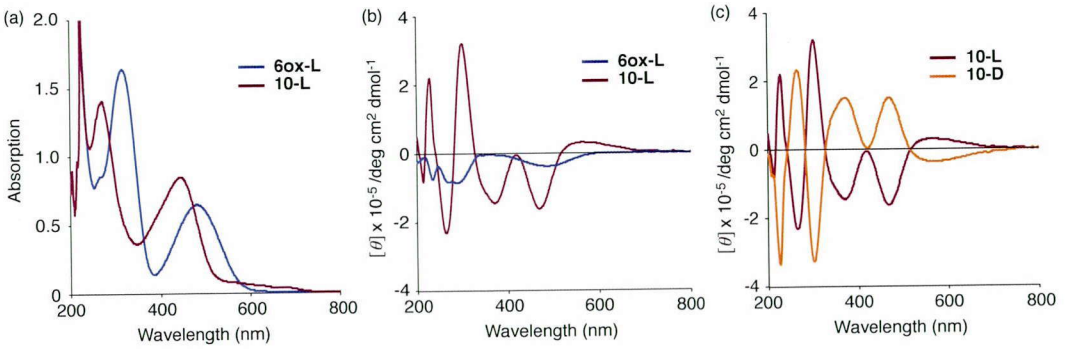


Figure 14. a) The electronic spectra of **6ox-L** and **10-L**. b) CD spectra of **6ox-L** and **10-L**. c) CD spectra of **10** in acetonitrile (1.0 x 10^{-4} M) at 25 °C under an argon atmosphere.

The redox property of **6ox-L** and **10-L** were investigated by cyclic voltammetry. The quinonediimine derivative **6ox-L** in DMSO showed two reduction waves (E_{pc} = -0.86 and -1.12 V vs. Fc/Fc^{+}), which might be assigned to the successive reduction processes of the quinonediimine moiety (Figure 15a). The two reduction waves (E_{pc} = -0.57 and -0.91 V vs. Fc/Fc^{+}) based on the reduction processes of the quinonediimine moiety were also detected in the cyclic voltammogram of the homobimetallic palladium(II) complex **10-L** (Figure 15b). A substantial positive shift of the reduction waves compared with the hydrogen-bonded quinonediimine indicates that the complexed quinonediimine becomes more stabilized as an electron sink. From these results, the redox properties of the quinonediimine moiety are considered to be modulated by the complexation with palladium atoms.

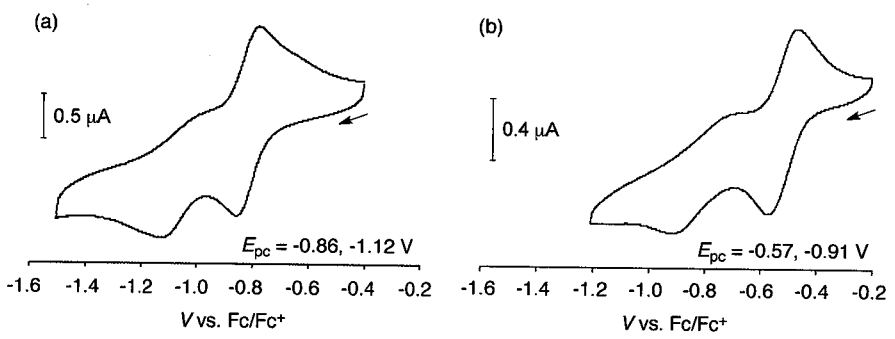


Figure 15. Cyclic voltammograms of a) **6ox-L** and b) **10-L** in DMSO (5.0×10^{-4} M) containing 0.1 M Bu_4NClO_4 at a glassy carbon working electrode with scan rate 10 mVs^{-1} at 25 °C under an argon atmosphere.

2-3. Summary

Hydrogen-bonding induced chirality organization of polyaniline-unit molecules through intramolecular hydrogen bonding was achieved by the introduction of amino acid moieties. The formation of the intramolecular hydrogen bonding was found to play an important role in the stabilization of the redox species of these polyaniline-unit molecules, wherein the chirality-organized structures are preserved through the intramolecular hydrogen bonding. The substituent position of the amino acid moieties shows that conformational changing between *syn*/*anti* conformer. Furthermore, quinonediimine derivatives bearing amino acid moieties were performed to serve as a π-conjugated bridging ligand to afford the conjugated chiral homobimetallic palladium(II) complexes with palladium(II) salt. Chirality organization through intramolecular hydrogen bonding or complexation is, therefore, an efficient and feasible strategy for the construction of chiral redox-active π-conjugated molecules.

2-4. Experimental Section

General Methods

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Solvents employed were dried by refluxing in the presence of appropriate drying reagents, distilled under argon atmosphere, and stored in the drybox. ^{1}H NMR spectra were recorded on a JEOL JNM-ECP 400 or a JNM-ECS 400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS DX-303 spectrometer. UV-vis. spectra were recorded using a HITACHI U-3500 spectrophotometer monitoring under argon atmosphere at 25 °C. Fluorescence emission spectra were recorded using a SHIMADZU RF-5300PC spectrofluorometer under argon atmosphere at 25 °C. ESR spectrum was taken on a JEOL X-band spectrometer (JES-RE1XE). CD spectra were recorded using a JASCO J-720 spectropolarimeter. UV-vis. and CD measurements were conducted using 1-cm pathlength quartz cuvettes. Cyclic voltammograms were recorded on a BAS CV-50W voltammetry analyzer under argon atmosphere at 25 °C.

General Procedure for Synthesis of Phenylenediamines 6red

A mixture of diethyl 2,5-bis(phenylamino)terephthalate (607 mg, 1.5 mmol) and sodium hydroxide (c.a. 132 mg) in tetrahydrofuran (15 mL) was refluxed for 24 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1N HCl aqueous solution. The violet precipitate was isolated by filtration, washed with

water, and dried in vacuo. Anhydrous dichloromethane (50 mL) was added to a mixture of the thus-obtained violet solid, 1-hydroxybenzotriazole (676 mg, 5.0 mmol), L- or D-alanine methyl ester hydrochloride (698 mg, 5.0 mmol), and triethylamine (diluted, 4.4 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (959 mg, 5.0 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 48 h. The resulting mixture was diluted with dichloromethane (20 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 1:1) to give **6red** (**6red-L**: 620 mg; **6red-D**: 607 mg) as an orange solid, R_f = 0.28 (ethyl acetate). The obtained compound was recrystallized from ethyl acetate/hexane.

6red-L: Isolated yield 95%; mp 161-163 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.04 (s, 2H), 7.58 (s, 2H), 7.27 (t, J = 7.5 Hz, 4H), 7.07 (d, J = 7.5 Hz, 4H), 6.93~6.98 (m, 4H), 4.63 (quint, J = 7.2 Hz, 2H), 3.69 (s, 6H), 1.39 (d, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2), 173.5, 167.5, 143.5, 136.8, 129.8, 125.8, 121.9, 119.2, 118.8, 52.8, 48.9, 18.2 ppm; IR (KBr) 3374, 3323, 2990, 2951, 1750, 1630, 1602, 1588, 1534, 1498, 1437, 1263 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3426, 3343, 2986, 2955, 1741, 1649, 1600, 1587, 1530, 1496, 1437, 1262, 1212 cm^{-1}; HRMS (FAB) m/z: $[M]^+$

518.2177, $C_{28}H_{30}N_4O_6$ (calc. 518.2165); Anal. Calcd. for $C_{28}H_{30}N_4O_6$: C, 64.85; H, 5.83; N, 10.80; Found: C, 64.64; H, 5.67; N, 10.75.

6red-D: Isolated yield 93%; mp 161-163 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.04 (s, 2H), 7.58 (s, 2H), 7.27 (t, J = 7.5 Hz, 4H), 7.07 (d, J = 7.5 Hz, 4H), 6.93~6.98 (m, 4H), 4.63 (quint, J = 7.2 Hz, 2H), 3.69 (s, 6H), 1.39 (d, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2), 173.5, 167.5, 143.5, 136.8, 129.8, 125.8, 121.9, 119.2, 118.8, 52.8, 48.9, 18.2 ppm; IR (KBr) 3374, 3323, 2990, 2951, 1750, 1630, 1602, 1588, 1534, 1498, 1437, 1263 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3426, 3343, 2986, 2955, 1741, 1649, 1600, 1587, 1530, 1496, 1437, 1262, 1212 cm^{-1}; HRMS (FAB) m/z: $[M]^+$ 518.2181, $C_{28}H_{30}N_4O_6$ (calc. 518.2165); Anal. Calc. for $C_{28}H_{30}N_4O_6$: C, 64.85; H, 5.83; N, 10.80; Found: C, 64.77; H, 5.56; N, 10.74.

General Procedure for Synthesis of Quinonediimines 6ox

A mixture of phenylenediamine **6red** (51.8 mg, 0.1 mmol) and iodosylbenzene (44.0 mg, 0.2 mmol) in dry dichloromethane (10 mL) was refluxed under argon atmosphere for 3 h. The resulting mixture was filtered and the filtrate was evaporated in vacuo. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to ethyl acetate) to give **6ox** (**6ox-L**: 46.5 mg; **6ox-D**: 46.4 mg) as a red-brown solid, R_f = 0.65 (ethyl acetate).

6ox-L: Isolated yield 90%; mp 193-196 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.34 (d, J = 7.2 Hz, 2H), 8.02 (s, 2H), 7.50 (t, J = 7.3 Hz, 4H), 7.33 (t, J = 7.3 Hz, 2H), 7.05 (d, J = 8.4 Hz, 4H), 4.61 (quint., J = 7.0 Hz, 2H), 3.71 (s, 6H), 1.45 (d,

J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2), 173.4, 162.6, 157.4, 148.2, 134.4, 130.3, 129.7, 127.3, 122.0, 52.7, 49.4, 18.4 ppm; IR (KBr) 3454, 3184, 1739, 1663, 1570, 1552, 1481, 1452, 1147, 693 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3207, 1743, 1662, 1571, 1526, 1482, 1452, 1216, 1149, 696 cm^{-1}; HRMS (FAB) m/z: $[M+2H]^{2+}$ 518.2164, $[M+H]^+$ 517.2086, $[M]^+$ 516.2003, $C_{28}H_{28}N_4O_6$ (calc. 516.2009); Anal. Calc. for $C_{28}H_{28}N_4O_6$: C, 65.12; H, 5.43; N, 10.85; Found: C, 64.83; H, 5.32; N, 10.87.

6ox-D: Isolated yield 91%; mp 193-196 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 10.34 (d, J = 7.2 Hz, 2H), 8.02 (s, 2H), 7.50 (t, J = 7.3 Hz, 4H), 7.33 (t, J = 7.3 Hz, 2H), 7.05 (d, J = 8.4 Hz, 4H), 4.61 (quint., J = 7.0 Hz, 2H), 3.71 (s, 6H), 1.45 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2), 173.4, 162.6, 157.4, 148.2, 134.4, 130.3, 129.7, 127.3, 122.0, 52.7, 49.4, 18.4 ppm; IR (KBr) 3454, 3184, 1739, 1663, 1570, 1552, 1481, 1452, 1147, 693 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3207, 1743, 1662, 1571, 1526, 1482, 1452, 1216, 1149, 696 cm^{-1}; HRMS (FAB) m/z: $[M+2H]^{2+}$ 518.2166, $[M+H]^+$ 517.2094, $[M]^+$ 516.2010, $C_{28}H_{28}N_4O_6$ (calc. 516.2009).

Synthesis of Phenylenediamine 7red

A mixture of diethyl 2,5-bis(phenylamino)terephthalate (606 mg, 1.5 mmol) and sodium hydroxide (c.a. 132 mg) in tetrahydrofuran (15 mL) was refluxed for 24 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1N HCl aqueous solution. The violet precipitate was isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture

of the thus-obtained violet solid, 1-hydroxybenzotriazole (676 mg, 5.0 mmol), L-proline methyl ester hydrochloride (828 mg, 5.0 mmol), and triethylamine (diluted, 4.4 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (959 mg, 5.0 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 60 h. The resulting mixture was diluted with dichloromethane (20 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 1:4) to give **7red** (583 mg) as a yellow solid, R_f = 0.50 (ethyl acetate: hexane = 4:1).

7red: Isolated yield 78%; mp 154-156 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 (s, 2H), 7.26 (t, J = 7.8 Hz, 4H), 7.12 (s, 2H), 7.08 (d, J = 7.8 Hz, 4H), 6.91 (t, J = 7.3 Hz, 2H) 4.56-4.59 (m, 2H), 3.73 (s, 6H), 3.47-3.60 (m, 4H), 2.24-2.33 (m, 2H), 2.00-1.81 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2), 173.2, 168.5, 143.5, 134.5, 129.8, 127.6, 121.2, 118.0, 117.3, 59.3, 52.8, 49.9, 29.8, 25.6 ppm; IR (KBr) 3279, 3195, 2970, 2954, 1750, 1618, 1549, 1498, 1456, 1289, 1175, 750 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3360, 2992, 2982, 1732, 1632, 1600, 1586, 1559, 1497, 1477, 1274, 1178, 754 cm^{-1}; HRMS (EI) m/z: $[M+Na]^+$ 593.2384, $C_{32}H_{34}N_4O_6Na$ (calc. 593.2376); Anal. Calc. for $C_{32}H_{34}N_4O_6$: C, 67.40; H, 6.00; N, 9.80; Found: C, 67.27; H, 5.90; N, 9.70.

Synthesis of Phenylenediamine 7ox

A mixture of phenylenediamine **7red** (54.2 mg, 0.1 mmol) and iodosylbenzene (26.4 mg, 0.1 mmol) in dry dichloromethane (5.0 mL) was refluxed under an argon atmosphere for 6 h. The resulting mixture was filtered and the filtrate was evaporated in vacuo. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to ethyl acetate) to give **7ox** (45.4 mg) as a red-brown solid, R_f = 0.38 (ethyl acetate: hexane = 4: 1).

7ox: Isolated yield 80%; mp 94-95 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2) as mixture of two *syn/anti* isomers, δ 7.45-7.40 (m, 4H), 7.25-7.22 (m, 2H), 6.94-6.84 (m, 6H), 4.51-4.49 (m, 1.5H), 4.31 (d, J = 8.2 Hz, 0.5H), 3.66-3.65 (m, 2H), 3.60-3.46 (m, 2H), 2.27-2.17 (m, 2H), 2.04-1.89 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2) as mixture of two *syn/anti* isomers, 172.8, 172.6, 165.8, 165.8, 155.8, 155.5, 155.4, 149.9, 149.8, 149.7, 144.6, 144.1, 129.5, 126.3, 126.2, 122.6, 121.9, 121.0, 60.7, 58.9, 52.7, 52.5, 48.7, 46.4, 31.4, 29.8, 29.5, 25.1, 23.0 ppm; IR (KBr) 2953, 1742, 1647, 1574, 1430, 1200, 1175, 699 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 2955, 1744, 1643, 1575, 1435, 1200, 1177, 703 cm^{-1}; HRMS (EI) m/z: $[M+Na]^+$ 591.2225, $C_{32}H_{32}N_4O_6Na$ (calc. 591.2220); Anal. Calc. for $C_{32}H_{32}N_4O_6 \cdot 0.5\ H_2O$: C, 65.55; H, 5.71; N, 9.70; Found: C, 66.51; H, 5.66; N, 9.60.

Synthesis of 2-phenyl-4,7-bis(phenylamino)isoindoline-1,3-dione

To a mixture of cesium carbonate (3.9 g, 12 mmol), palladium(II) acetate (66 mg, 0.3 mmol), (±)-BINAP (311 mg, 0.5 mmol), 3,6-dibromophtalic anhydride (766 mg, 2.5

mmol), and aniline (1.1 mL, 12 mmol) was added anhydrous toluene (50 mL). The mixture was stirred at 100 °C for 20 h under an argon atmosphere. After cooling to ambient temperature, dichloromethane (40 mL) was added to the red-brown suspension and filtered. After evaporation of the solvent, a residue was purified by silica-gel column chromatography (from hexane to hexane/EtOAc = 5:2) to give the target compound (162 mg, 0.4 mmol) as a red crystal, R_f = 0.45 (hexane/EtOAc = 5:2).

2-phenyl-4,7-bis(phenylamino)isoindoline-1,3-dione; Isolated yield 17%; mp 195-198 °C (uncorrected.); IR (KBr) 3358, 3048, 2933, 1731, 1685, 1645, 1599, 1508, 1475, 1396, 1351, 1319, 1278, 1239, 1195, 1099 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 7.97 (s, 2H), 7.53 (t, J = 7.3 Hz, 2H), 7.46 (s, 2H), 7.47-7.40 (m, 3H), 7.36 (t, J = 7.3 Hz, 4H), 7.24 (d, J = 7.3 Hz, 4H), 7.10 (t, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 168.8, 140.7, 136.9, 132.4, 129.9, 129.4, 128.2, 127.1, 123.9, 123.0, 121.3, 111.7 ppm; HRMS (FAB) *m/z*: $[M]^+$ 405.1480, $C_{26}H_{19}N_3O_2$ (calc. 405.1477); Anal. Calcd. for $C_{20}H_{14}N_2O_3 \cdot 0.25\ H_2O$: C, 76.17; H, 4.79; N, 10.25. Found: C, 75.99; H, 4.57; N, 10.32.

Synthesis of Phenylenediamine 8red

A mixture of 2-phenyl-4,7-bis(phenylamino)isoindoline-1,3-dione (122 mg, 0.3 mmol) and sodium hydroxide (c.a. 95 mg) in tetrahydrofuran (15 mL) was refluxed for 24 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) and methanol (20 mL) were added to the residue, and the solution was acidified with 1N HCl aqueous solution. The purple precipitate was

isolated by filtration, washed with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture of the thus-obtained purple solid, 1-hydroxybenzotriazole (189 mg, 1.4 mmol), L-alanine methyl ester hydrochloride (195 mg, 1.4 mmol), and triethylamine (diluted, 3.2 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (268 mg, 1.4 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 24 h. The resulting mixture was diluted with dichloromethane (20 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 5:2) to give **8red** (41 mg) as a red solid, R_f = 0.28 (ethyl acetate).

8red: Isolated yield 33%; mp 108-110 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 7.82 (s, 2H), 7.40 (s, 2H), 7.34 (t, J = 7.6 Hz, 4H), 7.20 (d, J = 7.6 Hz, 4H), 7.08 (t, J = 7.6 Hz, 2H), 4.92 (q, J = 7.6 Hz, 1H), 3.73 (s, 3H), 1.67 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M), 169.8, 167.7, 139.6, 135.4, 128.7, 122.5, 121.7, 120.0, 110.9, 51.8, 46.0, 14.4 ppm; IR (KBr) 3370, 3001, 2952, 1752, 1728, 1686, 1645, 1614, 1599, 1505, 1398, 1348, 1319, 1223, 1204, 1158 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3373, 3051, 2986, 1686, 1646, 1600, 1500, 1400, 1348, 1319, 1203, 1045 cm^{-1}; HRMS (FAB) *m/z*: $[M]^+$ 415.1538, $C_{24}H_{21}N_3O_4$ (calc. 415.1532).

Synthesis of Phenylenediamine 8ox

A mixture of phenylenediamine **8red** (41.5 mg, 0.1 mmol) and lead(IV) acetate (44.3 mg, 0.1 mmol) in dichloromethane (10 mL) was refluxed under argon atmosphere at for 3 h. The resulting mixture was filtered and the filtrate was evaporated in vacuo. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to ethyl acetate) to give **8ox** (37 mg) as a red-brown solid, $R_f = 0.65$ (ethyl acetate).

8ox: Isolated yield 90%; mp 102-104 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 7.42 (t, J = 7.6 Hz, 4H), 7.24 (t, J = 7.6 Hz, 2H), 6.93 (d, J = 7.6 Hz, 4H), 6.85 (s, 2H), 4.95 (q, J = 7.3 Hz, 1H), 3.76 (s, 3H), 1.69 (d, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M), 170.4, 165.8, 153.6, 150.4, 135.2, 129.5, 126.7, 125.9, 120.7, 53.1, 47.9, 15.3 ppm; IR (KBr) 2999, 2953, 1724, 1590, 1574, 1480, 1384, 1238, 697 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 2999, 2956, 1725, 1576, 1387, 1239, 694 cm^{-1}; HRMS (FAB) *m/z*: $[M+2H]^{2+}$ 415.1544, $[M+H]^+$ 414.1462, $[M]^+$ 413.1381, $C_{24}H_{19}N_3O_4$ (calc. 413.1376).

Synthesis of Phenylenediamine 9red

A mixture of 2-phenyl-4,7-bis(phenylamino)isoindoline-1,3-dione (122 mg, 0.3 mmol) and sodium hydroxide (c.a. 95 mg) in tetrahydrofuran (15 mL) was refluxed for 24 h. After the reaction was completed, the solvent was evaporated and the residue was dried in vacuo. Water (15 mL) was added to the residue, and the solution was acidified with 1N HCl aqueous solution. The purple precipitate was isolated by filtration, washed

with water, and dried in vacuo. Anhydrous dichloromethane (40 mL) was added to a mixture of the thus-obtained purple solid, 1-hydroxybenzotriazole (189 mg, 1.4 mmol), L-proline methyl ester hydrochloride (265 mg, 1.6 mmol), and triethylamine (diluted, 3.2 mL). The mixture was stirred at 0 °C, and a solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (268 mg, 1.4 mmol) in anhydrous dichloromethane (40 mL) was dropwise added to the mixture over 1 h. Then, the mixture was stirred at ambient temperature for 72 h. The resulting mixture was diluted with dichloromethane (20 mL), washed with saturated $NaHCO_3$ aqueous solution (30 mL x 2), water (30 mL), and saturated NaCl aqueous solution (30 mL). After separating and discarding the water phase, the organic phase was dried on Na_2SO_4. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 1:4) to give **9red** (133 mg) as a yellow solid, R_f = 0.50 (ethyl acetate: hexane = 4:1).

9red: Isolated yield 78%; mp 153-156 °C (uncorrected); ^{1}H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 7.36 (s, 2H), 7.26 (t, J = 7.8 Hz, 4H), 7.15 (d, J = 7.8 Hz, 4H), 6.90 (t, J = 7.8 Hz, 2H), 6.81 (s, 2H) 4.60-4.56 (m, 2H), 3.78 (s, 6H), 3.62-3.56 (m, 2H), 3.45-3.39 (m, 2H), 2.37-2.30 (m, 2H), 1.98-1.79 (m, 6H); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M), 173.6, 167.0, 143.5, 132.7, 129.3, 124.9, 120.7, 118.7, 117.5, 58.2, 52.6, 48.2, 29.6, 24.9 ppm; IR (KBr) 3355, 3338, 3041, 2972, 2952, 2886, 1736, 1635, 1599, 1511, 1500, 1416, 1335, 1224, 1200, 1026 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3354, 3051, 2987, 2956, 1736, 1636, 1601, 1508, 1498, 1415, 1361, 1223, 1202, 1028 cm^{-1}; HRMS (EI) *m/z*: $[M]^+$ 570.2465, $C_{32}H_{34}N_4O_6$ (calc. 570.2478).

Synthesis of Quinonediimine 9ox

A mixture of phenylenediamine **9red** (57.0 mg, 0.1 mmol) and lead(IV) acetate (44.3 mg, 0.1 mmol) in dry dichloromethane (5.0 mL) was refluxed under argon atmosphere at for 6 h. The resulting mixture was filtered and the filtrate was evaporated in vacuo. After evaporation of the solvent, a mixture was purified by silica-gel column chromatography (from hexane to ethyl acetate) to give **9ox** (51.1 mg) as a red-brown solid, R_f = 0.38 (ethyl acetate : hexane = 4 : 1).

9ox: Isolated yield 80%; mp 103-105 °C (uncorrected); ^{1}H NMR (600 MHz, CD_3COCD_3, 1.0 x 10^{-2} M, *syn/anti* = 5:1) δ 7.43-7.38 (m, 5H), 7.21-7.17 (m, 2.4H), 6.95 (d, 1H), 6.91-6.86 (m, 4H), 6.84 (s, 2H), 4.85-4.84 (m, 1H), 4.74-4.73 (m, 0.2H), 4.52-4.50 (m, 0.2H), 4.41-4.39 (m, 1H), 4.05-4.00 (m, 1.2H), 3.85-3.82 (m, 1.2H), 3.77-3.72 (m, 0.2H), 3.69 (s, 3H), 3.61 (s, 1.2H), 3.54-3.49 (m, 1.2H), 3.46 (s, 3H), 2.31-2.13 (m, 2.4H), 2.03-1.87 (m, 7,2H); ^{13}C NMR (100 MHz, CD_3COCD_3, 1.0 x 10^{-2} M, *syn/anti* = 5:1) 173.1, 172.7, 172.6, 165.3, 164.9, 163.9, 163.6, 157.5, 156.6, 156.5, 156.2, 156.1, 150.8, 150.7, 140.6, 140.2, 138.2, 129.9, 129.8, 129.7, 126.4, 126.2, 126.1, 125.4, 125.3, 125.2, 125.1, 121.6, 121.4, 121.3, 121.2, 61.0, 60.9, 59.3, 59.0, 52.2, 52,1, 51.9, 48.4, 48.3, 46.2, 30.9, 30.8, 25.4, 25.3, 23.2 ppm; IR (KBr) 3058, 2952, 2879, 1747, 1650, 1575, 1436, 1280, 1198, 1172, 1090 cm^{-1}; IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3053, 2954, 2883, 1749, 1645, 1577, 1437, 1280, 1199, 1175, 1026 cm^{-1}; HRMS (EI) *m/z*: $[M+2H]^{2+}$ 570.2492, $[M+H]^+$ 569.2420, $[M]^+$ 568.2316, $C_{32}H_{32}N_4O_6$ (calc. 568.2322).

General Procedure for Synthesis of the Chiral Homobimetallic Palladium(II) Complexes 10

A mixture of the quinonediimine derivative **6ox-L** or **6ox-D** (21.1 mg, 0.04 mmol) and $Pd(OAc)_2$ (19.3 mg, 0.09 mmol) in acetonitrile (5 mL) was stirred at ambient temperature for 5 h under an atmosphere of argon in the dark. After filtration and evaporation the solvent, the palladium(II) complexes **10** (**10-L:** 21.8 mg; **10-D:** 19.3 mg) were isolated by recrystallization from acetonitrile/ether as a brown crystal.

10-L: Isolated yield 70%; mp 152-154 °C (uncorrected); ^{1}H NMR (400 MHz, CD_3CN, 1.0 x 10^{-2} M): δ 7.58 (s, 2H), 7.53 (t, J = 7.3 Hz, 4H), 7.46 (t, J = 7.3 Hz, 4H), 7.05 (t, J = 7.3 Hz, 2H), 4.34 (q, J = 6.9 Hz, 2H), 2.09 (s, 6H), 1.31 (d, J = 6.9 Hz, 6H); IR (KBr): 3064, 2973, 2924, 1627, 1599, 1555, 1448, 1395, 1371, 1340, 1264, 1123 cm^{-1}; Anal. Calcd. for $C_{30}H_{26}N_6O_6Pd_2$: C, 46.23; H, 3.36; N, 10.78; Found: C, 45.99; H, 3.41; N, 10.90.

10-D: Isolated yield 62%; mp 152-154 °C (uncorrected); ^{1}H NMR (400 MHz, CD_3CN, 1.0 x 10^{-2} M): δ 7.58 (s, 2H), 7.53 (t, J = 7.3 Hz, 4H), 7.46 (t, J = 7.3 Hz, 4H), 7.05 (t, J = 7.3 Hz, 2H), 4.34 (q, J = 6.9 Hz, 2H), 2.09 (s, 6H), 1.31 (d, J = 6.9 Hz, 6H); IR (KBr): 3064, 2973, 2924, 1627, 1599, 1555, 1448, 1395, 1371, 1340, 1264, 1123 cm^{-1}; Anal. Calcd. for $C_{30}H_{26}N_6O_6Pd_2$: C, 46.23; H, 3.36; N, 10.78; Found: C, 45.95; H, 3.48; N, 10.90.

Proton Magnetic Resonance Nuclear Overhauser Effect Measurements

A sample was prepared under nitrogen atmosphere. Nuclear Overhauser effect experiments were performed with 1 second irridiation of a freeze-pump-thaw degassed CD_2Cl_2 solution of **9red**. The 400 MHz ^1H NMR spectra were recorded at 25 °C. Nuclear Overhauser enhancements were obtained by saturation of the desired resonance. Irradiation of the pyrrolidine protons at the 5-position enhanced the phenyl protone at the 2-position (see Figure 7).

UV/vis Measurements

UV/vis spectra were measured using a Hitachi U-3500 spectrophotometer in a deaerated dichloromethane or acetonitrile solution under a nitrogen atmosphere at 25 °C.

CD Measurements

CD spectra were measured using a JASCO J-720 spectropolarimeter in a deaerated dichloromethane or acetonitrile solution under a nitrogen atmosphere at 25 °C.

General Procedures of Electrochemical Experiments

The cyclic voltammetry of **6-L**, **7**, **8red** and **9red** were performed in a deareted dichloromethane solution (5.0×10^{-4} M) containing 0.1 M Bu_4NClO_4 as a supporting electorate at 25 °C with a three-electrode system consisting of a platinum working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/Ag^+ (0.01 M)

reference electrode (BAS) at 100 mVs^{-1} scan rate. The cyclic voltammetry of **6ox-L** and **10-L** were performed in a deareted dimethyl sulfoxide solution (5.0 x 10^{-4} M) containing 0.1 M Bu_4NClO_4 as a supporting electorate at 25 °C with a three-electrode system consisting of a glassy carbon working electrode (BAS), a platinum auxiliary electrode (BAS), and an Ag/Ag^+ (0.01 M) reference electrode (BAS) at 10 mVs^{-1} scan rate. Redox potentials are given *vs.* Fc/Fc^+.

Generation of 6ox-L$^{\bullet-}$.

For spectroscopic purposes, **6ox-L$^{\bullet-}$** was generated by treatment of **6ox-L** with 1.0 equiv. of cobaltcene in acetonitrile. The cobaltocene and cobaltocenium ion presented in the reaction mixture did not significantly interfere with the electronic spectrum because of their low extinction coefficient below 400 nm.

Generation of 6red-L$^{\bullet+}$, 8red $^{\bullet+}$,and 9red $^{\bullet+}$.

For spectroscopic purposes, **6red-L$^{\bullet+}$, 8red $^{\bullet+}$** , and **9red $^{\bullet+}$** were generated by treatment of **6red-L, 8red**, and **9red** with 1.0 equiv. of nitrosonium tetrafluoroborate in acetonitrile, respectively.

ESR Measurements

ESR spectra of **6red-L$^{\bullet+}$; 6ox-L$^{\bullet-}$, 8red$^{\bullet+}$** , and **9red$^{\bullet+}$** were measured using a JEOL X-band spectrometer (JES-RE1XE) under a nitrogen atmosphere at 25 °C. **6red-L** was measured in a deaerated acetonitrile solution with the concentration 1.0 x

10^{-4} M under nonsaturating microwave power conditions (1.0 mW) operating at 9.0610 GHz. **8red**$^{\bullet+}$ was measured in a deaerated acetonitrile solution with the concentration 1.0 x 10^{-4} M under nonsaturating microwave power conditions (1.0 mW) operating at 8.9928 GHz. **9red**$^{\bullet+}$ was measured in a deaerated acetonitrile solution with the concentration 1.0 x 10^{-4} M under nonsaturating microwave power conditions (1.0 mW) operating at 9.0478 GHz. **6ox-L**$^{\bullet-}$ was measured in a deaerated dichloromethane solution with the concentration 1.0 x 10^{-4} M under nonsaturating microwave power conditions (1.5 mW) operating at 9.0546 GHz.

X-ray Structure Analysis

Measurements for **6red-L** and **10** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Ka radiation and measurements of **6red-D** and **9red** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Ka radiation. All measurements for **3red** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractmeter with graphite monochromated Mo Ka radiation. The structures of **6red**, **9red** and **10** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 1 and 3. Hydrogen bonds are listed in Table 2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-816048 for **6red-L**, CCDC-816049 for **6red-D**, CCDC-832415 for **9red**, CCDC-888392 for **10-L**, and CCDC-888393 for **10-D** Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for **6red** and **9red**.

	6red-L	**6red-D**	**9red**
Empirical formula	$C_{28}H_{30}N_4O_6$	$C_{28}H_{30}N_4O_6$	$C_{32}H_{34}N_4O_6$
Formula weight	518.57	518.57	570.64
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$ (No. 4)	$P2_1$ (No. 4)	$P2_1$ (No. 4)
a [Å]	14.8203(6)	14.8463(3)	11.8520(4)
b [Å]	5.0199(2)	5.03545(9)	5.03545(9)
c [Å]	17.7205(7)	17.7458(3)	14.5076(6)
β [deg]	95.8060(17)	95.7702(10)	91.710(1)
V [Å^3]	1311.58(9)	1319.91(4)	1470.81(9)
Z	2	2	2
D_{calcd} [g cm^{-3}]	1.313	1.305	1.288
μ(Mo Kα) [cm^{-1}]	0.94		0.90
μ(Cu Kα) [cm^{-1}]		7.672	
T [°C]	4.0	4.0	4.0
λ(Mo Kα) [Å]	0.71069		0.71069
λ(Cu Kα) [Å]		1.54186	
$R1$ [a]	0.0832	0.0389	0.0472
$wR2$ [b]	0.2456	0.1182	0.1447

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Hydrogen bondings for **6red** and **9red**.

crystal	type [a]	donor	acceptor	D • • • A (Å)	D–H • • • A (°)
6red-L	intra	N(1)	O(1)	2.756(5)	135(4)
	intra	N(2)	O(11)	2.749(5)	136(3)
	inter	N(3)	O(1)	2.832(5)	138(2)
	inter	N(13)	O(11)	2.842(5)	152.1(19)
6red-D	intra	N(1)	O(1)	2.761(2)	131(2)
	intra	N(2)	O(11)	2.747(2)	132(2)
	inter	N(3)	O(1)	2.845(2)	141.8(16)
	inter	N(13)	O(11)	2.844(2)	152.2(16)
9red	intra	N(1)	O(2)	3.049(3)	156(2)
	intra	N(2)	O(12)	2.989(3)	162(2)

[a] inter: intermolecular, intra: intramolecular.

Table 3. Crystallographic data for **10**.

	10-L	**10-D**
Empirical formula	$C_{30}H_{26}N_6O_6Pd_2$	$C_{30}H_{26}N_6O_6Pd_2$
Formula weight	779.37	779.37
Crystal system	tetragonal	tetragonal
Space group	$I4_1$ (No. 80)	$I4_1$ (No. 80)
a [Å]	19.172(2)	19.292(5)
c [Å]	16.5460(17)	16.516(3)
V [Å^3]	6081.8(11)	6147.1(23)
Z	8	8
D_{calcd} [g cm^{-3}]	1.702	1.684
μ(Mo Kα) [cm^{-1}]	12.366	12.234
T [°C]	-100	-100
λ(Mo Kα) [Å]	0.71075	0.71075
$R1$ [a]	0.0534	0.0708
$wR2$ [b]	0.1737	0.1672

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 4. Selected bond length and angles of **10**.

	10-L	**10-D**
	Bond lengths / Å	
Pd(1)-N(1)	2.008(8)	1.944(9)
Pd(1)-N(2)	1.989(8)	1.940(8)
Pd(1)-N(3)	2.060(10)	2.006(10)
Pd(1)-O(2)	1.988(7)	1.988(8)
Pd(11)-N(11)	1.994(8)	2.021(9)
Pd(11)-N(12)	1.947(8)	1.940(9)
Pd(11)-N(13)	2.026(9)	2.014(11)
Pd(11)-O(12)	1.986(7)	1.972(8)
N(1)-C(1)	1.295(14)	1.356(14)
N(1)-C(4)	1.454(12)	1.473(14)
N(11)-C(21)	1.333(13)	1.298(15)
N(11)-C(24)	1.440(12)	1.433(14)
	Bond angles / °	
N(1)-Pd(1)-N(2)	93.9(3)	93.4(4)
N(1)-Pd(1)-N(3)	94.2(3)	93.8(4)
N(2)-Pd(1)-O(2)	83.4(3)	82.9(4)
N(3)-Pd(1)-O(2)	88.5(3)	89.8(4)
N(11)-Pd(11)-N(12)	93.3(3)	93.4(4)
N(11)-Pd(11)-N(13)	94.7(3)	93.5(4)
N(12)-Pd(11)-O(12)	83.6(3)	84.2(4)
N(13)-Pd(11)-O(12)	88.4(3)	88.8(4)
C(1)-N(1)-Pd(1)	127.3(6)	128.0(7)
C(4)-N(1)-Pd(1)	114.7(6)	115.4(9)
C(10)-N(2)-Pd(1)	126.8(7)	130.9(7)
C(11a)-N(2)-Pd(1)	111.9(6)	112.2(6)
C(12)-O(2)-Pd(1)	113.7(6)	115.2(7)
C(21)-N(11)-Pd(11)	126.7(6)	126.1(8)
C(24)-N(11)-Pd(11)	114.6(6)	114.1(7)
C(30)-N(12)-Pd(11)	131.2(6)	130.4(8)
C(31a)-N(12)-Pd(11)	111.0(6)	113.1(7)
C(32)-O(12)-Pd(11)	115.1(7)	114.3(7)

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Chapter 3. Luminescent properties of phenylenediamines and quinonediimines based on their redox states

3-1. Introduction

π-Conjugated compounds with luminescent properties have paid much attention because of their applications to electronic materials such as light-emitting diodes (LEDs).[1] Solution processing is possible with organic materials, permitting the easy and low-cost fabrication of optoelectronic devices. The emission colors of π-conjugated molecules are closely related to their π-conjugated electronic states.

Phenylenediamines are molecular units of polyanilines as π-conjugated polymers. The redox-active phenylenediamine exists in three different redox forms: the reduced phenylenediamine, the partially oxidized phynylenediamine radical cation, and the oxidized quinonediimine. Hirao's group has demonstrated the redox switching of the emission properties of Ru(II) dipyridyl complexes bearing the phenylenediamine moieties by changing their redox states of the phenylenediamine moieties.[2] On the other hand, 2,5-bis(arylamino)terephthalate derivatives have been reported to show luminescent properties.[3] The luminescent properties of phenylenediamine derivatives are expected to be regulated by changing their redox states. However, these compounds are hardly found in the literature, although they are brilliant dyes with pronounced fluorescence behavior. Thereby, the luminescent properties of phenylenediamines for redox switching were elucidated.

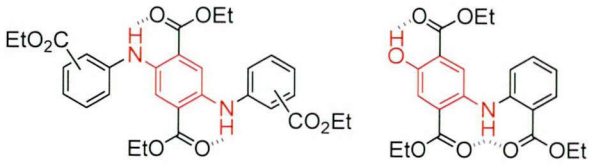
3-2. Results and Discussion

3-2-1. Syntheses and luminescence properties of phenylenediamine and phenylaminophenol derivatives bearing ethoxycarbonyl groups

The phenylenediamine derivatives **11red** were synthesized by the reaction of diethyl 2,5-dioxo-1,4-cyclohexanedicarboxylate with the corresponding substituted anilines. Phenylaminophenol **12red-*o*** was also obtained as a by-product from the synthesis of **11red-*o*** (Figure 1). The thus-obtained phenylenediamines and phenylaminophenol are stable under ambient air and light, and were fully characterized by spectroscopically and elemental analyses.

In the ^{1}H NMR spectrum of **11red-*o*** in CD_2Cl_2 (1.0×10^{-2} M), the NH signals for the phenylenediamine moiety were hardly perturbed by the addition of aliquot of DMSO-d_6 to CD_2Cl_2 (CD_2Cl_2: 10.56 ppm, CD_2Cl_2-DMSO-d_6 (9:1): 10.51 ppm). The FT-IR spectrum of **11red-*o*** in CH_2Cl_2 (1.0×10^{-2} M) showed a hydrogen-bonded NH stretching at 3116 cm^{-1}. From these observations, the NH moieties are indicated to participate in intramolecular hydrogen bonding in solution. The intramolecular hydrogen bonding was observed in the case of **11red-*m*** and **11red-*p***. Furthermore, the OH of **12red-*o*** was found to participate in intramolecular hydrogen bonding with the CO moiety as shown in Figure 1.

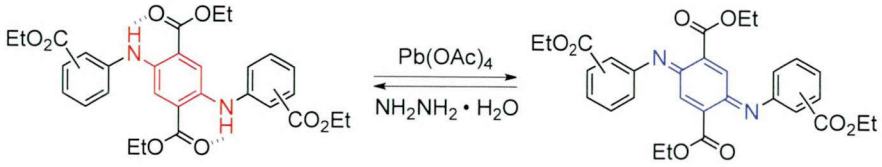
The phenylenediamine **11red** was oxidized into the quinonediimine **11ox** by treatment with lead(IV) acetate as an oxidant. The oxidized form **11ox** could be again reduced to **11red** with hydrazine monohydrate (Scheme 1).



11red-*o*: *ortho*
11red-*m*: *meta*
11red-*p*: *para*

12red-*o*

Figure 1. Phenylenediamine and phenylaminophenol derivatives.



11red-*o*: *ortho*
11red-*m*: *meta*
11red-*p*: *para*

11ox-*o*: *ortho*
11ox-*m*: *meta*
11ox-*p*: *para*

Scheme 1.

The crystal structure of diethyl *N*,*N'*-diphenyl 2,5-diaminoterephtalate was reported to show the formation of the intramolecular hydrogen bondings between NH and CO at the central benzene ring. The single-crystal X-ray structure determination of **11red-*o*** also confirmed the formation of the intramolecular hydrogen bonding between the NH and CO at the central benzene ring (Table 1). The *anti*-conformation of the π-conjugated moiety is formed (Figure 2), and another hydrogen bondings were observed between NH and CO at the terminal benzene rings. The terminal and central benzene rings are oriented with a dihedral angle of 43.82(8)°. This is probably due to the steric repulsion between the *ortho*-hydrogen atoms despite the formation of the intramolecular hydrogen bondings, which might induce a coplanar structure of theπ-conjugated moiety. The crystal structure of **11ox-*o*** revealed the *anti*-conformation with a dihedral angle of 99.22(5)° between the terminal and central benzene rings as

Table 1. Intramolecular hydrogen bondings for **11red-*o*** and **12red-*o***.

crystal	donor	acceptor	D···A (Å)	D-H···A (°)
11red-*o* [a]	N(1)	O(1*)	2.700(1)	123(2)
	N(1)	O(3)	2.713(2)	129(1)
	N(1*)	O(1)	2.700(1)	123(2)
	N(1*)	O(3*)	2.713(2)	129(1)
12red-*o*	N(1)	O(1*)	2.760(2)	120(1)
	N(1)	O(3)	2.686(2)	127(1)
	O(5)	O(1)	2.611(2)	136(2)

[a] The molecule sites on an inversion center.

shown in Figure 2b. This structure is considered to be caused by the steric repulsion between the *ortho*-hydrogen atoms at each benzene ring due to the short imine bond length. Phenylaminophenol **12red-*o*** was found to form intramolecular hydrogen bonding between not only OH and CO but also NH and CO in a crystal structure (Figure 2c).

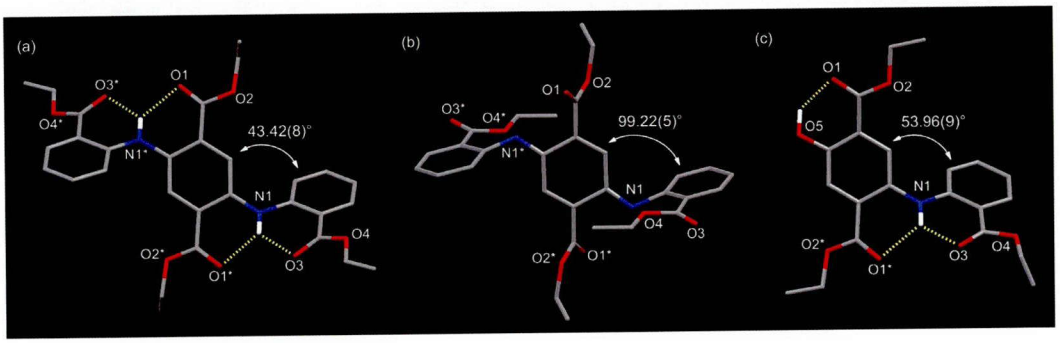


Figure 2. Crystal structures of (a) **11red-*o***, (b) **11ox-*o***, and (c) **12red-*o***.

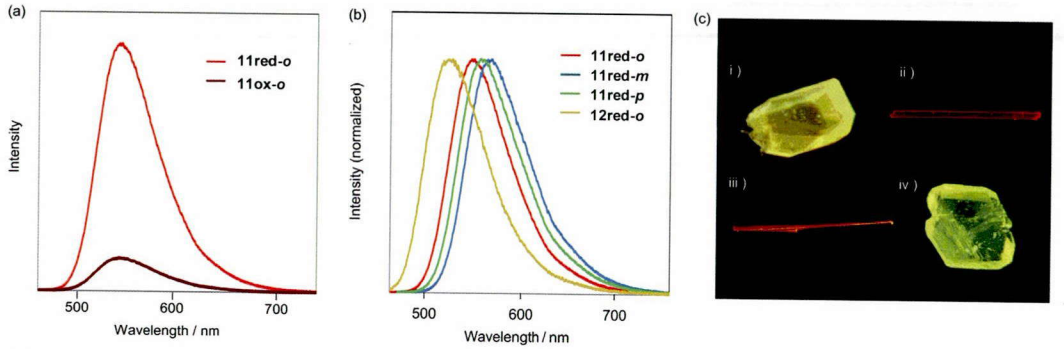


Figure 3. a) Emission spectra of **11red-*o*** (λ_{ex} = 430 nm) and **11ox-*o*** (λ_{ex} = 449 nm) and b) **11red-*o*** (λ_{ex} = 430 nm), **11red-*m***, (λ_{ex} = 458 nm), **11red-*p*** (λ_{ex} = 446 nm), and **12red-*o*** (λ_{ex} = 415 nm) in dichloromethane (1.0 x 10-5 M). c) Photographs (under 365 nm) of i) **11red-*o***, ii) 11red-m, iii) **11red-*p***, and iv) **12red-*o***.

The reduced form **11red-*o*** exhibited strong luminescence at 536 nm (Figure 3a). On the contrary, weak luminescence was observed with **11ox-*o***. These findings indicate that redox switching of the luminescent properties is achieved by changing the redox states of the π-conjugated moiety. The redox switching was also observed between **11red-*m*** and **11ox-*m*** or **11red-*p*** and **11ox-*p*** (Figure 3b, and c). In the present π-conjugated systems, emission wavelength is largely dependent on the substituent position of the ethoxycarbonyl group on the terminal benzene rings. Phenylenediamine **11red-*p*** showed a red-shift of the maximum emission wavelength as compared with **11red-*o*** (Table 2 and Figure 3d). Further red-shift of the maximum emission wavelength was observed in the case of **11red-*m***. This result might be contributed to the difference of the π-conjugated electronic states. Phenylaminophenol **12red-*o*** showed the maximum wavelength at 511 nm, wherein the luminescent intensity was lower as compared with that of **11red-*o*** (Table 2).

Table 2. Emission data for **11** and **12red-*o***.

	CH_2Cl_2 [a]		In a solid state	
	$\lambda_{em,\,max}$ (nm)	Φ_F [b]	$\lambda_{em,\,max}$ (nm)	Φ_F [c]
11red-*o*	536	0.58	543	0.47
11red-*m*	554	0.27	589	0.08
11red-*p*	543	0.39	604	0.17
12red-*o*	511	0.20	531	0.26
11ox-*o*	536	0.15		
11ox-*m*	552	0.01		
11ox-*p*	543	0.01		

The phenylenediamine **11red-*o*** exhibits an intense yellow emission at 543 nm even in a solid state (Figure 3c). The quantum yield of **11red-*o*** at ambient temperature, measured in an interesting sphere for packed powder samples, is 0.47 using λ_{ex} = 450 nm (Table 2). Rigid π-conjugated frameworks without conformational disorder have been reported to provide attractive photophysical properties. In the case of **11red-*o***, a rigid π-conjugated structure is considered to be increased by the formation of intramolecur hydrogen bondings between NH and CO at the terminal benzene rings.

3-2-2. Luminescent properties of phenylenediamine derivatives bearing amino acid moieties

In the preceding section, the luminescent switching properties of phenylenediamines bearing ethoxycarbonyl groups has been demonstrated. Phenylenediamine derivatives bearing amino acid moieties **6red**, **7red**, **8red** and **9red** (Figure 5) exhibited strong luminescence 500-600 nm (Figure 6). On the contrary, weak luminescence was observed with the oxidized quinonediimine derivatives **6ox**, **7ox**, **8ox** and **9ox** (Figure 6). These findings indicate that redox switching of the luminescent properties was achieved by changing the redox states of the π-conjugated moiety.

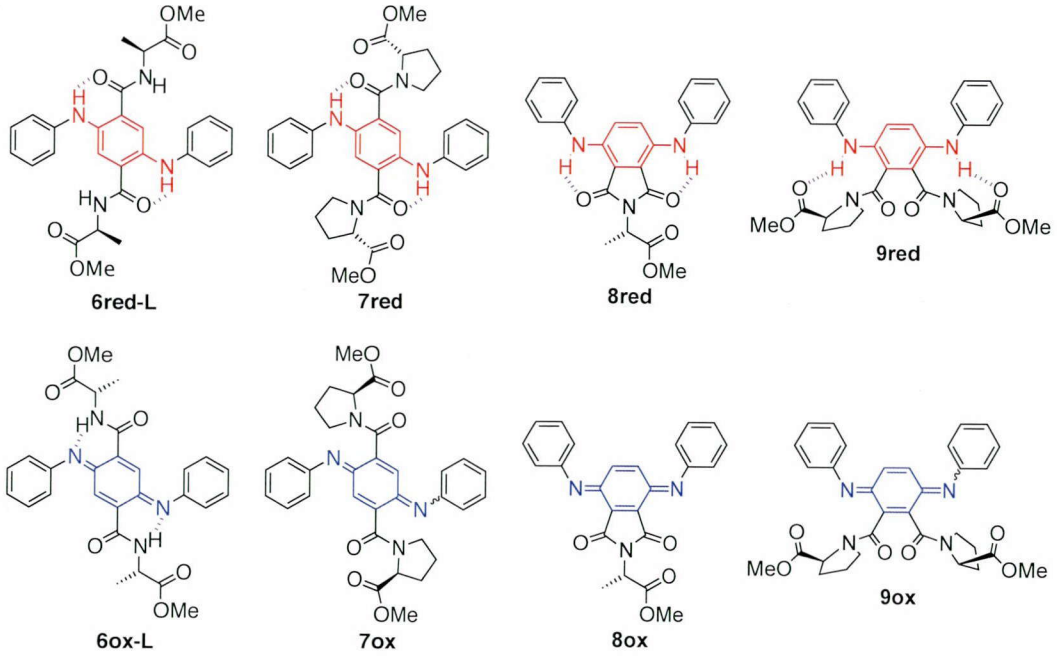


Figure 5. Phenylenediamines and quinonediimines bearing amino acid moieties.

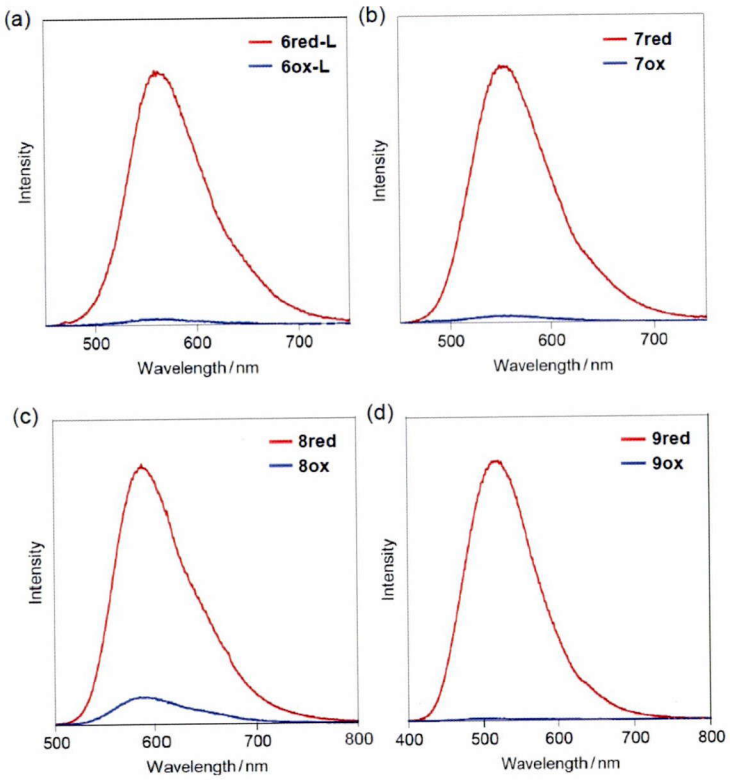


Figure 6. a) Emission spectra of **6red-L** (λ_{ex} = 430 nm) and **6ox-L** (λ_{ex} = 449 nm), (b) **7red** (λ_{ex} = 430 nm) and **7ox** (λ_{ex} = 458 nm), (c) **8red** (λ_{ex} = 409 nm) and **8ox** (λ_{ex} = 409 nm), and (d) **9red** (λ_{ex} = 375 nm) and **9ox** (λ_{ex} = 375 nm) in dichloromethane (1.0×10^{-5} M) at 25 °C under a nitrogen atmosphere.

3-3. Summary

In conclusion, a series of luminescent phenylenediamines and its analogue were synthesized to control the luminescent properties. The luminescent switching was demonstrated by changing the redox states of the π-conjugated phenylenediamines. Emission wavelength of phenylenediamines was tuned by the substituent position of ethoxycarbonyl group on the terminal benzene rings. Chirality-organized phenylenediamines were also shown the luminescent switching properties based on the redox states of the π-conjugated moieties.

3-4. Experimental Section

General Methods

Fluorescence emission was recorded using a SHIMADZU RF-5300PC spectrofluorometer under an argon atmosphere at 25 °C. Fluorescence measurements were conducted using 1-cm pathlength quartz cuvettes.

Synthesis of Phenylenediamine and phenylaminophenol 11red-*o* and 12red-*o*

Ethyl 2-aminobenzoate (793 mg, 4.8 mmol) was added to a solution of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (505 mg, 2.0 mmol) in acetic acid (10 mL). The mixture was stirred at 100 °C for 25 h and then cooled to ambient temperature. The orange solution was neutralized with saturated $NaHCO_3$ aqueous solution (20 mL x 2) and extracted with dichloromethane. After separating and discarding the water phase, the organic phase was dried on Na_2SO_4 and filtered. After evaporation of the solvent, a mixture of **11red-*o***, **12red-*o***, and unreacted substrate were obtained as a yellow-orange solid. The mixture was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 4:1) to give **11red-*o*** (289 mg, 0.53 mmol) as a pale-orange solid, R_f= 0.59 (hexane/ethyl acetate = 5:2), and **12red-*o*** (50.1 mg, 0.12 mmol) as a yellow solid, R_f = 0.65 (hexane/ethyl acetate = 5:2).

11red-*o*: Isolated yield 27%; mp 148-149 °C (uncorrected); IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3316, 1696, 1578, 1522, 1443, 1414, 1313, 1237, 1211 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 10.57 (s, 2H), 8.13 (s, 2H), 8.00 (d, 2H, J = 8.1 Hz), 7.42-7.36 (m, 4H), 6.86 (t, 2H, J = 7.3 Hz), 4.38 (q, 4H, J = 7.3 Hz), 4.33 (q, 4H, J = 7.3 Hz), 1.40

(t, 6H, J = 7.3 Hz), 1.32 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 167.8, 166.5, 145.8, 136.4, 133.8, 132.1, 124.2, 123.2, 119.2, 116.3, 61.8, 61.2, 14.5, 14.3 ppm; HRMS (FAB) *m/z*: $[M]^+$ 548.2175, $C_{30}H_{32}N_2O_8$ (calc. 548.2159); Anal. Calcd. for $C_{30}H_{32}N_2O_8$: C, 65.68; H, 5.88; N, 5.11. Found: C, 65.45; H, 5.77; N, 5.05.

12red-*o*: Isolated yield 6%; mp 101 °C (uncorrected); IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3320, 3268, 2991, 1685, 1519, 1454, cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 10.35 (s, 1H), 10.34 (s, 1H), 8.02 (s, 1H), 7.98 (dd, 1H, J = 8.0, 1.6 Hz), 7.55 (s, 1H), 7.33 (dt, 1H, J = 7.8, 1.6 Hz), 7.25 (dd, 1H, J = 8.0, 1.1 Hz), 6.81 (dt, 1H, J = 7.8, 1.1 Hz), 4.41-4.32 (m, 6H), 1.39 (t, 3H, J = 7.0 Hz), 1.36 (t, 3H, J = 7.0 Hz), 1.35 (t, 3H, J = 7.0 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 169.6, 168.0, 166.2, 155.6, 146.8, 134.3, 133.9, 132.1, 128.3, 122.9, 120.1, 118.6, 116.6, 115.2, 62.5, 62.0, 14.5, 14.3, 14.2 ppm; HRMS (FAB) *m/z*: $[M]^+$ 401.1499, $C_{21}H_{23}NO_7$ (calc. 401.1475); Anal. Calcd. for $C_{21}H_{23}NO_7$: C, 62.83; H, 5.78; N, 3.49. Found: C, 62.67; H, 5.77; N, 3.52.

Synthesis of Phenylenediamine 11red-*m*

Acetic acid (10 mL) was added to a mixture of ethyl 3-aminobenzoate (330 mg, 2.0 mmol) and diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (252 mg, 1.0 mmol). The mixture was stirred at 100 °C for 25 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with cooled ethanol, and dried in vacuo. Phenylenediamine **11red-*m*** (236 mg, 0.43 mmol) was obtained as an orange-needle crystal by recrystallization from ethyl acetate.

11red-*m*: Isolated yield 27%, mp 179-180 °C (uncorrected); IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3395, 3345, 3318, 3175, 1714, 1694, 1605, 1586, 1538, 1216 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 8.93 (s, 2H), 8.05 (s, 2H), 7.85 (s, 2H), 7.64 (m, 2H), 7.39-7.38 (m, 4H), 4.37-4.30 (m, 8H), 1.37 (t, 6H, J = 7.1 Hz), 1.32 (t, 6H, J = 7.1 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 167.6, 166.6, 142.8, 137.9, 132.3, 129.7, 123.6,123.4, 120.3, 119.1, 61.8, 61.3, 14.5, 14.3 ppm; HRMS (FAB) *m/z* $[M]^+$ 548.2165, $C_{30}H_{32}N_2O_8$ (calc. 548.2159); Anal. Calcd. for $C_{30}H_{32}N_2O_8$: C, 65.68; H, 5.88; N, 5.11. Found: C, 65.49; H, 5.64; N, 5.18.

Synthesis of Phenylenediamine 11red-*p*

Acetic acid (10 mL) was added to the mixture of ethyl 4-aminobenzoate (330 mg, 2.0 mmol) and diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (252 mg, 1.0 mmol). The mixture was stirred at 100 °C for 25 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with cooled ethanol, and dried in vacuo. Phenylenediamine **11red-*p*** (249 mg, 0.45 mmol) was obtained as an orange-needle crystal by recrystallization from ethyl acetate.

11red-*p*: Isolated yield 45%, mp 157 °C (uncorrected); IR (CH_2Cl_2, 1.0 x 10^{-2} M) 3414, 3403, 3349, 3318, 3179, 1700, 1605, 1534, 1470, 1397, 1370 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 9.13 (s, 2H), 8.17 (s, 2H), 7.96 (d, 4H, J = 8.7 Hz), 7.19 (d, 4H, J = 8.7 Hz), 4.35 (q, 4H, J = 7.3 Hz), 4.32 (q, 4H, J = 7.3 Hz), 1.37 (t, 6H, J = 7.3 Hz), 1.35 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 167.5, 166.5, 146.8, 137.1, 133.2, 131.6, 123.4, 121.1, 120.7, 117.1, 62.2, 61.0, 14.6, 14.4

ppm; HRMS (FAB) *m/z* $[M]^+$ 548.2162, $C_{30}H_{32}N_2O_8$ (calc. 548.2159); Anal. Calcd. for $C_{30}H_{32}N_2O_8$: C, 65.68; H, 5.88; N, 5.11. Found: C, 65.50; H, 5.78; N, 5.07.

General Procedure for Synthesis of Quinonediimine derivative 11ox

A mixture of phenylenediamine **11red** (54.9 mg, 0.10 mmol) and lead(IV) acetate (53.2 mg, 0.12 mmol) in dry dichloromethane (5.0 mL) was stirred under an argon atmosphere at ambient temperature for 3 h. The resulting mixture was filtered and the filtrate was evaporated in vacuo. The quinonediimine **11ox** was isolated quantitatively as a brown solid and by recrystallization from acetone (**11ox-*o***: 54.5 mg; **11ox-*m***: 54.8 mg; **11ox-*p***: 54.7 mg).

11ox-*o*: Isolated yield quant.; mp 114-115 °C (uncorrected); IR (KBr) 2984, 1733, 1704, 1596, 1473, 1445, 1379, 1297, 1266, 1076 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 8.00 (d, 2H, J = 8.0 Hz), 7.54 (t, 2H, J = 7.6 Hz), 7.25 (t, 2H, J = 7.6 Hz), 6.81 (s, 2H), 6.73 (d, 2H, J = 7.6 Hz), 4.23 (q, 4H, J = 7.3 Hz), 4.22 (q, 4H, J = 7.3 Hz), 1.27 (t, 6H, J = 7.3 Hz), 1.25 (t, 6H, J = 7.3 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 166.1, 165.5, 154.7, 150.5, 139.9, 133.2, 131.6, 125.1, 123.8, 121.2, 119.8, 62.3, 61.5, 14.3, 14.2 ppm; HRMS (FAB) *m/z* $[M+H]^+$ 547.2093, $C_{30}H_{31}N_2O_8$ (calc. 547.2080); Anal. Calcd. for $C_{30}H_{30}N_2O_8$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.67; H, 5.18; N, 5.24.

11ox-*m*: Isolated yield quant.; mp 132-134 °C (uncorrected); IR (KBr) 2979, 1721, 1577, 1384, 1364, 1288, 1100, 1080, 1022 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 7.89 (d, 2H, J = 7.8 Hz), 7.55 (s, 2H), 7.51 (t, 2H, J = 7.8 Hz), 7.09 (d, 2H 7.8 Hz),

7.00 (s, 2H), 4.37 (q, 4H, J = 7.1 Hz), 4.27 (q, 4H, J = 7.1 Hz), 1.39 (t, 6H, J = 7.1 Hz), 1.28 (t, 6H, J = 7.1 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 166.3, 165.6, 155.7, 149.8, 140.6, 132.2, 129.7, 127.0, 124.7, 123.2, 121.4, 62.4, 61.7, 14.5, 14.3 ppm; HRMS (FAB) m/z $[M+2H]^+$ 548.2153, $C_{30}H_{32}N_2O_8$ (calc. 548.2159).

11ox-*p*: Isolated yield quant.; mp 140-141 °C (uncorrected); IR (KBr) 2981, 1714, 1603, 1529, 1453, 1400, 1367, 1276, 1173, 1102 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) δ 8.08 (d, 4H, J = 8.5 Hz), 6.98 (s, 2H), 6.94 (d, 4H, J = 8.5 Hz), 4.37 (q, 4H, J = 7.1 Hz), 4.27 (q, 4H, J = 7.1 Hz), 1.39 (t, 6H, J = 7.1 Hz), 1.28 (t, 6H, J = 7.1 Hz); ^{13}C NMR (100 MHz, CD_2Cl_2, 1.0 x 10^{-2} M) 166.3, 165.4, 155.3, 153.5, 140.5, 131.0, 128.3, 123.6, 120.2, 62.5, 61.4, 14.6, 14.3 ppm; HRMS (FAB) m/z $[M+2H]^+$ 548.2170, $C_{30}H_{32}N_2O_8$ (calc. 548.2159).

General Procedure for Preparation of Phenylenediamine derivative 11red

To a dichloromethane (5 mL) solution of **11ox** (5.46 mg, 0.01 mmol) was dropwise added hydrazine monohydrate (0.5 mL, 100 mmol) under an argon atmosphere at ambient temperature. The mixture was stirred at ambient temperature for 30 h. After evaporation of this solution, the resulting mixture was purified by silica-gel column chromatography (from hexane to hexane/ethyl acetate = 4:1) to give **11red** (**11red-*o***: 4.81 mg, 88%; **11red-*m***: 4.54 mg, 83%; **11red-*p***: 4.70 mg, 86%.).

UV/vis and Emission Measurements

UV/vis spectra of **6-L**, **7**, **8**, **9**, **11**, and **12red-*o*** were measured using a Hitachi U-3500 spectrophotometer in a deaerated dichloromethane solution with the concentration 1.0 x 10^{-5} M under an argon atmosphere at 25 °C. Emission spectra of **6-L**, **7**, **8**, **9**, **11** and **12red-*o*** were measured using a SHIMADZU RF-5300PC spectrofluorophotometer in a deaerated dichloromethane solution with the concentration 1.0 x 10^{-5} M under an argon atmosphere at 25 °C.

X-ray Structure Analysis

Measurements for **11red-*o*** and **12red-*o*** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation and measurements of **11ox-*o*** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractmeter with graphite monochromated Cu Kα radiation. The structures of **11red-*o*,** **11ox-*o*,** and **12red-*o*** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-755547 for **11red-*o***, CCDC-755548 for **11ox-*o***, and CCDC-755549 for **12red-*o***. Copies of the data can be obtained free of charge on

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystallographic data for **11-*o***, **12red-*o***

	11red-*o*	**11ox-*o***	**12red-*o***
formula	$C_{30}H_{32}N_2O_8$	$C_{30}H_{30}N_2O_8$	$C_{21}H_{23}N_1O_5$
formula weight	548.59	546.58	369.42
crystal system	triclinic	monoclinic	triclinic
space group	*P*-1 (No. 2)	$P2_1/c$ (No. 14)	*P*-1 (No. 2)
a, Å	8.1742(5)	9.2400(2)	8.3035(6)
b, Å	8.7541(6)	15.0566(3)	10.3553(8)
c, Å	10.8412(8)	10.4578(2)	12.899(1)
α, deg	100.156(2)		73.132(3)
β, deg	109.775(2)	102.5477(8)	88.385(3)
γ, deg	97.572(2)		75.938(2)
V, Å^3	703.06(8)	1420.17(5)	1028.6(2)
Z	1	2	2
D_{calcd}, g cm^{-3}	1.296	1.278	1.193
μ(Mo Kα), cm^{-1}	0.94		0.85
μ(Cu Kα), cm^{-1}		7.76	
T, °C	4.0	4.0	4.0
λ(Mo Kα), Å	0.71075		0.71075
λ(Cu Kα), Å		1.54186	
*R*1 [a]	0.079	0.039	0.071
*wR*2 [b]	0.240	0.165	0.271

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

3-5. References

1. a) *Organic Light-Emitting Devices. Synthesis, Properties and Applications* (Eds.: K. Müllen, U. Scherf), Wiley-VCH: Weinheim, **2006**; b) *Highly Efficient OLEDs with Phosphorescent Materials* (Ed.: H. Yersin), Wiley-VCH: Weinheim, **2008**; c) A. C. Grimsdale, K. L. Chan, R. E. Martin, P. G. Jokisz, A. B. Holms, *Chem. Rev.* **2009**, *109*, 897-1091.
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Conclusions

In this dissertation, the development of chirality-organized redox-active conjugates with oligoanilines is described. The formation of the intramolecular hydrogen bondings based on the introduction of amino acid moieties was found to play an important role in the structural and conformational regulation of the π-conjugated aniline backbones. Furthermore, the intramolecular hydrogen bonds were shown to play an important role in the stabilization of the redox species of polyaniline-unit molecules, wherein the chirality-organized structures are preserved through intramolecular hydrogen bondings. The strategy for chirality organization through intramolecular hydrogen bondings provides an efficient and feasible route to chiral redox-active molecule, in which hydrogen bonding is envisioned to play an important role as a proton dopant and a binding unit for the controlled assembly of π-conjugated moieties. These chirality-organized oligoanilines and their derivatives are considered to have potential as promising functionalized materials and asymmetric redox catalysts.

In chapter 1, polyaniline bearing amino acid moieties was synthesized by oxidative polymerization of aniline derivative. The chirality organization of the π-conjugated moieties was revealed spectroscopically. Furthermore, the formation of the intramolecular hydrogen bondings was shown to play the important role in the conformational and chiral regulation of the oligoanilines through the studies of oligoanilines bearing amino acid moieties.

In chapter 2, the chirality organization of polyaniline-unit molecules was achieved by the introduction of amino acid moieties through intramolecular hydrogen bonding. Furthermore, the formation of the intramolecular hydrogen bondings was found to play an important role in the stabilization of the redox species of these polyaniline-unit molecules, wherein the chirality-organized structures are preserved by the intramolecular hydrogen bondings. On the other hand, the chirality-organized quinonediimine derivatives by the introduction of amino acid moieties were performed to serve as a π-conjugated bridging ligand to afford the conjugated chiral palladium(II) complexes.

In chapter 3, the phenylenediamine derivatives show the luminescence properties with moderate quantum yields. It is noteworthy that the luminescence-switching properties based on the redox states of the phenylenediamine moiety were revealed.

These results and findings provide a significant contribution toward not only the fundamental information for the chirality-organized polyanilines and their redox properties, but also their potential applications for materials and asymmetric catalysts.

List of Publications

(1) "Luminescent Properties of Phenylenediamine Derivatives Depending on the Redox States"
Satoshi D. Ohmura, Toshiyuki Moriuchi, and Toshikazu Hirao
Tetrahedron Lett. **2010**, *51*, 3190-3192

(2) "Chirality Organization of Aniline Oligomers through Hydrogen Bonds of Amino Acid Moieties"
Satoshi D. Ohmura, Toshiyuki Moriuchi, and Toshikazu Hirao
J. Org. Chem. **2010**, *75*, 7909-7912

(3) "Hydrogen-Bonding Induced Chirality Organization and Stabilization of Redox Species of Polyaniline-Unit Molecules by Introduction of Amino Acid Pendant Groups"
Toshiyuki Moriuchi, Satoshi D. Ohmura, Kenji Morita, and Toshikazu Hirao
Chem. Asian J. **2011**, *6*, 3206-3213

(4) "Chirality Organization in Phenylenediamines Induced by a Nonpeptidic Reverse-Turn"
Toshiyuki Moriuchi, Satoshi D. Ohmura, Kenji Morita, and Toshikazu Hirao
Asian J. Org. Chem. **2012**, *1*, 52-59

(5) "Chiral Homobimetallic Palladium(II) Complexes Composed of Chirality-Organized Quinonediimines Bearing Amino Acid Moieties"
Satoshi D. Ohmura, Toshiyuki Moriuchi, and Toshikazu Hirao
J. Inorg. Organomet. Polym. **2013**, *23*, 251-255

Supplementary Publications

(1) "Design and Characterization of Ferrocene-Peptide-Oligoaniline Conjugates"
Toshiyuki Moriuchi, Nami Kikushima-Honda, Satoshi D. Ohmura, and Toshikazu Hirao
Tetrahedron Lett. **2010**, *51*, 4530-4533

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