



Luminescent properties of phenylenediamine derivatives depending on the redox states

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ABSTRACT

Phenylenediamines bearing the ethoxycarbonyl groups were synthesized to modulate luminescent properties. Switching of the luminescent properties was achieved by redox change between the phenylenediamine and quinonediimine derivatives.

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Since the last decade, π -conjugated compounds with luminescent properties have paid much attention because of the 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 redox forms: the reduced phenylenediamine, the partially oxidized phenylenediamine radical cation, and the oxidized quinonediimine. In previous papers, we have already demonstrated the redox switching of the emission properties of Ru(II) dipyridyl complexes bearing the phenylenediamine moieties by changing the 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 the phenylenediamine derivatives are expected to be regulated by changing their redox states. Herein, we report luminescent phenylenediamines for redox switching (Fig. 1).

The phenylenediamine derivatives **1-red** were synthesized by the reaction of diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate with the corresponding anilines.^{4,5} Phenylaminophenol **2o-red** was also obtained as a byproduct from the synthesis of **1o-red**. The thus-obtained phenylenediamines and phenylaminophenol are stable under air and light, and were fully characterized by spectral data and elemental analyses.

In the ¹H NMR spectrum of **1o-red** in CD₂Cl₂ (1.0 × 10⁻² M), the NHs of the phenylenediamine moiety were hardly perturbed by the addition of aliquot DMSO-*d*₆ to CD₂Cl₂ (CD₂Cl₂: 10.56 ppm, CD₂Cl₂-DMSO-*d*₆ (9:1): 10.51 ppm). The FT-IR spectrum of **1o-red** in CH₂Cl₂ (1.0 × 10⁻² M) showed a hydrogen-bonded NH stretching at 3316 cm⁻¹. From these observations, the NH moieties are indi-

cated to participate in intramolecular hydrogen bonding in solution. The intramolecular hydrogen bonding was also observed in the case of **1m-red** and **1p-red**. Furthermore, the OH of **2o-red** was found to participate in intramolecular hydrogen bonding with the CO moiety as shown in Figure 1.

The phenylenediamine **1-red** was oxidized into the quinonediimine **1-ox** by treatment with lead(IV) acetate as an oxidant.⁶ The oxidized form **1-ox** could be again reduced to **1-red** with hydrazine monohydrate (Fig. 2).

The crystal structure of diethyl *N,N'*-diphenyl 2,5-diaminoterephthalate was reported to show the formation of the intramolecular hydrogen bonds between NH and CO at the central benzene ring.⁷ The single-crystal X-ray structure determination⁸ of **1o-red** also confirmed the formation of the intramolecular hydrogen bonds between the NH and CO at the central benzene ring (Table 1). The *anti*-conformation of the π -conjugated moiety (Fig. 3a) is formed, and another hydrogen bonds 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 bonds, which might induce a coplanar structure of the π -conjugated moiety. The crystal structure of **1o-ox** revealed the *anti*-conformation with a dihedral angle of 99.22(5)° between

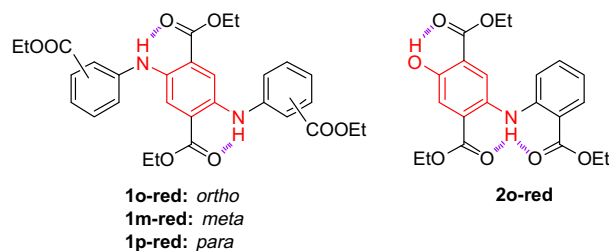


Figure 1. Phenylenediamine and phenylaminophenol derivatives.

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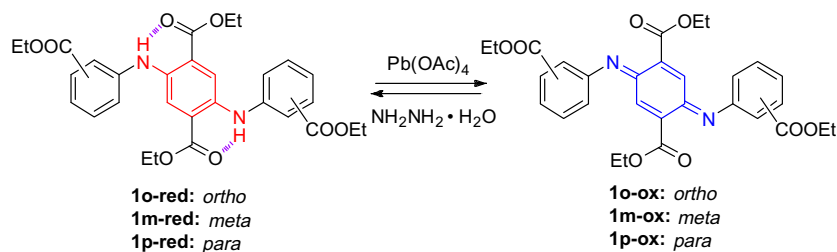


Figure 2. Redox interconversion between the phenylenediamines and quinonediiimines.

Table 1
Intramolecular hydrogen bonds for **1o-red** and **2o-red**

Crystal	Donor	Acceptor	D...A (Å)	D-H...A (°)
1o-red ^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)
2o-red	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 sits on an inversion center.

the terminal and central benzene rings as shown in Figure 3b. 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 **2o-red** was found to form intramolecular hydrogen bonds between not only OH and CO but also NH and CO in a crystal structure (Fig. 3c).

The reduced form **1o-red** exhibited strong luminescence at 536 nm (Fig. 4a). On the contrary, weak luminescence was observed with **1o-ox**. 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 **1m-red** and **1m-ox** or **1p-red** and **1p-ox** (Supplementary data Fig. S1). 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 **1p-red** showed a red-shift of the maximum emission wavelength as compared with **1o-red** (Table 2 and Fig. 4b). Further red-shift of the maximum emission wavelength was observed in the case of **1m-red**. This result might be contributed to the difference of the π -conjugated electronic states. Phenylaminophenol **2o-red** showed the maximum wavelength at 511 nm, wherein the luminescent intensity was lower as compared with that of **1o-red** (Table 2).

The phenylenediamine **1o-red** exhibits an intense yellow emission at 543 nm even in a solid state (Fig. 4c). The quantum yield of

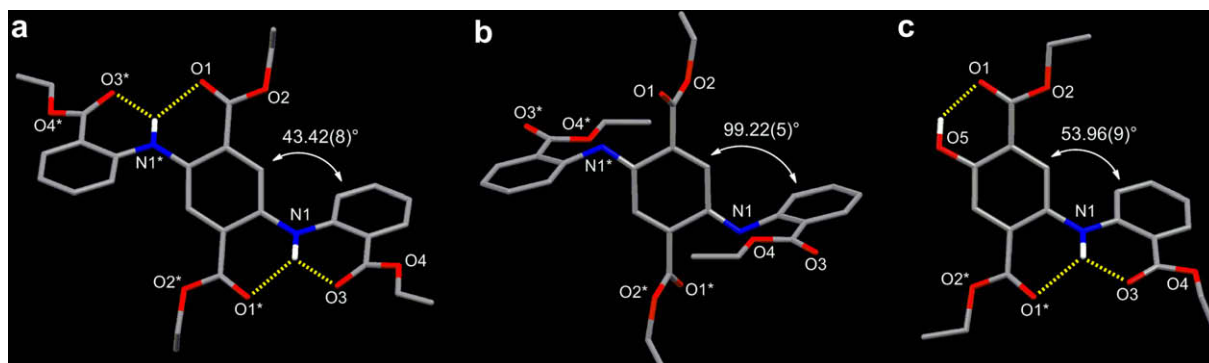


Figure 3. Crystal structures of (a) **1o-red**, (b) **1o-ox**, and (c) **2o-red**.

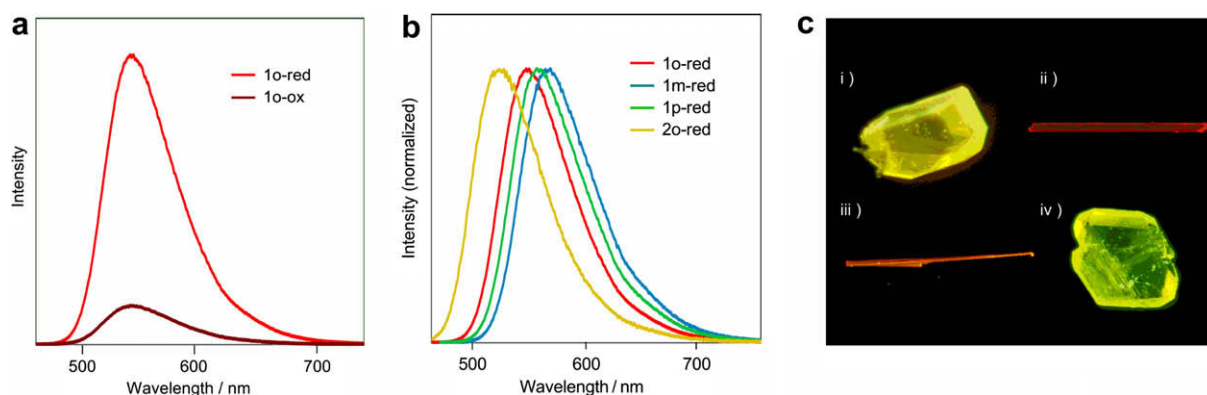


Figure 4. (a) Emission spectra of **1o-red** ($\lambda_{\text{ex}} = 430$ nm) and **1o-ox** ($\lambda_{\text{ex}} = 449$ nm) and (b) **1o-red** ($\lambda_{\text{ex}} = 430$ nm), **1m-red** ($\lambda_{\text{ex}} = 458$ nm), **1p-red** ($\lambda_{\text{ex}} = 446$ nm), and **2o-red** ($\lambda_{\text{ex}} = 415$ nm) in CH_2Cl_2 (1.0×10^{-5} M). (c) Photographs (under 365 nm) of (i) **1o-red**, (ii) **1m-red**, (iii) **1p-red**, and (iv) **2o-red**.

Table 2
Emission data for **1** and **2o-red**

	CH ₂ Cl ₂ ^a		In a solid state	
	$\lambda_{em, max}$ (nm)	Φ_F^b	$\lambda_{em, max}$ (nm)	Φ_F^c
1o-red	536	0.58	543	0.47
1m-red	554	0.27	589	0.08
1p-red	543	0.39	604	0.17
2o-red	511	0.20	531	0.26
1o-ox	536	0.15		
1m-ox	552	0.01		
1p-ox	543	0.01		

^a 1.0×10^{-5} M.

^b The relative fluorescence quantum yield was determined with Ru(bpy)₃Cl₂ ($\lambda_{ex} = 450$ nm).

^c The quantum yield was measured in an integrating sphere for packed powder samples at ambient temperature ($\lambda_{ex} = 450$ nm).

1o-red at ambient temperature, measured in an integrating sphere for a packed powder samples, is 0.47 using $\lambda_{ex} = 450$ nm (Table 2). Rigid π -conjugated frameworks without conformational disorder have been reported to provide attractive photophysical properties.⁹ In the case of **1o-red**, a rigid π -conjugated structure is considered to be induced by the formation of intramolecular hydrogen bonds between NH and CO at the central and terminal benzene rings.

In conclusion, a series of luminescent phenylenediamines were synthesized to control the luminescent properties. The luminescent switching was demonstrated by changing the redox states of the π -conjugated phenylenediamines. Further investigation including tuning of the color is now in progress.

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Supplementary data

Supplementary data (general information, synthesis, procedure, and spectral data) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.04.028.

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5. **1o-red** and **2o-red**: 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 AcOH (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 NaHCO₃ aqueous solution (20 mL \times 2) and extracted with CH₂Cl₂. After separating and discarding the water phase, the organic phase was dried on Na₂SO₄ and filtered. After evaporation of the solvent, a mixture of **1o-red**, **2o-red**, and unreacted substrate was obtained as a yellow–orange solid. The mixture was purified by silica gel column chromatography (from hexane to 4/1, hexane/EtOAc) to give **1o-red** (289 mg, 0.53 mmol) as a pale-orange solid, $R_f = 0.59$ (5/2, hexane/EtOAc) and **2o-red** (50.1 mg, 0.12 mmol) as a yellow solid, $R_f = 0.65$ (5/2, hexane/EtOAc).
- 1m-red**: A mixture of ethyl 3-aminobenzoate (330 mg, 2.0 mmol) and diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (252 mg, 1.0 mmol) in AcOH (10 mL) was stirred at 100 °C for 25 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with EtOH, and dried in vacuo. The phenylenediamine **1m-red** (236 mg, 0.43 mmol) was obtained as an orange-needle crystal by recrystallization from EtOAc.
- 1p-red**: A mixture of ethyl 4-aminobenzoate (330 mg, 2.0 mmol) and diethyl 2,5-dioxocyclohexane-1,4-dicarboxylate (252 mg, 1.0 mmol) in AcOH (10 mL) was stirred at 100 °C for 25 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with EtOH, and dried in vacuo. The phenylenediamine **1p-red** (249 mg, 0.45 mmol) was obtained as an orange-needle crystal by recrystallization from EtOAc.
6. **1o-ox**: A mixture of the phenylenediamine **1-red** (54.9 mg, 0.10 mmol) and Pb(IV) acetate (53.2 mg, 0.12 mmol) in dry CH₂Cl₂ (5.0 mL) was stirred under argon atmosphere at ambient temperature for 3 h. The resulting mixture was filtered and the filtrate was evaporated in vacuo. The quinonediimine **1o-ox** was isolated quantitatively as a brown solid and by recrystallization from acetone (**1o-ox**: 54.5 mg, quant.; **1m-ox**: 54.8 mg, quant.; **1p-ox**: 54.7 mg, quant.).
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8. *Crystal data for 1o-red*: C₃₀H₃₂N₂O₈, $M = 548.59$, triclinic, space group $P - 1$ (No. 2), $a = 8.1742(5)$ Å, $b = 8.7541(6)$ Å, $c = 10.8412(8)$ Å, $\alpha = 100.156(2)^\circ$, $\beta = 109.775(2)^\circ$, $\gamma = 97.572(2)^\circ$, $V = 703.06(8)$ Å³, $Z = 1$, $T = 4.0$ °C, $D_{calcd} = 1.296$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.94$ cm⁻¹, MoK α radiation ($\lambda = 0.71075$ Å), $R_1 = 0.079$, $wR_2 = 0.240$. *Crystal data for 1o-ox*: C₃₀H₃₀N₂O₈, $M = 546.58$, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.2400(2)$ Å, $b = 15.0566(3)$ Å, $c = 10.4578(2)$ Å, $\beta = 102.5477(8)^\circ$, $V = 1420.17(5)$ Å³, $Z = 2$, $T = 4.0$ °C, $D_{calcd} = 1.278$ g cm⁻³, $\mu(\text{CuK}\alpha) = 7.76$ cm⁻¹, CuK α radiation ($\lambda = 1.54186$ Å), $R_1 = 0.039$, $wR_2 = 0.165$. *Crystal data for 2o-red*: C₂₁H₂₃N₁O₅, $M = 369.42$, triclinic, space group $P - 1$ (No. 2), $a = 8.3035(6)$ Å, $b = 10.3553(8)$ Å, $c = 12.899(1)$ Å, $\alpha = 73.132(3)^\circ$, $\beta = 88.385(3)^\circ$, $\gamma = 75.938(2)^\circ$, $V = 1028.6(2)$ Å³, $Z = 2$, $T = 4.0$ °C, $D_{calcd} = 1.193$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.85$ cm⁻¹, MoK α radiation ($\lambda = 0.71075$ Å), $R_1 = 0.071$, $wR_2 = 0.271$. Crystallographic data (excluding structure factors) for the structures reported in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-755547 for **1o-red**, CCDC-755548 for **1o-ox**, and CCDC-755549 for **2o-red**. 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].
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