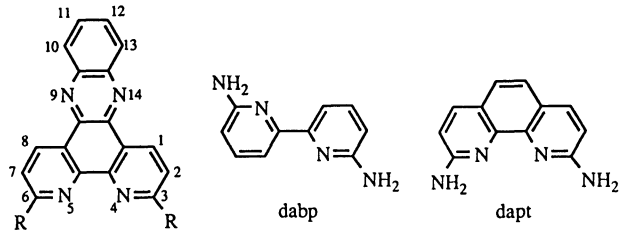
Synthesis and Properties of Diamino-Substituted Dipyrido [3,2-*a*: 2′,3′-*c*]phenazine

Masaki YAMADA,* Yoshihito TANAKA, Yasuyuki YOSHIMOTO, Shigeyasu KURODA, and Ichiro SHIMAO
Department of Materials Science and Engineering, Faculty of Engineering, Toyama University, 3190 Gofuku, Toyama 930
(Received November 30, 1991)

A heteroaromatic compound 3,6-diaminodipyrido[3,2-*a*: 2′,3′-*c*]phenazine was synthesized with an improved method to convert 1,10-phenanthroline derivatives to the corresponding 5,6-diones. It was shown that the electron-donating effects of amino substituents were extended not only to pyridine rings but also to the phenazine ring.

Recently Chambron et al. reported that a heteroaromatic compound dipyrido[3,2-*a*:2′,3′-*c*]phenazine (phenazino-bpy)[1] was a metal ligand with attractive features.[2–4] The formal π-conjugated system of phenazino-bpy resembles a combination of those of 2,2′-bipyridine (bpy) and phenazine systems.[2,5] In most cases, phenazino-bpy forms metal complexes as an N_2-type ligand by using the bpy part,[2–6] and the phenazine part acts as an electron-withdrawing group to the bpy part.[2,3,5,6] In photochemistry of ruthenium(II) complexes, an electron exited at the metal center is transferred rapidly to the phenazine part, resulting in an efficient charge separation.[2,3]

On the other hand, we have reported strong and characteristic electron-donating effects of amino substituents in bpy and 1,10-phenanthroline (phen) systems, 6,6′-diamino-2,2′-bipyridine (dabp)[7] and 2,9-diamino-1,10-phenanthroline (dapt).[8] One of the notable effects of amino substituents was the drastic and characteristic red shifts of absorption bands.[7,8] In this regard, it is interesting to introduce amino substituents into the corresponding positions of the phenazino-bpy system, 3- and 6-positions. In this work, we synthesized such a compound, 3,6-diaminodipyrido[3,2-*a*: 2′,3′-*c*]phenazine (phenazino-dabp). A key step to synthesize phenazino-dabp in good yield was an improvement in the synthesis of 1,10-phenanthroline-5,6-diones (phen-5,6-diones).[1,4,9–12] The effects of amino substituents in phenazino-dabp were investigated and discussed in terms of their electron donation to the bpy and phenazine parts.

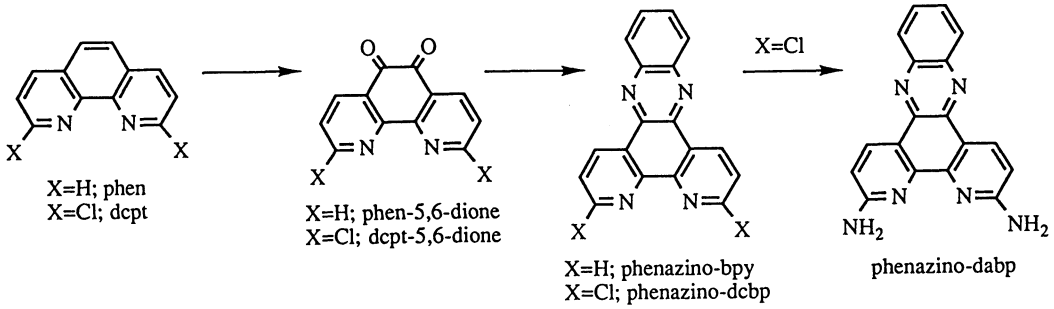


R=H; phenazino-bpy
R=NH_2; phenazino-dabp

Results and Discussion

Synthesis. Phenazino-bpy is prepared from phen via phen-5,6-dione (Scheme 1).[1] To synthesize phenazino-dabp, we subjected 2,9-dichloro-1,10-phenanthroline (dcpt)[13,14] to an analogous procedure yielding a dichloro precursor phenazino-dcbp, followed by conversion of the chloro substituents into amino substituents (Scheme 1).

A small amount of phen-5,6-dione can be obtained as a by-product by the nitrating reaction of phen.[3,9] However, a three-step reaction consisting of nitration of the 5-position, reduction of the nitro group, and final oxidation is needed to obtain phen-5,6-dione in sufficient yield.[1,10,11] Though nitration of the 5-position of dcpt was carried out similarly,[15] preparation of 2,9-dichloro-1,10-phenanthroline-5,6-dione (dcpt-5,6-dione)

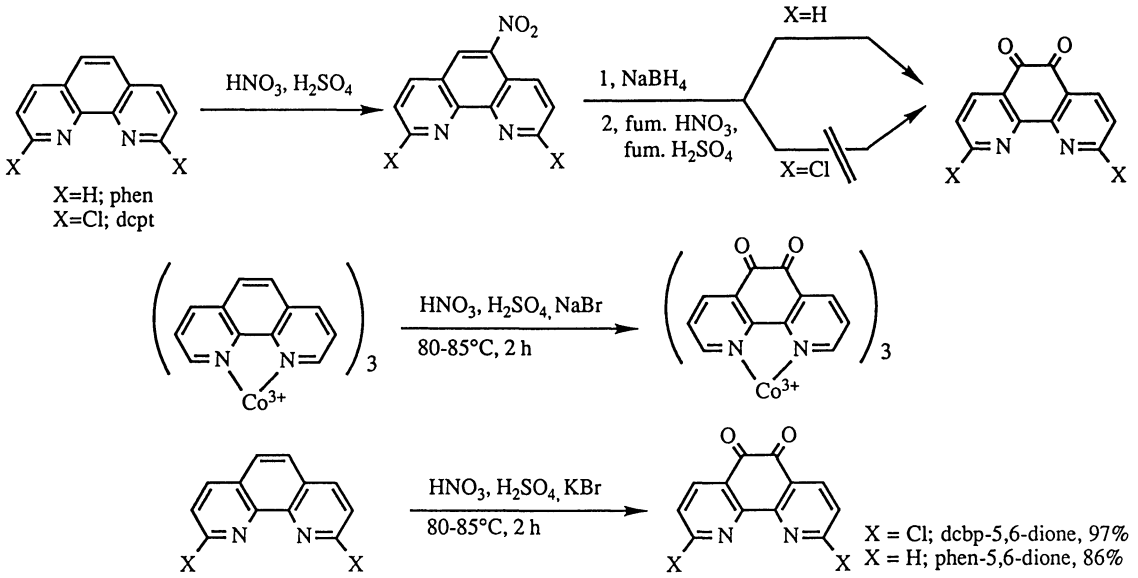


Scheme 1.

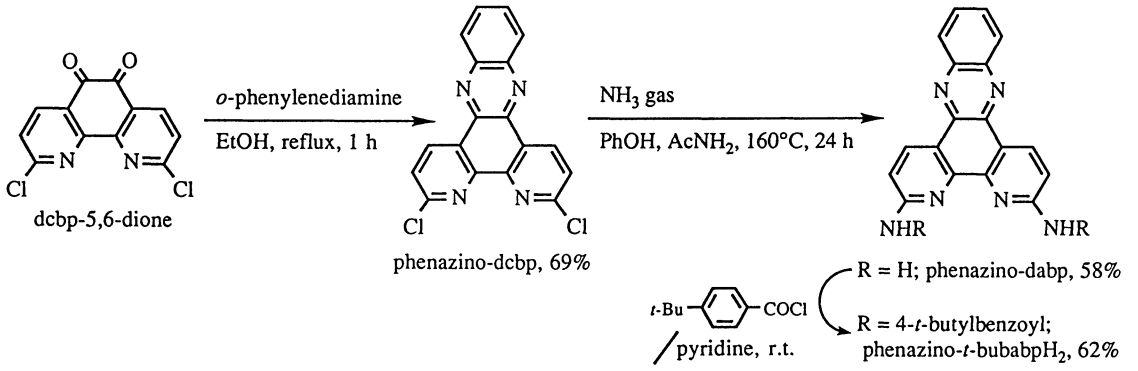
by a similar procedure was unsuccessful, i.e., reduction of 5-nitro-dcpt with sodium borohydride followed by oxidation with a nitrating reagent gave only unidentified brown solid (Scheme 2). Chloro substituents might be affected under reductive conditions. Dcpt-5,6-dione was successfully synthesized by a simpler one-step procedure. Gillard et al. reported that phen coordinated to the cobalt(III) center was converted into the corresponding 5,6-dione by a one-step procedure, namely by treating with a nitrating reagent *containing bromide ion*.[10-12] This method, however, was not applicable to metal-free phen.[10,11] We found this method was effective for dcpt, yielding dcpt-5,6-dione almost quantitatively (Scheme 2). It is noteworthy that this method is applicable to metal free phen if carried out *carefully* (see Experimental section). This should be a convenient method to convert a series of phen derivatives into the corresponding 5,6-diones.

5,6-Dione of dcpt was converted into phenazino-dcbp by condensation with *o*-phenylenediamine in ethanol (Scheme 3).[1,16] Treatment of phenazino-dcbp with gaseous ammonia in a mixture of phenol and acetamide[13,17] gave phenazino-dabp in high yield (Scheme 3). Though contamination of a trace amount of 3-amino-6-phenoxy product was revealed by mass spectrometry, this impurity was completely removed after washing with hot benzene (see Experimental section). On the other hand, we have found that an analogous treatment of bpy derivatives suffered from the production of a large amount of phenoxy-substituted products,[18] while phen derivatives gave only amino-substituted products in high yield. Judging from these results, the activity and selectivity of chloro substituents at 3- and 6-positions of the phenazino-bpy system for nucleophilic substitutions resemble those of the corresponding chloro substituents in the phen system[13,17] rather than those in the bpy system.

Properties. ^{1}H NMR chemical shifts for phenazino-dabp in dimethyl-d_6 sulfoxide (DMSO-d_6) are summarized in Table 1 (pyridine rings) and Table 2 (phenazine ring) in comparison with related compounds. Large high-field shifts caused by the presence of amino substit-



Scheme 2.



Scheme 3.

Table 1. ^{1}H NMR Chemical Shifts for Pyridine Rings of Phenazino-dabp and Related Compounds in DMSO-d_6

Compound	δ(Position)				Ref.
Phenazino-dabp	—	7.00 (2,7)	9.11 (1,8)	—	
Phenazino-bpy	9.20 (3,6)	7.93 (2,7)	9.52 (1,8)	—	This Work
Δδ	—	−0.93 (2,7)	−0.41 (1,8)	—	
dabp	—	6.38 (5,5′)	7.36 (4,4′)	7.36 (3,3′)	
bpy	8.43 (6,6′)	7.24 (5,5′)	7.72 (4,4′)	8.15 (3,3′)	7)
Δδ	—	−0.86 (5,5′)	−0.36 (4,4′)	−0.79 (3,3′)	
dapt	—	6.81 (3,8)	7.88 (4,7)	—	
phen	9.12 (2,9)	7.77 (3,8)	8.50 (4,7)	—	8)
Δδ	—	−0.96 (3,8)	−0.62 (4,7)	—	

Table 2. ^{1}H NMR Chemical Shifts for Phenazine Ring of Phenazino-dabp and Related Compounds in DMSO-d_6

Compound	δ (Position)	
Phenazino-bpy (A)	8.04 (11,12)	8.37 (10,13)
Phenazino-dabp (B)	7.84 (11,12)	8.20 (10,13)
$\delta_B-\delta_A$	−0.20	−0.17
Phenazino-*t*-bubabpH$_2$ (C)	7.89 (11,12)	8.37 (10,13)
$\delta_C-\delta_B$	0.09	0.17

uents are observed in pyridine rings ($\Delta\delta$=0.93 for 2- and 7-positions and $\Delta\delta$=0.41 for 1- and 8-positions, Table 1), indicating that electron donation to pyridine rings ocurrs to a similar magnitude as in dabp[7,8,19] and dapt.[8] High-field shifts caused by amino substituents are also noted in the phenazine part ($\Delta\delta$=0.20 for 11 and 12 positions an $\Delta\delta$=0.17 for 10 and 13 positions, Table 2). Electron donation of amino substituents should be extended to the phenazine part.

Electron donation of amino substituents to the phenazine part was corroborated by the redox potentials. A single quasi-reversible reduction was observed in cyclic voltammetry of phenazino-dabp ($E_{1/2}$=−1.40 V vs. SCE in DMSO). Because the corresponding processes were also detected in phenazino-bpy[2,3,5,6] but not in dabp and dapt, this process should be assigned to reduction of the phenazine moiety. That this reduction potential is negative of the corresponding values for phenazino-bpy and phenazine ($E_{1/2}$=−1.14 and −1.11 V vs. SCE in DMSO, respectively) indicates that electron donation of amino substituents extends to the phenazine ring.

The electronic spectrum of phenazino-dabp reveals more characteristic effects of amino substituents (Fig. 1). The spectrum of phenazino-bpy in DMSO exhibits three peaks (λ_{max}=381, 362, and 270 nm, with $\log\varepsilon_{max}$=4.13, 4.10, and 4.73, respectively) and five shoulder peaks (λ_{max}=ca. 370, 355, 345, 305, and 295 nm) in the 260—500 nm region. Introduction of chloro substituents at 3- and 6-positions caused only a small red shift without changing the spectral pattern. A notable spectral change was caused by the presence of amino substituents at these positions. The spectrum of phenazino-dabp in the 260—500 nm region exhibits four

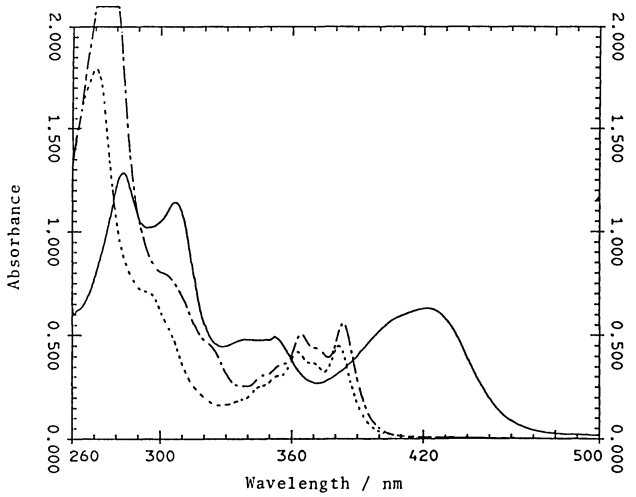


Fig. 1. Electronic spectra of phenazino-dabp (——), phenazino-bpy (----), and phenazino-dcbp (— - —) in DMSO.

peaks (λ_{max}=422, 350, 306, and 283 nm, with $\log\varepsilon_{max}$=4.29, 4.18, 4.56, and 4.62, respectively) and two shoulder peaks (λ_{max}=ca. 400 and 340 nm), and the absorption tail at longer wavelengths extends to around 470 nm. Solute–solute interactions such as the formation of dimeric species are absent because the spectral pattern remained unchanged over a wide range of concentration. Since the absorption bands showed a large blue shift in methanol (λ_{max} in methanol=408, 344, 299, and 277 nm), solvent–solute interactions, interactions between polar solvents and amino substituents, are present.[7,20] The spectral pattern in DMSO and methanol, however, was quite similar to each other, indicating these interactions did not affect the spectral pattern.

Amino substituents in dabp[7] and dapt[8] cause a large bathochromic shift of the π–π* transition band, but did not affect the spectral patterns. The calculated π–MO's of dabp are in agreement with this observation.[7] The π–MO's of dabp had a character quite similar to that of the corresponding π–MO's of bpy, though the energy levels of some π–MO's increased largely and characteristically. In the case of the phenazino-bpy system, amino substituents at 3- and 6-positions caused

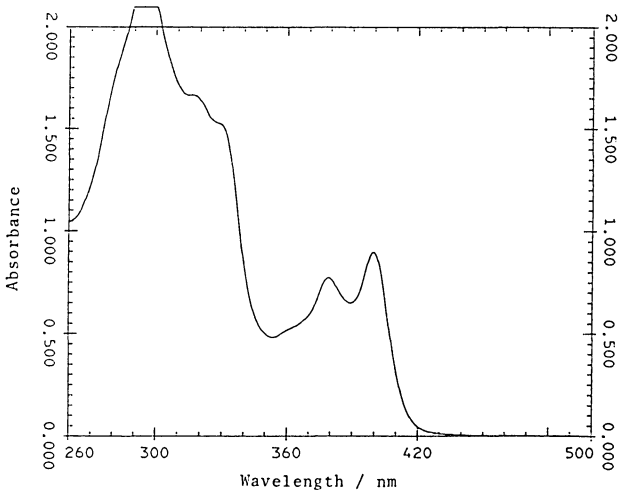


Fig. 2. Electronic spectrum of phenazino-*t*-bubabpH$_2$ in DMSO.

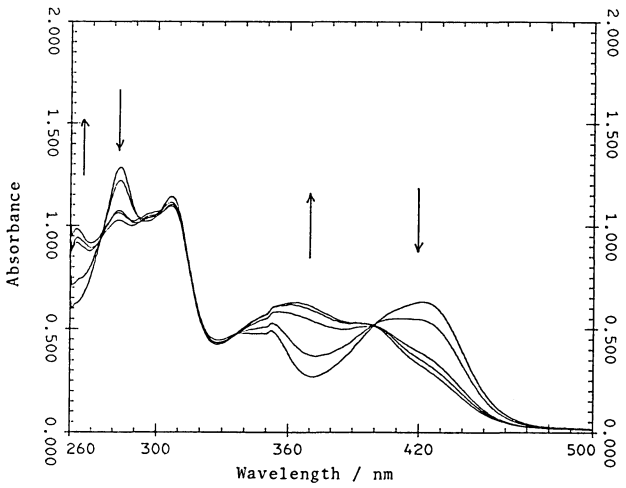


Fig. 3. Spectral change of phenazino-dabp in DMSO by addition of hydrochloric acid, at hydrochloric acid/phenazino-dabp molar ratios of 0, 3, 4.5, 6, and 24.

a drastic spectral change including the spectral pattern. Since the observed strong absorption bands could be assigned to the π–π^* transition bands, the character of some π–MO's of phenazino-bpy, a combination of those of bpy and the phenazine system,[2,5] might be affected.

The effects of amino substituents were drastically counteracted by acylation. Treatment of phenazino-dabp with 4-*t*-butylbenzoyl chloride in pyridine[21] gave a 3,6-bis(4-*t*-butylbenzoylamino) derivative phenazino-*t*-bubabpH$_2$ (Scheme 3).[22] The δ-values of phenazine protons in ^{1}H NMR of phenazino-*t*-bubabpH$_2$ were shifted to low field again (Table 2). The electronic spectrum of phenazino-*t*-bubabpH$_2$ resembles that of phenazino-bpy rather than that of phenazino-dabp (Fig 2).

Such a counteraction was also observed in the protonated form. A set of isosbestic points exhibited during

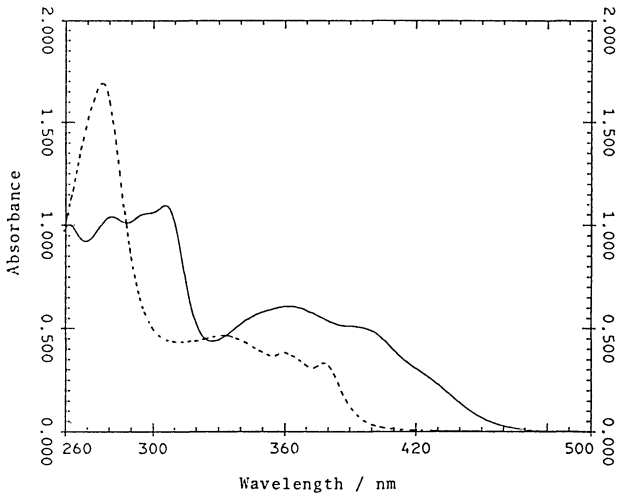


Fig. 4. Spectral comparison of phenazino-dabp (——) and phenazino-bpy (------) in protonated forms.

spectrometric titration of phenazino-dabp with hydrochloric acid in DMSO (Fig 3). Protonation to ring nitrogens in the pyridine ring should be taking place.[7,8,19] An analogous behavior was noted also in phenazino-bpy. In protonated forms, the spectral patterns of phenazino-dabp and phenazino-bpy at longer wavelengths resemble each other (Fig. 4). The electron-donating effect of the amino substituent should not be strong enough to affect the character of some π–MO's in the protonated form.

In conclusion, phenazino-dabp was synthesized with three-step procedure from dcpt. The electron-donating effects of amino substituents extend not only toward pyridine rings but also toward the phenazine ring, affecting the character of the π–MO's. These effects could be counteracted by acylation of amino groups or protonation to ring nitrogens in pyridine rings.

Experimental

^{1}H NMR spectra were recorded on a JEOL FX-90Q Spectrometer or JEOL JNM-GX270 (phenazino-dcbp) at room temperature. Electronic spectra were taken on a Shimadzu UV2100S Spectrophotometer at room temperature at a concentration of 3.33×10^{-5} mol dm^{-3}. IR Spectra were recorded on a JASCO IR-810 Spectrometer. Elemental analyses were carried out with a Yanaco CHN Corder Model MT-5. Thermal analyses were done with a Rigaku TAS 100 system at 5 °C min^{-1} under nitrogen atmosphere.

Cyclic voltammetry was made with a Yanaco Polarographic Analyzer Model P-1100 at room temperature at a scan rate of 50 mV s^{-1} under nitrogen atmosphere. A platinum wire, a glassy carbon stick, and a saturated caromel electrode were used as a working electrode, a counter electrode, and a reference electrode, respectively.

Materials. 1,10-Phenanthroline (phen) hydrate and phenazine were commercially obtained and used without purification. Preparation of 2,9-dichloro-1,10-phenanthroline (dcpt) was reported elsewhere.[14] Other chemicals were obtained commercially, and some of them were purified by conven-

tional methods prior to use.

2,9-Dichloro-1,10-phenanthroline-5,6-dione (dcpt-5,6-dione): A round-bottom flask containing 1.33 g (5.34 mmol) of dcpt and 6.35 g (53.4 mmol) of potassium bromide was placed in an ice bath. Concentrated sulfuric acid (20 cm^3) was added in small portions, and then was added 10 cm^3 of concentrated nitric acid. The resulting solution was heated for 2 h at 80—85 °C, was cooled to room temperature, and then was poured into 400 cm^3 of water. Yellow precipitates were collected by filtration, air-dried, and then were subjected to column chromatography (Merck Kieselgel 60-acetone). The residual brown solid obtained by removal of the solvent was extracted with hot benzene. Removal of benzene gave 1.45 g (97%) of dcpt-5,6-dione as yellow needles. Mp (acetone) 267—268 °C. MS (EI, 70 eV) m/z (rel intensity) 282 (M^{**+}, 0.6), 280 (M^{**+}, 3.5) 278 (M^+, 5.1), 254 (11), 252 (67), and 250 (100). HRMS Found: m/z 277.9665, 279.9625, and 281.9677. Calcd for $C_{12}H_4Cl_2N_2O_2$, $C_{12}H_4ClCl^*N_2O_2$, and $C_{12}H_4Cl^*{}_2N_2O_2$: M, 277.9650, 279.9620, and 281.9591, respectively. Elemental analysis, Found: C, 50.89; H, 1.56; N, 10.26%. Calcd for $C_{12}H_4Cl_2N_2O_2$: C, 51.65; H, 1.44; N, 10.04%. IR ν_{max} (KBr) 1682s, 1560s, 1428s, 1360s, 1300s, 1140s, 1112s, 878s, and 840s cm^{-1}. ^{1}H NMR ($CDCl_3$) δ_H=7.62 (2H, d, H-3 and H-8), 8.44 (2H, d, H-4 and H-7).

In this series of procedure, addition of sulfuric acid must be carried out most carefully. We successfully performed this step by addition through the ice-cooled wall of flask. If sulfuric acid was added directly onto the mixture of dcpt and potassium bromide, desired 5,6-dione was not obtained at all.[24]

1,10-Phenanthroline-5,6-dione (phen-5,6-dione): Phen hydrate (1.00 g, 5.04 mmol), potassium bromide (5.95 g, 50.0 mmol), concentrated sulfuric acid (20 cm^3), and concentrated nitric acid (10 cm^3) were subjected to an analogous procedure. The reaction mixture was poured into 400 cm^3 of water. The solution was neutralized with sodium hydrogencarbonate, and then was extracted with dichloromethane. Removal of dichloromethane gave 0.91 g (86%) of phen-5,6-dione as yellow needles. Mp (methanol) 271—272 °C (lit,[1] 258 °C).

3,6-Dichlorodipyrido[3,2-*a*:2′,3′-*c*]phenazine (phenazino-dcbp):[1] A mixture of dcpt-5,6-dione (1,51 g, 5.41 mmol) and *o*-phenylenediamine (1.51 g, 14.0 mmol) was refluxed in ethanol for 1 h. Brown solid precipitated after cooling to room temperature was collected by filtration, and was washed successively with ethanol and acetone. Yield 1.32 g (69 %). Mp (benzene) 375 °C (decomp, DTA peak). MS (EI, 70 eV) m/z (rel intensity) 354 (M^{**+}, 12), 352 (M^{**+}, 68), 350 (M^+, 100). HRMS Found: m/z 350.0121, 352.0122, and 354.0077. Calcd for $C_{18}H_8Cl_2N_4$, $C_{18}H_8Cl^*ClN_4$, and $C_{18}H_8Cl^*{}_2N_4$: M, 350.0124, 352.0097, and 354.0067, respectively. Elemental analysis, Found: C, 60.76; H, 2.55; N, 15.74%. Calcd for $C_{18}H_8Cl_2N_4$: C, 61.56; H, 2.30; N, 15.95%. IR ν_{max} (KBr) 1568s, 1480s, 1360s, 1102s, and 750 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ_H=7.82 (2H, d, H-2 and H-7), 7.95 (2H, dd, H-11 and H-12), 8.37 (2H, dd, H-10 and H-13), 9.62 (2H, d, H-1 and H-8).

Dipyrido[3,2-*a*:2′,3′-*c*]phenazine (phenazino-bpy). This was obtained from phen-5,6-dione and *o*-phenylenediamine according to a method described in the literature.[1] Mp (benzene) 260—265 °C (lit,[1] 250 °C).

3,6-Diaminodipyrido[3,2-*a*:2′,3′-*c*]phenazine (phenazino-dabp):[13] A stream of gaseous ammonia was bubbled through a solution of phenazino-dcbp (850 mg, 2.42 mmol) in a mixture of phenol (22.8 g) and acetamide (7.14 g), maintaining the solution at 160 °C for 24 h. The resulting reaction mixture was cooled to room temperature, and was poured into 100 cm^3 of 1 equiv-sodium hydroxide. Yellow precipitates were collected by filtration, and were extracted with hot ethanol. The residual brown solid obtained by removal of ethanol was washed with hot benzene to remove the contaminating 3-amino-6-phenoxy product. Yield 437 mg (58%). Mp (5:1 (v/v)-benzene/ethanol) 356 °C (decomp, DTA peak). MS (EI, 70 eV) m/z (rel intensity) 312 (100, M^+). HRMS Found: m/z 312.1137. Calcd for $C_{18}H_{12}N_6$: M, 312.1124. IR ν_{max} (KBr) 3320m, 1600s, 1480s, 1440s, 1400s, 754s cm^{-1}.

Though most of analytical and characterization data were consistent with the structure of phenazino-dabp, there were large errors between the observed and calculated values of elemental analysis. For example, an analysis gave the figures C, 61.64; H, 4.00; and N, 22.80 %, while the formula $C_{18}H_{12}N_6$ should give C, 69.22; H, 3.87; and N, 26.91%. Removal of inorganic impurities by repeated recrystallization from a mixture of ethanol and benzene did not improve the observed values. The electronic spectrum (Fig. 1), which is sensitive to the presence of impurity, was not changed by repeated recrystallization. Presence of a large amount of residual solvents was ruled out because the weight loss in TG analysis was only 3% even at 250 °C. Furthermore, since a benzoylated product phenazino-*t*-bubabpH_2 was obtained in high yield under ordinary conditions (see below), we concluded that phenazino-dabp was obtained in a pure form. Large errors found in elemental analysis should be due to the measurement itself rather than to impurity.

3,6-Bis(4-*t*-butylbenzoylamino)dipyrido[3,2-*a*:2′,3′-*c*]phenazine (phenazino-*t*-bubabpH_2):[21] Into a solution of phenazino-dabp (100 mg, 0.32 mmol) in 30 cm^3 of dry pyridine was added 630 mg (3.2 mmol) of 4-*t*-butylbenzoyl chloride under stirring at room temperature and the mixture was stirred for 1 h at room temperature. Then the mixture was poured into 100 cm^3 of methanol. Yellow precipitates were collected by filtration, and were washed successively with diluted hydrochloric acid, acetone, diluted aqueous ammonia, and methanol. Yield 125 mg (62%). Mp (benzene) 355 °C (DTA peak). MS (EI, 70 eV) m/z (rel intensity) 632 (M^+, 42), 161 (100). HRMS Found: m/z 632.2906. Calcd for $C_{40}H_{36}N_6O_2$, M, 632.2900. Elemental analysis, Found: C, 74.10; H, 5.96; N, 12.80%. Calcd for $C_{40}H_{36}N_6O_2 \cdot H_2O$: C, 73.83; H, 5.89; N, 12.91%. IR ν_{max} (KBr) 3380m, 2950m, 1684s, 1584s, 1508s, 1480s, 1422s, and 1376 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ_H=1.37 (18H, s, *t*-butyl groups) 7.55 (4H, d, H-2 and H-6 of benzoyl groups), 7.89 (2H, dd, H-11 and H-12), 8.07 (4H, d, H-3 and H-5 of benzoyl groups), 8.29 (2H, dd, H-10 and H-13), 8.92 (2H, d, H-2 and H-7), 9.58 (2H, d, H-1 and H-8).

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