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3,11-Diaminodibenzo[*a,j*]phenazine: Synthesis, Properties, and Applications to Tröger's Base-Forming Ladder Polymerization

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Abstract: A new class of diamino-substituted π -extended phenazine compound was synthesized, and its photophysical properties were investigated. The U-shaped diaminophenazine displayed photoluminescence in solution with moderate quantum yield. The diamino aromatic compound was found applicable to the polycondensation with formaldehyde to form Tröger's base ladder polymer. The obtained microporous ladder polymer features high CO₂ adsorption selectivity against N₂, most likely due to the presence of basic nitrogen atoms in the phenazine rings.

polymerization to afford structurally well-defined ladder polymer (i.e., polymers of intrinsic microporosity; PIMs)^[5] that exhibits gas absorption and desorption in a reversible way.

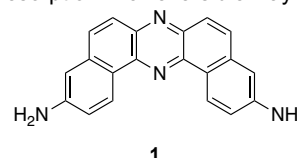


Figure 1. Structure of 3,11-diaminodibenzo[*a,j*]phenazine (1).

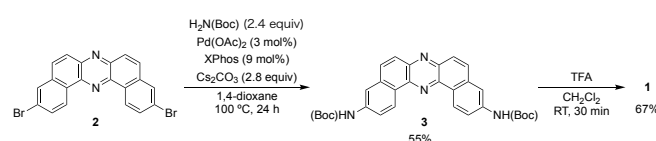
Introduction

Aminophenazines and their salts constitute a fundamental family of organic dyes, represented by mauveine discovered by Sir William Henry Perkin.^[1] By making the use of superb redox nature, diamino-functionalized phenazine serves as a promising electrode and active material for lithium ion batteries^[2] and aqueous organic redox flow batteries.^[3] Therefore, the synthesis and cultivation of properties of novel aminophenazine compounds is of highly importance from the viewpoint of materials sciences. Recently, we have developed a series of diarylamine-connected dibenzo[*a,j*]phenazine derivatives that exhibit various photophysical phenomenon such as thermally activated delayed fluorescence, mechanofluorochromism, and room temperature phosphorescence, which have rapidly emerged as emitters for highly efficient organic light-emitting diodes (OLEDs).^[4] As an interesting extension of our research of diamino-functionalized dibenzo[*a,j*]phenazine, herein we report the synthesis and the photophysical properties of a novel diaminodibenzo[*a,j*]phenazine (1, Figure 1) having highly reactive primary amino groups. Furthermore, the utility of the U-shaped compound with two primary amino groups was showcased by applying to Tröger's base-forming ladder

Results and Discussion

Synthesis of Materials

The target compound 3,11-diaminodibenzo[*a,j*]phenazine (1) was successfully synthesized through a Pd-catalyzed double Buchwald–Hartwig amination of 3,11-dibromodibenzo[*a,j*]phenazine (2)^[6] with *tert*-butyl carbamate (NH₂Boc) followed by deprotection of the N-Boc group of intermediate 3 with trifluoroacetic acid (TFA) in a good yield (Scheme 1). The newly synthesized compounds were fully characterized with NMR, IR, and MS spectroscopy (For the details, see the Supporting Information).



Scheme 1. Synthesis of diaminodibenzophenazine 1.

Photophysical properties

To investigate the photophysical properties of the new diaminophenazine **1**, absorption and photoluminescence (PL) spectra of diluted solutions of **1** ($c = 10^{-5}$ M) were acquired (Figure 2a and Table 1). In any solvents, the absorption spectra look similar, including two $\pi-\pi^*$ transitions in the higher regime between 300–370 nm and the lower regime between 400–500 nm (Figure 2a, dotted lines). It should be noted that the lowest absorption edge band was slightly shifted to the longer wavelength (the lower energy) region as the polarity of solvent increases (Figure 2a), indicating its $\pi-\pi^*$ transition nature. Quantum chemical calculations using the time-dependent density functional theory (TD-DFT) at the LC- ω HPBE/cc-pVDZ level ($\omega = 0.10$) with polarizable continuum model (PCM) (toluene) indicated that the energetically-lowest electronic transition observed at $\lambda_{\text{exp}} = 448$ nm is ascribed to the S_0-S_1 transition ($\lambda_{\text{calc}} = 453$ nm; $f = 0.432$). Natural transition orbital (NTO) analysis supported that the S_1 state is admixture of $\pi-\pi^*$ and weak intramolecular charge-transfer (hybrid CT) from the diamino groups to the phenazine core (Figure 2b) (for the details of theoretical calculations, see the SI).

In contrast to the absorption spectra, the photoluminescence spectra of **1** significantly red-shifted from 472 nm (sky blue emission) to 552 nm (yellow emission) as the function of polarity of solvent used (Figure 2a, solid lines). Also, shape of PL spectrum becomes broader as the polarity of solvent increases (Figure 2a). Taken together with the absorption properties, we can conclude that the emission of **1** in solutions is derived from the charge-transfer excited state, which is in consistent with the NTO analysis (Figure 2b). Importantly, the photoluminescence quantum yield (PLQY) of diluted solutions of **1** did not decrease even in a polar solvent such as DMF (Table 1), probably because of admixture of $\pi-\pi^*$ and CT character. Such significant positive luminochromism in response to dielectric constants along with good quantum yields would allow for the application to chemical probes to visualize environment conditions such as polarity and viscosity.^[7]

In contrast to the solutions, diaminodibenzophenazine **1** did not show PL in the solid state, probably due to strong intermolecular electronic interactions caused by its planar structure.

Figure 2. a) UV-Vis absorption spectra (dotted lines) and normalized photoluminescence spectra (solid lines) of diluted solutions ($c = 10^{-5}$) of **1** (cyan: toluene, moss green: chloroform, dark green: THF, magenta: DMF; $\lambda_{\text{ex}} = 400$ nm). The inset photographs show the solutions under the irradiation of UV lamp ($\lambda = 365$ nm). b) HONTO and LUNTO distributions of S_1 state of **1** in toluene.

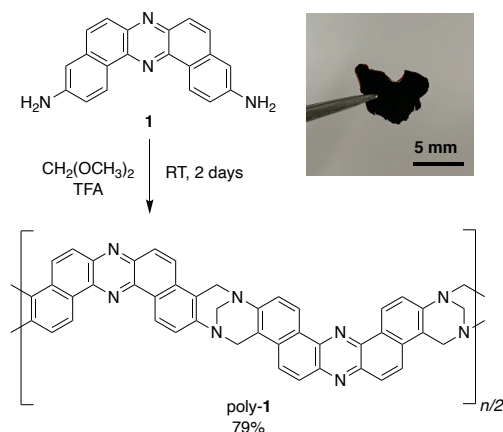
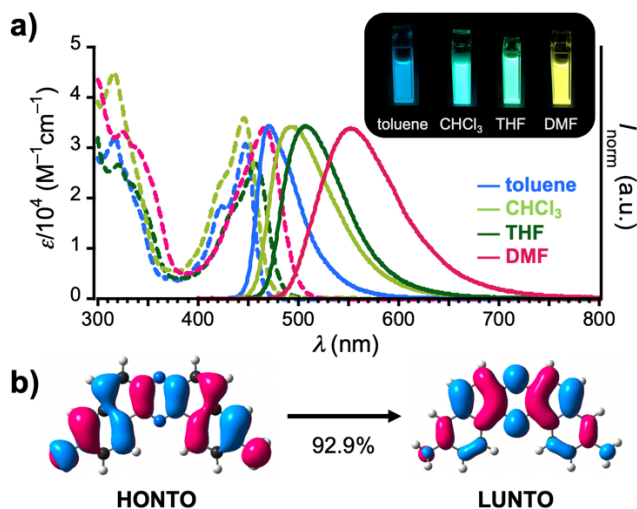
Table 1. Summary of the photophysical properties of diluted solutions of **1**^[a].

solvent	absorption		PL ^[b]	
	λ_{abs} [nm] ^[c]	ϵ [M ⁻¹ cm ⁻¹]	λ_{em} [nm]	ϕ_{PL} ^[d]
toluene	448	29,600	472	0.36
CHCl ₃	446	35,800	492	0.33
THF	458	26,000	508	0.35
DMF	467	33,100	552	0.52

[a] $c = 10^{-5}$. [b] PL spectra were acquired with $\lambda_{\text{ex}} = 400$ nm. [c] The longest maximum wavelength of the absorption spectrum. [d] The absolute photoluminescence quantum yield acquired with the integral sphere.

Application to the synthesis of Tröger's base-containing ladder polymer

With a new diaminophenazine in hand, we envisioned that the diamino functionality along with the unique U-shaped aromatic skeleton would allow for synthesizing a kinked ladder polymer by Tröger's base-forming ladder polymerization. According to Scheme 2, diamine **1** and dimethoxymethane as a precursor of formaldehyde were stirred in trifluoroacetic acid (TFA) at 25 °C for 2 days. After the reaction was quenched by neutralizing with ammonia aqueous solution, poly-**1** insoluble in common organic solvents except for highly acidic TFA was obtained in a high yield (Scheme 2).^[6] The complete neutralization was confirmed by FT-IR spectroscopy of poly-**1**, where C=O stretching absorption of CF₃CO₂⁻ counter anion at around 1680 cm⁻¹ was not observed (Figure S2). Although determination of degree of polymerization of poly-**1** with size-exclusion chromatography was prevented by its low solubility, we found that a free-standing film of poly-**1** was obtained by solvent casting from TFA solution (inset photograph in Scheme 2), indicating that the degree of polymerization of poly-**1** would be high enough to exhibits high membrane forming ability.



Scheme 2. Synthesis of ladder polymer. Inset photograph shows a free-standing film of poly-1.

To characterize the synthesized polymer, by comparing the ^1H NMR resonance of monomer **1** and poly-1, NMR charts of both materials in $\text{TFA-}d_1$ were acquired (Figure 3). Unexpectedly, sharp signals corresponding to dibenzo[*a,j*]phenazine core (H^a , H^b , H^d and H^e) were observed in the NMR chart of poly-1 (Figure 3), suggesting a progress of regioselective ladder polymerizations. In addition, three methylene protons (H^f and H^g), which are specific to Tröger's base polymers, were also detected in the 5–6 ppm regime (Figure 3b). Further characterization with ^1H - ^1H COSY analysis of poly-1 (Figure S3) showing the correlation between H^a and H^b of dibenzophenazine unit also supports well that ladder polymerization proceeds in a regioselective manner. In other words, the electrophilic aromatic substitution to form bicyclic ring of the Tröger's base skeleton exclusively occurs at the 4 (or 10) position of dibenzo[*a,j*]phenazine core not at the 2 (or 12) position. Theoretical calculation of the atomic charges on protonated diamine **1** (1-H^+ , which should be under an equilibrium with fully protonated form and serve as an intermediate for the polymerization, clearly suggested that the 4 (or 10) position is more nucleophilic than the 2 (or 12) position (Figure 3c). This would support the exclusive formation of regioregular poly-1.

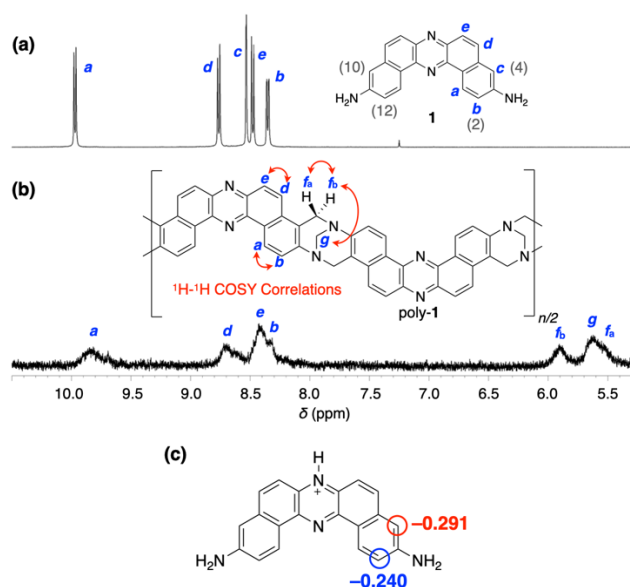


Figure 3. Comparison of the NMR charts of a) **1** and b) poly-1 in $\text{TFA-}d_1$. These compounds would exist as tricationic species in $\text{TFA-}d_1$, according to the theoretical calculations. The slight broadening of the signals of poly-1 should be due to the randomness of stereo structures of Tröger's base units in its mainchain. c) Calculated atomic charges of 1-H^+ using the Merz-Singh-Kollman (MK) Scheme @LC- ω HPBE/cc-pVDZ in THF.

The UV-vis absorption spectrum of the polymer in TFA nicely showed a similar one (black solid line in Figure 4) with that of monomer **1** in TFA (grey dotted line in Figure 4), with a slight red-shift of the absorption band. This would indicate some extension of effective π -conjugation length of the diaminophenazine core by hyperconjugation through methylene bridge. Figure 5 shows thermogravimetric analysis (TGA) of poly-1. Interestingly, we found that 5% weight loss temperature

(T_{d5}) of poly-1 is as high as 535 $^{\circ}\text{C}$, showing pronounced high thermal stability.

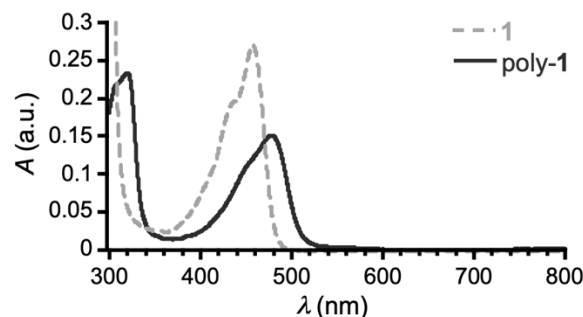


Figure 4. UV-Vis absorption spectra of poly-1 (in black solid line) and monomer **1** (in grey dotted line) in TFA.

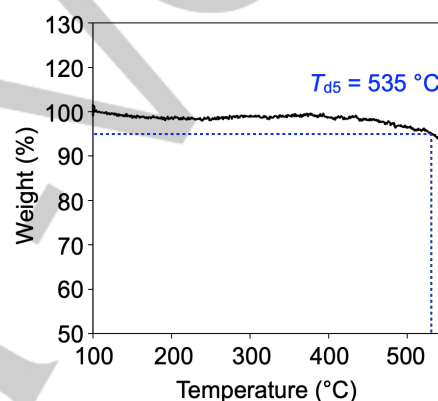


Figure 5. TGA profile of poly-1 measured at a scan rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2 flow (50 ml/min).

Gas adsorption/desorption property of the ladder polymer

We measured gas adsorption/desorption isotherms of poly-1 to investigate the microporous structure as PIMs (Polymers of Intrinsic Microporosity).^[5] The N_2 adsorption/desorption isotherms at 77 K (black plots in Figure 6a) is not typical for PIMs that usually show the isotherms of type-I,^[8] where rapid gas uptake occurs at lower relative pressure (P/P_0) region. The N_2 gas, that is hardly adsorbed at a lower P/P_0 region, showed rapid uptake above P/P_0 of ca. 0.6. The desorption isotherm of N_2 can be classified as type-I for microporous materials. This adsorption/desorption behavior is similar to so-called "gate-opening" behavior of third-generation metal-organic framework (MOF) materials.^[9] In the CO_2 adsorption measurement at 194 K (red plots in Figure 6), rapid adsorption from lower P/P_0 region was observed, that can be classified as type-I with a relatively large hysteresis. This suggested that poly-1 has micropores with specific affinity for CO_2 .^[10] The gradual CO_2 adsorption at the high P/P_0 region above 0.05 suggests the presence of mesopores. Thus, poly-1 was found to exhibit interesting gas sorption properties that differ from those of common PIMs.^[5] We measured adsorption/desorption isotherms for these gases at 298 K (Figure 6b). The adsorption/desorption isotherms of CO_2 are characterized by convex curves (Figure 6b, red plots), suggesting an attractive interaction between poly-1 and CO_2 . On the other hand, N_2 gas hardly adsorbed to poly-1 at 298 K (Figure 6a, black plots). The adsorption selectivity of CO_2

against N₂ for poly-1 at 1 atm (101.3 kPa) was ca. 26, which is relatively high value in comparison with other benchmark PIM materials.^[5e,11] Although the presence of basic nitrogen atoms of the phenazine ring of poly-1 might be responsible for these characteristic gas sorption behaviors, the details will be further investigated in the future.

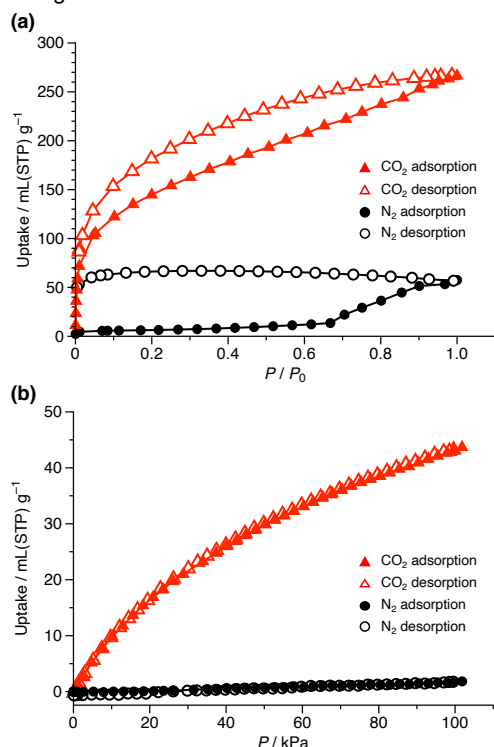


Figure 6. (a) Isotherms of N₂ (at 77 K, black plots) and CO₂ (at 194 K, red plots) adsorption/desorption of poly-1. (b) Isotherms of N₂ (at 298 K, black plots) and CO₂ (at 298 K, red plots) adsorption/desorption of poly-1.

Conclusion

In summary, we have developed a new diamino-substituted phenazine derivative and investigated their photophysical properties. The developed compound with highly reactive primary amino groups was found useful not only as a new luminophore with positive luminochromism in response to solvent polarity but also as a synthetic building block to construct functional material such as ladder polymers. The compound serves as a monomer for Tröger's base-forming ladder polymerization, giving a regioregular new ladder polymer. Although the polymer does not show PL in the protonated form, the polymer could be utilized as an active material for photovoltaic cells, due to the absorption ability of full-range (black color) of visible light in the solid state along with its π -conjugation. The obtained ladder polymer showed microporosity and high CO₂ adsorption selectivity of ca. 26 at ambient conditions against N₂, most likely due to the presence of basic nitrogen atoms in the phenazine rings. The detailed investigation of microporous structure, and gas sorption behavior of poly-1 and the development new materials using **1** as a synthetic intermediate via amide and imine formation are underway in our group.

Acknowledgements

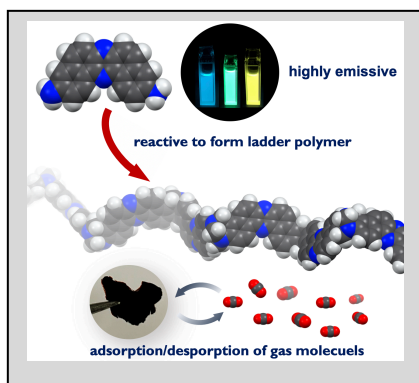
We acknowledge a Grant-in-Aid for Scientific Research on Innovative Areas "π-System Figuration: Control of Electron and Structural Dynamism for Innovative Functions" (JSPS KAKENHI Grant Number: JP17H05155), "Aquatic Functional Materials: Creation of New Materials Science for Environment-Friendly and Active Functions (Area No. 6104)" (JSPS KAKENHI Grant Number JP19H05716 for Y.T. and 22H04541 for F.I.), "Molecular Engine (Area No. 8006)" (JP21H00400 for F.I.) and "Coordination Asymmetry (Area No. 2802)" (JP19H04567 for F.I.) from the MEXT (Ministry of Education, Culture, Science and Technology, Japan), a Grant-in-Aid for Scientific Research (B) (JSPS KAKENHI Grant Number JP20H02813 for Y.T., and JP20H02784 for F.I.), a Grant-in-Aid for Challenging Research (Exploratory) (JSPS KAKENHI Grant Number JP21K18960 for Y.T.), Japan Science and Technology Agency (JST) PRESTO (JPMJPR21A2 for F.I.). Y.T. and S.M. acknowledge NIPPOH CHEMICALS for supplying *N,N*-diiodo-5,5-dimethylhydantoin (DIH). This work was also supported by Yazaki Memorial Foundation for Science, Technology, Iketani Science and Technology Foundation (ISTF), The Foundation for the Promotion of Ion Engineering, and the Research Program of "Five-Star Alliance" in "NJRC Mater. & Dev." The computation was performed using Research Center for Computational Science, Okazaki, Japan (Project: 22-IMS-C254, Y.T.).

Keywords: phenazine • luminescence • charge-transfer • ladder polymers • gas absorption

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- [10] The fitting of the CO₂ adsorption/desorption isotherms of poly-1 to Langmuir-type adsorption model was unsuccessful, implying the existence of ununiform adsorption sites and/or multilayer adsorption of CO₂.
- [11] The adsorption selectivities of CO₂ against N₂ for PIM-EA-TB and at 1 atm (101.3 kPa) was ca. 18.^[5e]

Entry for the Table of Contents



A new aminophenazine functional molecule has been developed. It displays efficient photoluminescence and positive luminochromism in organic solvent. Not only useful it is as luminophore, but also does it serve as a building block for Tröger's base regioregular ladder polymer. The ladder polymer nicely shows reversible adsorption/desorption behavior of carbon dioxide molecule.

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