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Synthesis and Physical Properties of Pyrido[1′,2′ : 1,2]imidazo[4,5-*b*]quinoxalines

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A series of 2-, 3-, or 4-substituted pyrido[1′,2′ : 1,2]imidazo[4,5-*b*]quinoxalines (PIQs) were synthesized in moderate-to-good yields by the reactions of 2-amino-3-chloroquinoxalines (ACQs) with substituted pyridines, and the structures were established. The reactions of ACQs with 3-phenoxycarbonyl and 3-benzoylpyridines gave the corresponding 2-substituted PIQs, while those with 3-methyl, 3-ethyl, 3-benzyl, 3-phenyl, 3-ethoxycarbonyl, and 3-acetylpyridines gave the corresponding 4-substituted PIQs. PIQ derivatives having substituents at the 2,4,8, and/or 9-positions were also studied. The spectroscopic and electrochemical properties of a series of PIQs derivatives were studied. PIQ showed a strong green fluorescence at 481.5 and 505 nm ($\Phi = 0.40$) in ethanol. The introduction of substituents at the 3 position of PIQ altered the color of the fluorescence from blue to green without deteriorating the high quantum yield of PIQ. All of the derivatives showed strong (blue to orange) fluorescence in both solution and the solid state.

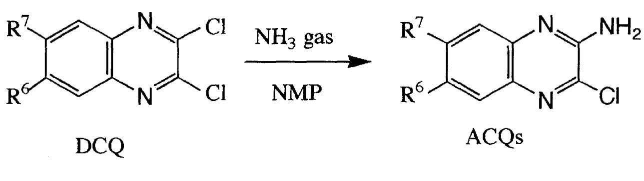
Nitrogen-containing fused polycyclic compounds, such as pyrido[1,2-*a*]benzimidazoles,[1] dipyrido[1,2-*a* : 2′,3′-*d*]imidazoles,[2] pyrido[1′,2′ : 1,2]imidazo[4,5-*b*]pyrazines,[3—5] and pyrido[1′,2′ : 1,2]imidazo[4,5-*b*]quinoxaline (PIQ), have the characteristic ring structures with a bridgehead nitrogen, and have been attracting much attention because of their use as pharmaceuticals and pesticides. Among them, however, relatively few have been known regarding the PIQ derivatives. Until recent reports by the authors[6] and Tanaka et al.,[7] a limited number of papers had reported on the synthesis of PIQ derivatives, only by the reaction of 2,3-dichloroquinoxaline (DCQ) and 2-aminopyridine under severe conditions.[8,9] We have established a convenient and facile synthetic method of 2-amino-3-chloroquinoxaline (ACQ) from DCQ,[10] and have developed a preparative procedure of 3-substituted PIQ derivatives by the reaction of ACQ with 4-substituted pyridines under mild conditions.[6] Most of the 3-substituted PIQs prepared showed strong fluorescence in both solution and the solid state.

Organic fluorescent compounds have been the focus of considerable interest because of their potential application in to a variety of fields, including fluorescent sensing[11] and opto-electronics,[12,13] and the development of a new series of fluorophores has been actively pursued.[14] Although a variety of organic pigments that are readily available have been examined, very few have been found to be promising for the purpose. Studies of a series of fluorescent compounds that have well-characterized structures and properties are essential to understand the structure-function relationship of the substances. The PIQ derivatives can be a potential candidate for this application because they show strong fluorescence in the solid state and have a relatively high thermal stability. In this report, we report here on the full details of the PIQ synthesis by the reaction of ACQs with substituted pyridines and a structural characterization of the series of the 2-, 3-, and 4-substituted PIQs. PIQ derivatives having substituents at the 8 and/or 9 positions are also included.[15] Most of the prepared compounds showed strong green or blue-green fluorescence in both solution and the solid state. We also examined the spectroscopic and electrochemical properties of a series of PIQ derivatives.

Results and Discussion

Synthesis of 2-Amino-3-chloroquinoxalines (ACQs). The ACQ derivatives were synthesized by controlled amination of the corresponding DCQs according to a previously reported procedure (Scheme 1).[10]

The amination of DCQs with ammonia proceeded succes-



	R6	R7
1a	H,	H
1b	NO_2,	H
1c	COPh,	H
1d	Cl	Cl
1e	Me,	Me

Scheme 1.

sively to give monoamino (ACQs) and diamino products. A higher reaction temperature and the prolonged reaction time gave diamino products and/or the ACQs regioisomer. Controlled amination of the DCQs gave ACQs in fare yields (Table 1). The substituents showed a noticeable effect on the reactivity of DCQs with ammonia; i.e., although the reactions of DCQs with electron-donating substituents required a higher temperature and longer reaction time, those of DCQs with electron-withdrawing groups took place readily under moderate conditions. The structures of the obtained ACQs were established by ^{1}H NMR, ^{13}C NMR, MS, and the IR spectra.

Reactions of ACQ with 4-Substituted Pyridines. The reactions of ACQ with 4-substituted pyridines were conducted at a temperature not higher than 100 °C and for a prolonged reaction time, since the reaction above 100 °C caused the self-condensation of ACQ.[10] The reactions gave the corresponding 3-substituted PIQs in moderate-to-good yield (Scheme 2, Table 2, #2—11). The reaction with 4-*t*-butyl- or 4-phenylpyridine afforded the product at more than 60% within 24 h. The reaction with 4-cyanopyridine in 1-methyl-2-pyrrolidone (NMP) gave 3-cyano PIQ in 42%, but only 3% in *N*,*N*-dimethylformamide (DMF), even after a longer reaction time. The reactions of 4-ethyl- and 4-isopropylpyridines with ACQ were carried out at 80 °C. The reactions at 100 °C resulted in the formation of uncharacterized by-products, which could not be separated from the reaction mixtures. Although reactions with 4-nitro-, 4-formyl-, 4-carboxy-, and 4-hydroxypyridines were attempted, no formation of PIQs was detected in any case, and the starting materials were recovered.

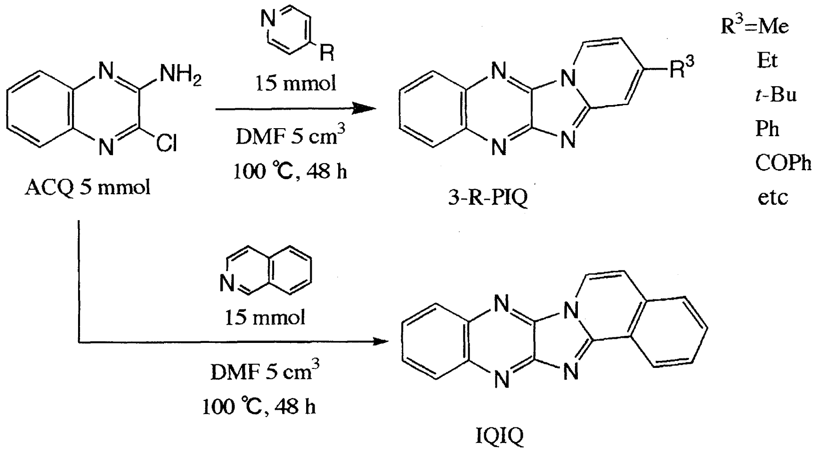
The substituted obtained PIQs were orange or pale-yellow crystals, or a powder; their melting points ranged from 200 to 320 °C without any sign of decomposition, thus showing high thermal stability. Their structures were confirmed by satisfactory elemental analyses, high-resolution mass spectrometry (HRMS, Table 2), ^{1}H NMR (Table 2), and IR spectra. Their solubility was generally poor in common solvents and ^{13}C NMR was not applied.

Reactions of ACQ with 3-Substituted Pyridines. The reaction of 3-substituted pyridine with ACQ might give two different products (regioisomers). One is the PIQ having a pyridine-originated substituent at the 4-position (4-R-PIQ) by an attack of the amino group of ACQ to the 2-position of 3-substituted pyridine moiety at the stage of ring closure; the other is the PIQ having the substituent at the 2-position (2-R-PIQ) by an attack of the amino group to the 6-position of 3-substituted pyridine (Scheme 3). When the substituent was phenoxycarbonyl or benzoyl, 2-R-PIQs were the isolated products (Table 3, #12,13). When the substituent was methyl, ethyl, benzyl, phenyl, ethoxycarbonyl, acetyl, hydroxymethyl or carbamoyl, 4-R-PIQs were exclusively obtained (Table 3, #15—20). 2-R-PIQ and 4-R-PIQ are easily distinguished by a difference in the ^{1}H NMR spectral pattern: the singlet-doublet-doublet pattern of the 1-, 3-, and 4-protons of the 2-R-PIQ and the doublet-triplet-doublet pattern of the 1-, 2-, and 3-protons of the 4-R-PIQ. The structure of the

Table 1. Characterization of 2-Amino-3-chloroquinoxalines (ACQs)

Run	DCQ		Solvent	Temp	Time	Yield	Mp	^{1}H NMR (DMSO-d_6–TMS)	^{13}C NMR (DMSO-d_6–TMS)	FTIR (KBr)
	R^6	R^7		°C	min	%	°C	∂	∂	cm^{-1} (NH$_2$)
1a[10)]	H	H	DMF	100—110	180	66	143—145	7.75 (d-1H), 7.64 (d-1H), 7.60 (t-1H), 7.41 (t-1H), 7.30 (s-NH$_2$) [7.85 (d-1H), 7.68 (d-1H), 7.62 (t-1H), 7.46 (t-1H), 5.50 (s-NH$_2$)][b]	150.0 141.2 137.2 136.0 130.0 127.4 125.0 124.5	3483, 3296
1b[16a)]	NO$_2$	H	DMF	1—5	40	59	290—293 (289)[a]	8.57 (s-1H), 8.35 (d-1H), 7.69 (d-1H), 8.00 (s-NH$_2$)	151.7 145.5 143.1 140.2 134.0 126.0 123.8 123.5	3447, 3310
1c[16b)]	COPh	H	DMF	50—60	70	63	261[a] (Reaction)	8.01—7.99 (m-2H), 7.80—7.56 (m-8H), [8.24 (s-1H), 8.16 (d-1H), 7.83 (d-2H), 7.76 (d-1H), 7.62 (t-1H), 7.51 (t-2H), 5.54 (s-NH$_2$)][b]	194.4 151.2 144.1 138.7 137.2 134.5 132.4 132.2 130.4 130.0 129.4 128.5 125.3	3406, 332
1d	Cl	Cl	NMP	20	80	71	241—243	8.03 (s-1H), 7.80 (s-1H), 7.56 (s-NH$_2$)	150.7 140.6 139.0 134.7 132.5 128.2 126.2 125.7	3484, 3391
1e	CH$_3$	CH$_3$	NMP	110—120	360	61	243—244	7.50 (s-1H), 7.36 (s-1H), 7.07 (s-NH$_2$), 2.35 (s-3H), 2.33 (s-3H)	149.5 139.9 139.6 135.8 134.5 133.9 126.5 124.4	3464, 3298

a) Melting point was measured with DSC. b) CDCl$_3$.



Scheme 2.

4-methyl PIQ was further confirmed by comparing it with 2-methyl PIQ (Table 3, #14), which was independently synthesized from the reaction of 2,3-dichloroquinoxaline with 2-amino-5-methylpyridine. The yields of the reactions leading to 2-R-PIQ or 4-R-PIQ were generally lower compared with those leading to 3-R-PIQ, and the starting materials were recovered. The reaction with 3-cyanopyridine gave neither 2- nor 4-cyano PIQ.

At present, we have no evidence to explain the observed product-selectivity of the 3-substituted pyridines. A semi-empirical MO calculation (AM1) revealed that the phenoxycarbonyl- and benzoyl-substituted pyridines have a lower LUMO (lowest unoccupied molecular orbital) energy (Table 4). However, the LUMO coefficients or partial charges on the 2 and 6-positions of the pyridines could not explain the product-selectivity, and still have to be studied in order to understand the observed selectivity.

Reactions of ACQ with Other Substituted Pyridines. ACQ did not react with 2-methylpyridine or 2-chloropyridine under the reaction conditions employed, and the starting materials were recovered. This implies that the 2-substituent sterically prevented a nucleophlic attack of the pyridine nitrogen atom to the 3-carbon atom of the quinoxaline ring. A reaction with 3,5-dimethylpyridine yielded 2,4-dimethyl PIQ in 33% yield. Although ACQ did not react with quinoline, a reaction with isoquinoline gave isoquino[2′,1′ : 1,2]-imidazo[4,5-*b*]quinoxaline (IQIQ) in 33% yield (Scheme 2). The different reactivity of quinoline might be due to a steric hindrance of the hydrogen atom at the 8 position of quinoline, and also due to the lower basicity of the ring nitrogen of quinoline (pK_a 4.90) than isoquinoline (pK_a 5.42). Pyrazine (pK_a 0.65), pyrimidine, and quinoxaline (pK_a 0.56) showed no reactivity toward ACQ, which might also have been due to their low basicity.

Reactions of Substituted ACQs with Pyridines. The results of the reaction of 6- and/or 7-substituted ACQs with pyridines were also investigated (Table 5). Although the ACQ having electron-donating 6,7-dimethyl substituents showed poor reactivity, and the reaction required a very long reaction time, those having electron-withdrawing groups, e.g. 6-nitro, 6-benzoyl, and 6,7-dichloro, reacted readily with pyridines. The obtained PIQs had a very limited solubility to common organic solvents, showing that the introduction of substituents to the quinoxaline ring lowered the solubility of the PIQs.

Redox Potentials. Cyclic voltammograms of the PIQs examined in this study show a pair or two pairs of reversible or quasi-reversible redox waves in a range between 0 and -1.5 V. Reduction potentials ($E_{1/2}$) were determined as the mean of the oxidation and reduction peaks and are summarized in Table 6. The first reduction potentials of the PIQs range from -0.73 to -1.31 V vs. SCE. 3-Alkyl substituted PIQs show a slightly lower $E_{1/2}$ value than does that of the parent PIQ because of the electron-donating nature of the alkyl group (Table 6, #2—5). However, those having electron-withdrawing groups, such as cyano and acetyl, on the pyrido-ring show a higher $E_{1/2}$ value (Table 6, #9—11); second redox peak was also observed within the sweep range down to -1.5 V.

The influence of introducing the 8- and/or 9-substituents to the 3-*t*-butyl PIQ was investigated (Table 6, #6—8). Introduction of electron-donating methyl groups slightly lower the reduction potential, while electron-withdrawing chloro or benzoyl caused an increase in the reduction potential (Table 6).

For some PIQ derivatives of limited solubility in ethanol, DMF was used as a solvent. The redox potentials in ethanol (Table 6, #1—12) and DMF (Table 6, #13—18) were substantially the same, and no appreciable solvent effect was observed. 4-Methyl PIQ showed a slightly lower reduction potential than did the parent PIQ, whereas isoquino-[2′,1′ : 1,2]imidazo[4,5-*b*]qinoxaline (IQIQ) exhibited a tendency similar to the case of alkyl substituents at the 3-position (Table 6).

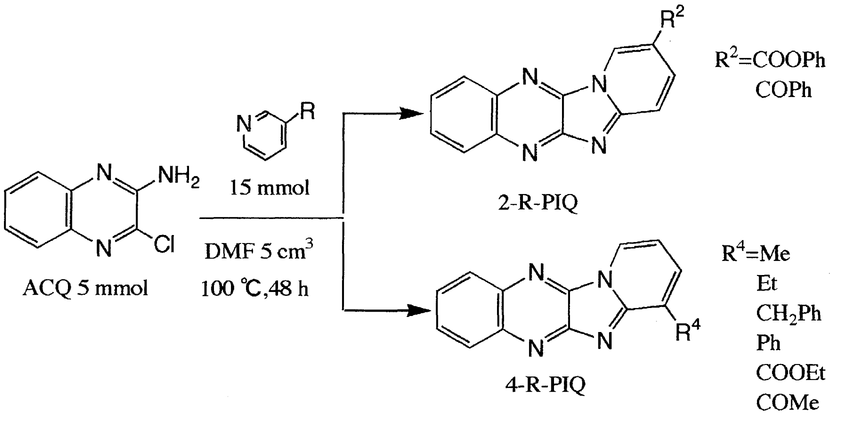
Spectroscopic Properties of 3-*t*-Butyl PIQ. The absorption spectra of 3-*t*-butyl PIQ in ethanol showed two absorption bands at around 356 and 418 nm, the latter consisting of three peaks (Fig. 1). In aprotic solvents, like dichloromethane and DMF, the band of the longer wavelength red-shifted from 418 to 429 nm (Fig. 2), while practically no change was observed for the former band.

Excitation at any of the absorption bands of 3-*t*-butyl PIQ

Table 2. Characterization of 3-Substituted Pyridoimidazoquinoxaline Derivatives

Compound						Yield	Mp	^{1}H NMR ($CDCl_3$–TMS) 1	2	3	4	7,10	8,9	R	E.A./% Calcd (H, C, N)	HRMS (m/z) Calcd	
No.	R^2	R^3	R^4	R^8	R^9	%	°C	δ							Found	Found	
1	H	H	H	H	H	49.0	293—294	8.92 (d)	7.02 (t)	7.72 (t)	7.80 (d)	8.37 (d)	7.86 (t)		3.66 70.89 25.45	220.0749	$C_{13}H_8N_4$
												8.27 (d)	7.79 (t)		3.47 71.06 25.44	220.0748	
2	H	Me	H	H	H	25.6	284—285	8.71 (d)	6.80 (d)	—	7.50 (s)	8.32 (d)	7.81 (t)	2.52 (s) 3H-CH_3	4.30 71.78 23.92	234.0905	$C_{14}H_{10}N_4$
												8.20 (d)	7.73 (t)		4.12 71.86 24.30	234.0907	
3	H	Et	H	H	H	38.4[a]	245—247	8.70 (d)	6.81 (d)	—	7.49 (s)	8.30 (d)	7.79 (t)	2.80 (q) 2H-CH_2	4.87 72.56 22.57	248.1062	$C_{15}H_{12}N_4$
												8.17 (d)	7.71 (t)	1.35 (t) 3H-CH_3	4.71 72.71 22.45	248.1061	
4	H	i-Pr	H	H	H	37.6[a]	202—204	8.65 (d)	6.84 (d)	—	7.48 (s)	8.27 (d)	7.74 (t)	3.00 (m) 1H-CH	5.38 73.26 21.36	262.1219	$C_{16}H_{14}N_4$
												8.09 (d)	7.65 (t)	1.33 (d) 6H-CH_3	5.48 73.54 21.28	262.1216	
5	H	t-Bu	H	H	H	66.4	281—282	8.69 (d)	7.03 (d)	—	7.63 (s)	8.28 (d)	7.76 (t)	1.41 (s) 9H-CH_3	5.84 73.88 20.28	276.1375	$C_{17}H_{16}N_4$
												8.12 (d)	7.67 (t)		5.77 73.45 20.15	276.1373	
6	H	Ph	H	H	H	65.3	321—322	8.95 (d)	7.32 (d)	—	7.99 (s)	8.37 (d)	7.86 (t)	7.80 (d) 2H-Ph	4.08 77.01 18.91	296.1062	$C_{19}H_{12}N_4$
												8.27 (d)	7.78 (t)	7.61—7.50 (m) 3H-Ph	3.91 77.26 18.92	296.1063	
7	H	COMe	H	H	H	45.6	314—315	8.96 (d)	7.54 (d)	—	8.37 (s)	8.40 (d)	7.90 (t)	2.78 (s) 3H-CH_3	3.84 68.69 21.37	262.0854	$C_{15}H_{10}N_4O$
												8.30 (d)	7.85 (t)		3.74 68.44 21.15	262.0854	
8	H	COPh	H	H	H	24.5	257—258	9.04 (d)	7.47 (d)	—	8.13 (s)	8.40 (d)	7.94 (t)	7.94 (d) 2H-Ph	3.73 74.06 17.28	324.1011	$C_{20}H_{12}N_4O$
												8.31 (d)	7.85 (t)	7.72 (t) 1H-Ph	3.56 74.06 17.04	324.1012	
														7.58 (t) 2H-Ph			
9	H	COOEt	H	H	H	52.3	268—270	8.93 (d)	7.54 (d)	—	8.48 (s)	8.36 (d)	7.87 (t)	4.50 (q) 2H-CH_2	4.14 65.74 19.17	292.0960	$C_{16}H_{12}N_4O_2$
												8.25 (d)	7.81 (t)	1.48 (t) 3H-CH_3	3.92 65.51 19.36	292.0961	
10	H	COOPh	H	H	H	20.0	309—310	9.05 (d)	7.69 (d)	—	8.74 (s)	8.42 (d)	7.92 (t)	7.51 (t) 2H-Ph	3.55 70.58 16.47	340.0960	$C_{20}H_{12}N_4O_2$
												8.32 (d)	7.87 (t)	7.38—7.29 (m) 3H-Ph	3.43 70.67 16.55	340.0958	
11	H	CN	H	H	H	42.0[b]	367[c]	9.03 (d)	7.12 (d)	—	8.22 (s)	8.42 (d)	7.93 (t)	—	2.88 68.56 28.56	245.0701	$C_{14}H_7N_5$
												8.31 (d)	7.88 (t)		2.60 68.72 28.43	245.0702	

a) Reaction temperature: 80 °C. b) Solvent: NMP. c) Melting point was measured with DSC.



Scheme 3.

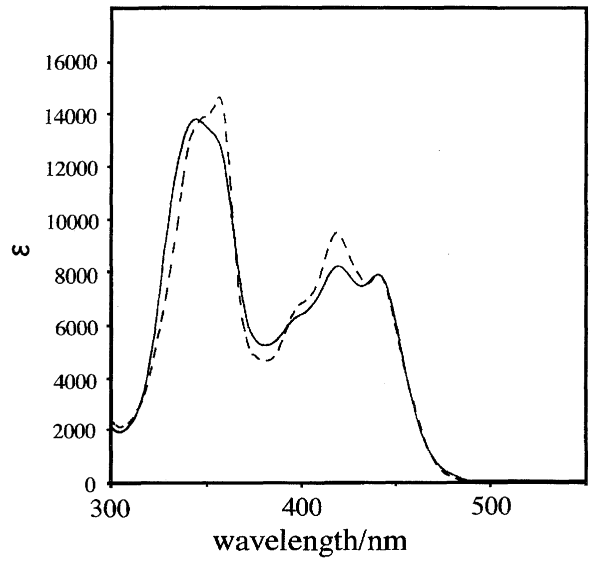


Fig. 1. The absorption and excitation spectra of 3-*t*-BuPIQ (3×10^{-5} mol dm^{-3}) in ethanol. --- absorption spectrum, —— excitation spectrum.

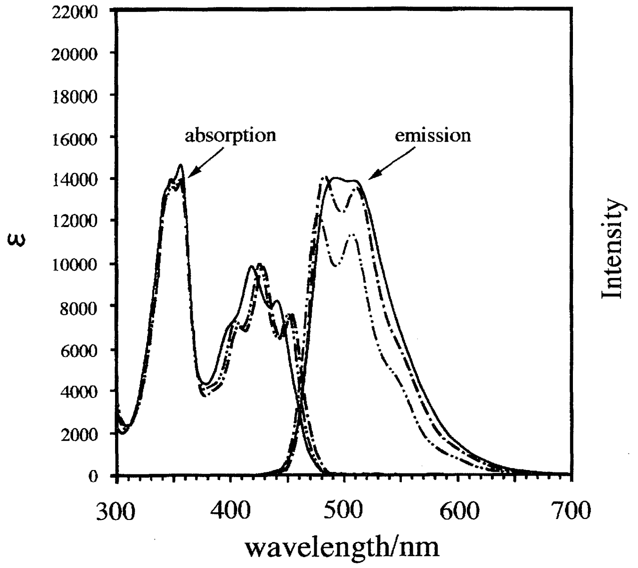


Fig. 2. The solvent effect on the absorption and fluorescence spectra of 3-*t*-BuPIQ (3×10^{-5} mol dm^{-3}) at 20 °C. —— Ethanol, – · – DMF, – ·· – CH_2Cl_2.

under an aerobic atmosphere caused strong blue-green fluorescence at around 500 nm in ethanol ($\Phi = 0.45$, $\lambda_{ex} = 366$ nm). Fluorescence under anaerobic conditions was only slightly stronger than under aerobic conditions, indicating that quenching by oxygen is not significant. Although the emission spectrum did not show any clear fine structure in ethanol, that in aprotic solvents showed the progression of a fine structure that can be regarded as being a mirror image of the absorption band at the longer wavelength side. Therefore, the emitting state is the excited state of the lowest energy absorption at 400—450 nm. The excitation spectrum monitored at 492.5 nm was slightly different from that of the absorption spectrum, showing efficient relaxation from the higher excited states to the emitting state (Fig. 1).

The acidification of a 3-*t*-butyl PIQ solution with an ethanolic hydrogen chloride solution resulted in a gradual decrease of the absorption strength of the band at around 440 nm (Fig. 3). The fluorescence intensity at around 500 nm dramatically decreased upon the addition of hydrochloric acid, and the protonated species showed no additional emission peak by the excitation of any of its absorption band. The addition of ethanolic sodium hydroxide to the solution restored the fluorescence intensity again (Fig. 4). These results showed that protonation of the basic ring-nitrogen suppressed the fluorescence.

Substituent Effect on the Spectroscopic Properties of PIQs. The introduction of various substituents at the 3-position caused a small or moderate change in their absorption and emission spectra. The results of the 3-substituted PIQs along with other substituted PIQs are summarized in Table 1. Alkyl groups at the 3-position induced only a small change (Table 6, #1—5). The absorption band at around 420—450 nm suffered a small blue-shift, while the emission band was slightly red-shifted. Electron-withdrawing groups, such as cyano and acetyl group, caused appreciable bathochromic shifts of both the absorption and emission peaks, and color of the fluorescence became reddish-green or orange (Table 6, #9—11). Except for 3-cyano PIQ, quantum yields ranged from 0.34 to 0.60; therefore, the introduction of substituents at the 3-position is a useful method for fine tuning the color

Table 3. Characterization of 2- or 4-Substituted Pyridoimidazoquinoxaline Derivatives

Compound						Yield	Mp	^{1}H NMR ($CDCl_3$–TMS)							E.A./%	HRMS (*m*/*z*)	
								1	2	3	4	7,10	8,9	R	Calcd (H, C, N)	Calcd	
No.	R^2	R^3	R^4	R^8	R^9	%	°C	δ							Found	Found	
12	COPh	H	H	H	H	15.2	324—325	9.35 (s)	—	8.39 (d)	7.72 (d)	8.28 (d)	7.86 (t)	7.92—7.85 (m) 3H-Ph	3.73 74.06 17.28	324.1011	$C_{20}H_{12}N_4O$
												8.25 (d)	7.82 (t)	7.63 (t) 2H-Ph	3.75 74.19 17.71	324.1012	
13	COOPh	H	H	H	H	16.9	304—308	9.86 (s)	—	8.41 (d)	7.93 (d)	8.35 (d)	7.50 (t)	7.89—7.83 (m) 2H-Ph	3.55 70.58 16.47	340.0960	$C_{20}H_{12}N_4O_2$
												8.31 (d)	7.50 (t)	7.41—7.27 (m) 3H-Ph	3.22 70.95 16.76	340.0959	
14*	Me	H	H	H	H	14.8[a]	281—282	8.71 (s)	—	7.59 (d)	7.73 (d)	8.35 (d)	7.84 (t)	2.48 (s) 3H-CH_3	4.30 71.78 23.92	234.0906	$C_{14}H_{10}N_4$
												8.25 (d)	7.81 (t)		4.13 71.96 23.90	234.0908	
15	H	H	Me	H	H	25.6	257—258	8.70 (d)	6.88 (t)	7.46 (d)	—	8.32 (d)	7.80 (t)	2.70 (s) 3H-CH_3	4.30 71.78 23.92	234.0906	$C_{14}H_{10}N_4$
												8.20 (d)	7.74 (t)		4.27 72.00 23.79	234.0903	
16	H	H	Et	H	H	14.6[a]	183—184	8.76 (d)	6.95 (t)	7.51 (d)	—	8.34 (d)	7.82 (t)	3.17 (q) 2H-CH_2	4.87 72.56 22.57	248.1062	$C_{15}H_{12}N_4$
												8.24 (d)	7.76 (t)	1.47 (t) 3H-CH_3	5.17 72.97 22.62	248.1061	
17	H	H	CH_2Ph	H	H	36.4	244—246	8.77 (d)	6.92 (t)	7.36 (d)	—	8.36 (d)	7.84 (t)	7.48 (d) 2H-Ph	4.55 77.40 18.06	310.1219	$C_{20}H_{14}N_4$
												8.26 (d)	7.78 (t)	7.32 (t) 3H-Ph	4.47 77.51 18.12	310.1218	
														4.48 (s) 2H-CH_2			
18	H	H	Ph	H	H	9.6	265—266	8.93 (d)	7.13 (t)	7.88 (t)	—	8.36 (d)	7.85 (t)	8.20 (d) 2H-Ph	4.08 77.01 18.91	296.1062	$C_{19}H_{12}N_4$
												8.29 (d)	7.80 (t)	7.59—7.45 (m) 3H-Ph	3.91 77.26 18.92	296.1065	
19	H	H	COMe	H	H	5.2	318—319	9.12 (d)	7.16 (t)	8.49 (d)	—	8.39 (d)	7.90 (t)	3.22 (s) 3H-CH_3	3.84 68.69 21.37	262.0855	$C_{15}H_{10}N_4O$
												8.30 (d)	7.84 (t)		3.64 69.20 21.31	262.0856	
20	H	H	COOEt	H	H	1.8	262—264	9.09 (d)	7.11 (t)	8.51 (d)	—	8.39 (d)	7.87 (t)	4.60 (q) 2H-CH_2	4.14 65.74 19.17	292.0960	$C_{16}H_{12}N_4O_2$
												8.26 (d)	7.82 (t)	1.54 (t) 3H-CH_3	3.92 65.51 19.36	292.0960	
21	Me	H	Me	H	H	47.5	278—279	8.56 (s)	—	7.38 (s)	—	8.34 (d)	7.82 (t)	2.43 (s) 3H-CH_3	4.87 72.56 22.57	248.1062	$C_{15}H_{12}N_4$
												8.24 (d)	7.76 (t)	2.71 (s) 3H-CH_3	4.90 72.37 22.61	248.1059	

a) Reaction temperature: 80 °C. b) Solvent: NMP. c) Melting point was measured with DSC.

Table 4. HOMO and LUMO Levels of 3-Substituted Pyridines[a)]

3-R-Pyridine R	HOMO Level/eV	LUMO Level/eV	Product
Me	−9.641	0.136	R^4-PIQ
CH$_2$Ph	−9.436	0.058	R^4-PIQ
Ph	−8.998	−0.512	R^4-PIQ
COMe	−10.245	−0.700	R^4-PIQ
COOEt	−10.314	−0.703	R^4-PIQ
COPh	−9.997	−0.736	R^2-PIQ
COOPh	−9.470	−0.817	R^2-PIQ

a) Calculated by MM2/AM1.

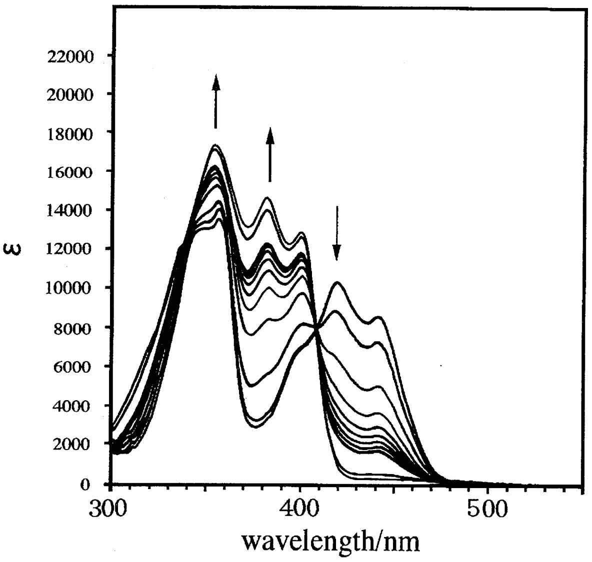


Fig. 3. The change in absorption spectrum of 3-*t*-BuPIQ (3×10^{-5} mol dm^{-3}) in ethanol with HCl/ethanol solution. 0.01 mol dm^{-3} HCl 20 μl (9 times), 0.1 mol dm^{-3} HCl 20 μl (2 times), 1 mol dm^{-3} HCl 20 μl (2 times).

and properties of the PIQ derivatives without deteriorating the high quantum yield of the parent PIQ.

Methyl-substitution at the 2- and/or 4-position caused bathochromic shifts of the fluorescence. The introduction of methyl, chloro, and benzoyl groups to the quinoxaline ring of the 3-*t*-butyl PIQ caused only a minor change in their absorption and emission properties. Though it is not included in Table 6, it is worth noting that the introduction of nitro at the 9-position decreased the quantum yield to below 0.01. Although IQIQ did not exercise any great influence on λ_{max}, the spectrum exhibited a shape elongated in the direction of the short wavelength.

Spectroscopic Properties of the PIQ Derivatives. To understand the absorption and emission properties of the PIQ derivatives, we carried out semi-empirical MO calculations. The electronic spectrum of PIQ was simulated by the ZINDO method (CI level 9) after geometrical optimization by successive MM2 and PM3 calculations (Fig. 5). The shape of the spectrum reproduced the observed spectrum, though the simulated spectrum shifted to the higher energy side. The band at the longer wavelength side of the simulated spectrum

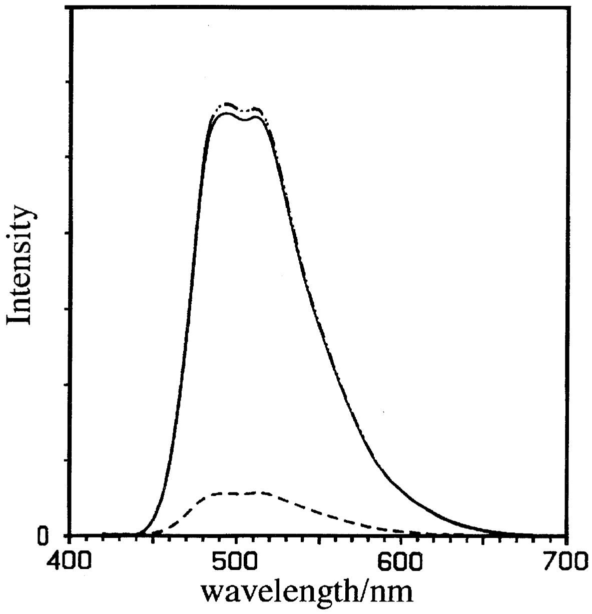


Fig. 4. Fluorescence spectra of 3-*t*-BuPIQ (3×10^{-5} mol dm^{-3}) in ethanol (–··–). After addition of 0.1 mol dm^{-3} HCl/ethanol (40 μl) (- - -), and subsequent addition of 0.1 mol dm^{-3} NaOH/ethanol (40 μl) (——).

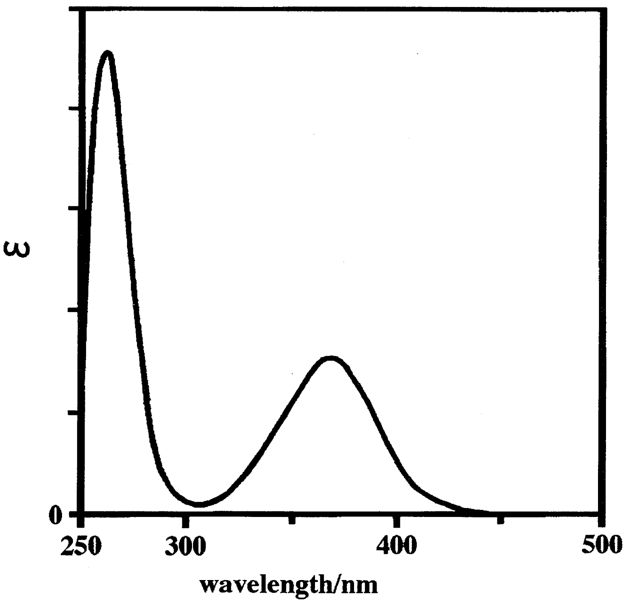


Fig. 5. Simulated electronic spectrum of PIQ by ZINDO method (CI level 9) after geometrical optimization by successive MM2 and PM3 calculations.

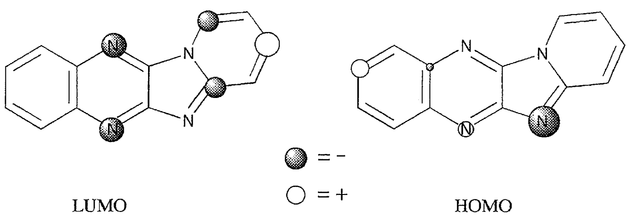


Fig. 6. The HOMO and LUMO orbitals of PIQ.

Table 5. Characterization of 8- and/or 9-Substituted Pyridoimidazoquinoxaline Derivatives

								^{1}H NMR (CDCl$_3$–TMS)							E.A./%	HRMS (m/z)	
Compound						Yield	Mp	1	2	3	4	7,10	8,9	R	Calcd (H, C, N)	Calcd	
No.	R^2	R^3	R^4	R^8	R^9	%	°C	δ							Found	Found	
22	H	H	H	H	NO$_2$	38.6	318—322	8.96 (d)	7.15 (m)	7.87 (m) 2H	—	8.46 (d)	8.62 (d)	—	2.67 58.86 26.41	265.0599	$C_{13}H_7N_5O_2$
						(24 h)	(344)$^{c)}$					9.22 (s)	—		2.69 58.36 26.10	265.0595	
23	H	*t*-Bu	H	H	NO$_2$	48.9	380 (decomp)$^{c)}$	8.83 (d)	7.19 (d)	—	7.75 (s)	8.42 (d)	8.59 (d)	1.46 (s) 9H-CH$_3$	4.71 63.54 21.80	321.1226	$C_{17}H_{15}N_5O_2$
						(24 h)						9.19 (s)	—		4.55 63.12 21.33	321.1218	
24	H	H	H	H	COPh	64.1	276—278	9.17 (d)	7.23 (d)	8.01 (d)	7.87 (m)	8.39 (d)	8.26 (d)	7.89 (m) *o*-2H	3.73 74.06 17.28	324.1011	$C_{20}H_{12}N_4O$
							(270)$^{c)}$					8.53 (s)	—	7.65 (t) *m*-2H	3.75 74.19 17.71	324.1013	
														7.76 (t) *p*-1H			
25	H	*t*-Bu	H	H	COPh	61.8	296—300	9.04 (d)	7.36 (d)	—	7.69 (s)	8.51 (s)	8.23 (d)	7.87 (d) *o*-2H	5.30 75.77 14.73	380.1637	$C_{24}H_{20}N_4O$
							(291)$^{c)}$					8.35 (d)	—	7.66 (t) *m*-2H	5.31 75.64 14.76	380.1619	
														7.75 (t) *p*-1H			
														1.42 (s) 9H-CH$_3$			
26	H	H	H	Cl	Cl	65.0	364—365	9.10 (d)	7.22 (t)	7.99 (t)	7.84 (d)	8.58 (s)	—	—	2.01 54.00 19.39	287.9970	$C_{13}H_6N_4Cl_2$
						(24 h)	(356)$^{c)}$					8.55 (s)	—		1.82 54.24 19.52	287.9952	
27	H	*t*-Bu	H	Cl	Cl	61.5	361$^{c)}$	8.75 (d)	7.12 (d)	—	7.69 (d)	8.44 (s)	—	1.44 (s) 9H-CH$_3$	4.09 59.14 16.23	344.0596	$C_{17}H_{14}N_4Cl_2$
												8.34 (s)	—		3.86 58.81 16.28	344.0600	
28	H	H	H	Me	Me	27.5	322-323	8.87 (d)	6.98 (t)	7.67 (d)	7.77 (d)	8.10 (s)	—	2.57 (s) 6H-CH$_3$	4.87 72.56 22.57	248.1062	$C_{15}H_{12}N_4$
						(120 h)	(315)$^{c)}$								4.86 72.70 22.44	248.1052	
29	H	*t*-Bu	H	Me	Me	41.5	298–299	8.75 (d)	6.90 (t)	—	7.67 (s)	8.08 (s)	—	2.56 (s) 6H-CH$_3$	6.62 74.97 18.41	304.1688	$C_{19}H_{20}N_4$
						(72 H)	(290)$^{c)}$					7.97 (s)	—	1.43 (s) 9H-CH$_3$	6.56 74.63 18.27	304.1689	

a) Reaction temperature: 80 °C. b) Solvent: NMP. c) Melting point was measured with DSC.

Table 6. Absorption and Emission Spectral and Electrochemical Data of PIQs

	Compound					Solvent	Absorbance				Emission			Φ	$E_{1/2}$/V		ν
Abreviation	R^2	R^3	R^4	R^8	R^9		λ_{max}/nm				λ_{max}/nm				vs. SCE		V
1[a)]	H	H	H	H	H	EtOH	355.5	424.5	448.5		481.5	505.0		0.40	−1.14		0.09
2	H	Me	H	H	H	EtOH	355.5	420.5	443.0		486.2	505.0		0.47	−1.23		0.08
3	H	*n*-Pr	H	H	H	EtOH	356.5	421.0	443.5		487.5	507.0		0.47	−1.22		0.12
4	H	*i*-Pr	H	H	H	EtOH	356.5	420.5	442.0		487.5	508.0		0.42	−1.22		0.08
5	H	*t*-Bu	H	H	H	EtOH	356.5	418.5	440.5		492.5	510.0		0.45	−1.22		0.06
6	H	*t*-Bu	H	Me	Me	EtOH	368.0	420.5	442.5		487.5	508.5		0.46	−1.30		0.08
7	H	*t*-Bu	H	Cl	Cl	EtOH	364.0	426.5	448.0		505.0			0.34	−1.01		0.06
8	H	*t*-Bu	H	H	COPh	EtOH	364.5	427.0	446.0		509.5			0.34	−1.01		0.09
9	H	CN	H	H	H	EtOH	369.5	448.0	475.5		481.2	527.5	565.0	0.26	−0.73	−1.44	0.08
10	H	COMe	H	H	H	EtOH	364.0	446.0	471.5		502.5	533.8		0.42	−0.79	−1.34	0.07
11	H	COOEt	H	H	H	EtOH	363.0	445.5	472.5		495.0	528.8		0.60	−0.82	−1.44	0.07
12	H	Ph	H	H	H	EtOH	368.0	437.0	462.5		482.5	523.8		0.42	−1.11		0.10
13	H	Ph	H	Me	Me	DMF	379.5	448.5	477.0			526.0		0.36	−1.16[b)]		0.09
14	H	H	Me	H	COPh	DMF	366.0	420.0	442.0	469.0		523.0		0.38	−0.98[b)]		0.06
15	H	H	H	H	COPh	DMF	366.0	442.0	469.0		516.5			0.48	−1.03[b)]		0.07
16	H	H	CH_2Ph	H	H	DMF	348.5	435.0	460.5		487.0	511.0		0.42	−1.17[b)]		0.07
17	H	H	Me	Me	Me	DMF	368.0	432.5	457.5		480.5	506.0		0.41	−1.31[b)]		0.06
18	H	H	H	Me	Me	DMF	368.0	434.5	461.5		471.0	501.5		0.32	−1.31[b)]		0.07
19	Me	H	H	H	H	EtOH	358.5	430.0	453.6		513			0.33	—[b)]		—
20	Me	H	Me	H	H	EtOH	357.2	429.0	450.0			520.0		0.14	−1.20		0.07
21	H	H	Me	H	H	EtOH	347.2	422.8	444.8		508			0.33	−1.19		0.08
IQIQ	H	−benzo	—	H	H	EtOH	365.5	397.0	418.5		485.0			0.45	−1.23		0.07

a) Lit, P. V. Tagiwala and D. W. Rangneckar, *Indian J. Chem.*, *Sect. B*, **25B**, 1057 (1986). Absorption (λ_{max}) 345 nm, Emission (λ_{max}) 520 nm.
b) Solvent: DMF.

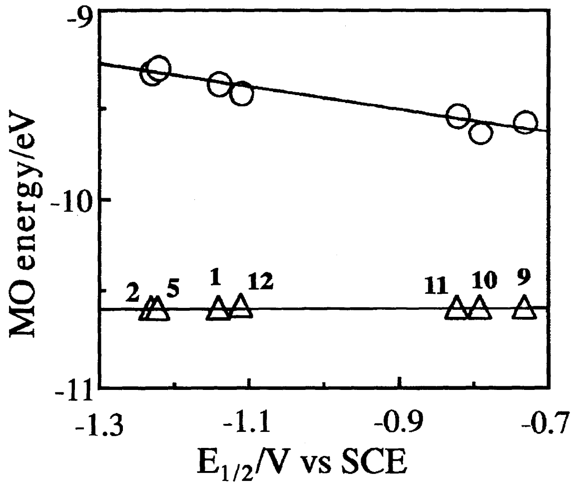


Fig. 7. The plots of HOMO (△) and LUMO (○) versus $E_{1/2}$ of 3-substituted PIQs. PIQs 1 : H, 2 : Me, 5 : *t*-Bu, 9 : CN, 10 : COMe, 11 : COOEt, 12 : Ph.

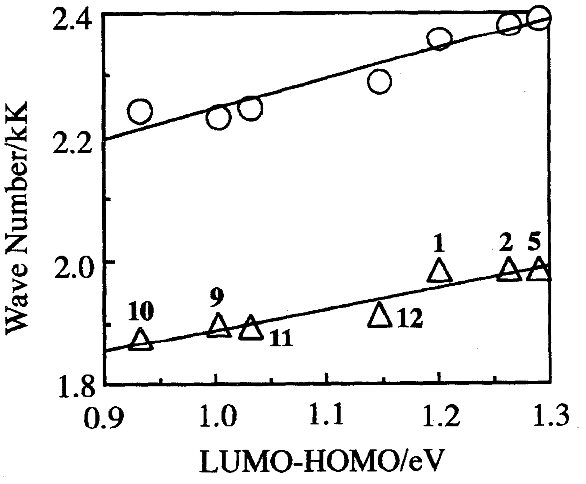


Fig. 8. The relationship of absorption (○) and fluorescence (△) spectra versus LUMO–HOMO energy difference of 3-substituted PIQs. PIQs 1 : H, 2 : Me, 5 : *t*-Bu, 9 : CN, 10 : COMe, 11 : COOEt, 12 : Ph.

consisted of three transitions from HOMO (π–π*), HOMO-3 (n–π*), and HOMO-1 (π–π*) to LUMO. Since the emitting state was the excited state of the lowest energy absorption, it is likely that the electronic state of the emitting state is not much different from the Frank–Condon LUMO state. The LUMO together with the HOMO of PIQ is shown in Fig. 6. The LUMO is a π* orbital having a relatively large coefficient on the quinoxaline nitrogens and on the pyrido ring.

The lower quantum yields of the PIQ derivatives in ethanol compared to those in DMF might have been due to the solvation of protic ethanol to the quinoxaline nitrogens by hydrogen bonding, the vibrational modes of which may act as an accepting mode for the energy from the emitting state of PIQ. As shown in Fig. 2, the fine structure of the emission observed in DMF and dichloromethane disappeared in ethanol. This further suggests the possible role of the solvation of ethanol by hydrogen bonding. Similar solvent effects have been reported for the emission of anthraquinone derivatives, in which hydrogen bonds with protic solvents caused a quenching of the excited S_1 state.[18] Methyl substitution at the 2- and/or 4-position resulted in smaller quantum yields compared to that for the 3-methyl derivative (Table 1), though the LUMO coefficients were found mostly at the 1- and 3-positions. The results suggest that the introduction of the substituent at the 3-position might be a better method for designing a variety of functionalized PIQ derivatives.

3-Substituted PIQ Derivatives. 3-Substituted derivatives show a strong fluorescence in both solution and the solid state, and their color of fluorescence covers from blue to orange. Except for cyano-substituted PIQ, the quantum yields are in the range between 0.34 and 0.6. Therefore, the introduction of substituents at the 3-position is a useful method for fine tuning the color of the PIQ derivatives without sacrificing the high quantum yield of the parent PIQ. 3-Substituted PIQ derivatives can be easily prepared by using 4-substituted pyridines. Though the PIQ derivatives generally show a high thermal stability, the relatively low solubility in common solvents may limit use as fluorescent organic materials. However, the introduction of a *t*-butyl group at the 3-position greatly increased the solubility, and 3-*t*-butyl PIQ became soluble in common solvents, like acetone and ethanol, though it retained high thermal stability (mp 281—282 °C). The results demonstrate than the series of 3-substituted PIQ derivatives reported here can be a new series of useful fluorophores.

The LUMO and HOMO levels of the 3-substituted PIQs were estimated by the extended Hückel method. Since the reduction potential is a good measure of the LUMO levels, we tested the correlation between the observed $E_{1/2}$ values and the calculated LUMO levels of the 3-substituted PIQs (Fig. 7). Although good linear correlation was observed between the calculated LUMO levels and the observed $E_{1/2}$ values ($r^2 = 0.9$), the HOMO levels of the PIQs remained practically unchanged. The results can be easily understood from the HOMO and LUMO orbitals shown in Fig. 6. A similar linear correlation was observed for the LUMO–HOMO energy difference with the lowest-energy absorption maxima and with the fluorescence maxima (Fig. 8). Therefore, the color of the fluorescence of the 3-substituted PIQ derivatives can be easily predicted by a simple extended Hückel estimation.

Experimental and Measurement

Practical grade 1,2-diaminobenzenes and pyridines were obtained commercially (Tokyo Kasei, Wako Junyaku, or Lancaster Synthesis), and were used without further purification. Analytical-grade DMF and NMP were used as solvents without further purification. The solvents used for spectroscopic measurements were the DOTITE fluorometric grade obtained from Dojindo. The melting points were measured with a Yazawa Kagaku micro melting-point apparatus and reported without any correction. The melting points were also measured with a Shimadzu DSC-50 under an argon atmosphere. Elemental analyses were performed on a Yanaco MT-2-CHN-corder. A Perkin–Elmer FTIR 1640 spectrophotometer was used to record the IR spectra as KBr pellets. The mass spectra were recorded on a JEOL JMS-DX303 spectrometer (70 eV) and the NMR spectra on a JEOL JNM-FX90Q, GX270, or A-400 spectrometer. The electronic absorption spectra of the PIQ derivatives in ethanol were recorded on a JASCO Ubest-50, and their emission spectra on a JASCO FP-770 spectrometer with a built-in spectral correction unit at 20 °C. For compounds having a low solubility in ethanol, DMF was used as a solvent. The fluorescence quantum yield (Φ) of 3-*t*-butyl PIQ was determined in reference to that of quinine sulfate ($\Phi = 0.55$), and those of substituted PIQs by using 3-*t*-butyl PIQ as the standard. The redox potentials of the PIQ derivatives were measured by cyclic voltammetry (CV), and were reported in V vs. SCE. Glassy carbon and platinum electrodes were used as working and auxiliary electrodes, respectively, and the potentials were referenced to SCE through a liquid junction. The PIQ derivatives in 0.1 mol dm^{-3} tetrabutylammonium perchlorate (n-Bu$_4$NClO$_4$)/ethanol or DMF solutions under a nitrogen atmosphere were subjected to a potential sweep between 0 and −1.5 V vs. SCE at a rate of 0.1 V s^{-1}. Details concerning the procedure have been reported elsewhere.[19]

Molecular-orbital calculations were carried out by MOPAC AM1/1 (CAChe system on an Apple Macintosh PowerPC 9500, Sony/Tektoronix Co.). The geometry of the molecules were optimized by MM2/AM1.

Synthesis. Quinoxaline-2,3(1*H*,4*H*)-diones, 2,3-dichloroquinoxalines, and 2-amino-3-chloroquinoxaline (ACQ **1a**) were prepared by a similar method as that already described.[10]

2-Amino-3-chloro-6-nitroquinoxaline (NO$_2$ACQ 1b). 2,3-Dichloro-6-nitroquinoxaline (30 mmol, 7.3 g) dissolved in DMF (300 cm^3) was placed in a three-neck flask, into which ammonia gas produced by heating aqueous ammonia (1 dm^3) was introduced for 40 min while keeping the reaction temperature at 1—5 °C. Then, the solution was poured into 5 dm^3 of water. The precipitate was collected by filtration and dried. Recrystallization from THF gave yellow crystals in 59% yield (4.0 g).

2-Amino-6-benzoyl-3-chloroquinoxaline (PhCOACQ 1c). To a DMF (150 cm^3) solution of 6-benzoyl-2,3-dichloroquinoxaline (15 mmol, 4.5 g), ammonia gas was introduced at 50—60 °C for 70 min. A similar work-up gave yellow crystals in 63% (2.7 g) yield.

2-Amino-3,6,7-trichloroquinoxaline (diClACQ 1d). 2,3,6,7-Tetrachloroquinoxaline (20 mmol, 5.4 g) in NMP (250 cm^3) was treated with ammonia gas at 20 °C for 80 min. Yellow crystals from benzene, 3.5 g (71%).

2-Amino-3-chloro-6,7-dimethylquinoxaline (diMeACQ 1e). The treatment of 2,3-dichloro-6,7-dimethylquinoxaline (30 mmol, 6.8 g) in NMP (150 cm^3) with ammonia gas at 110—120 °C for 6 h gave yellow crystals of 1e from benzene, 3.8 g (61%).

General Synthesis of 3-Substituted Pyridoimidazoquinoxalines (3-R-PIQ). 4-Substituted pyridines (7.5 mmol) were allowed to react with ACQ (2.5 mmol) in DMF or NMP (5 cm^3) at 100 °C for 48 h. After the reaction, the addition of water (5 cm^3) and a small amount of alcohol to the reaction mixture gave precipitates, which were collected by filtration and dried. Recrystallization from benzene, and subsequently from chloroform with activated charcoal gave the corresponding 3-substituted PIQ (3-R-PIQ).

2- and 4-Substituted Pyridoimidazoquinoxalines (2-R-PIQ and 4-R-PIQ). 3-Substituted pyridines (R = COOPh, COPh, Me, Et, CH$_2$Ph, COOEt, COMe, and CH$_2$OH) (7.5 mmol) were also allowed to react with ACQ (2.5 mmol) in DMF or NMP (5 cm^3) at 100 °C for 48 h. Then, water (5 cm^3) and a small amount of alcohol were added to the reaction mixture to give a precipitate, which was separated and recrystallized from benzene and subsequently from chloroform in the presence of activated charcoal.

9-NO$_2$-, PhCO-, 8,9-diCl-, and diMe- Pyridoimidazoquinoxalines from Substituted ACQs. Pyridine or 4-*t*-butyl-pyridine (7.5 mmol) was allowed to react with substituted ACQs; the reaction mixture was worked up by a procedure described in the general synthesis section above. PIQs having substituents at the corresponding positions were obtained (Table 4, #21—28).

Isoquinoimidazoquinoxaline (IQIQ). Isoquinoline (7.5 mmol) was allowed to react with ACQ (2.5 mmol) under similar conditions to those mentioned above, and isoquino[2′,1′:1,2]imidazo[4,5-*b*]quinoxaline was obtained in 33% yield. mp 263—264 °C; IR 1635 cm^{-1} (C=N); ^{1}H NMR $\delta = 8.99$ (d-1H), 7.22 (d-1H), 7.87—7.75 (m-3H), 8.59 (d-1H), 8.38 (d-1H), 8.28 (d-1H), 7.87—7.75 (m-2H). Found: C, 75.29; H, 3.62; N, 20.26%; M^+, 270.0908. Calcd for $C_{17}H_{10}N_4$: C, 75.54; H, 3.73; N, 20.73%; HRMS: 270.0906.

2-Methylpyridoimidazoquinoxaline (Table 3, #14*). The 2-amino-5-methylpyridine (7.5 mmol) was allowed to react with 2,3-dichloroquinoxaline (2.5 mmol) in DMF (5 cm^3) at 120 °C for 48 h. The addition of water and a small amount of alcohol gave a precipitate, which was recrystallized from benzene and subsequently from chloroform with activated charcoal.

Attempted Reactions of ACQ with Pyrazine, Pyrimidine, and Quinoxaline. Pyrazine, pyrimidine, or quinoxaline (7.5 mmol) was heated with ACQ (2.5 mmol) in DMF or NMP (5 cm^3) at 100 °C for 48 h. The solution was poured into water. The starting materials were recovered and/or 6,13-dihydropyrazino[2,3-*b*:5,6-*b*′]diquinoxaline (fluorubine) was formed by the self-condensation of ACQ.

Conclusions

In conclusion, we synthesized a series of substituted PIQs, and established their structures. PIQs having a well-characterized structure were afforded for a structure-function study. We described the spectroscopic and electrochemical properties of PIQ derivatives whose structures have been well established. Most of them showed strong blue to green fluorescence in both solution and the solid state. To be used as fluorescent materials having high functionality, the introduction of various functional groups is frequently required, i.e., reactive groups for the fluorescent labeling and bulky groups for the preparation of a smooth amorphous film. We reported on an efficient synthetic procedure, the structural information, and spectroscopic and electrochemical properties of a series of substituted PIQ derivatives. Since the PIQ unit has excellent properties as the novel fluorophore, we believe that the results obtained in this study provide essential and useful information for designing and developing novel functional fluorescent compounds based on the PIQ fluorophore.

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References

1) A. J. Hubert, *J. Chem. Soc. C*, **1969**, 1334.

2) C. Comber-Farnoux and M. Miocque, *J. Heterocycl. Chem.*, **22**, 369 (1985).

3) F. Uchimaru, S. Okada, A. Kosasayama, and T. Konno, *Chem. Pharm. Bull.*, **20**, 1834 (1972).

4) T. Suzuki, Y. Nagae, and K. Mitsuhashi, *J. Heterocycl. Chem.*, **23**, 1419 (1986).

5) K. Mitsuhashi, Y. Nagae, and T. Suzuki, *J. Heterocycl. Chem.*, **23**, 1741 (1986).

6) H. Tomoda, S. Saito, and S. Shiraishi, *Chem. Lett.*, **1990**, 267.

7) K. Tanaka, H. Takahashi, K. Takimoto, M. Sugita, and K. Mitsuhashi, *J. Heterocycl. Chem.*, **29**, 771 (1992).

8) A. K. El-Shafei, H. S. El-Kashef, and A-B. A. G. Ghattas, *Gazz. Chim. Ital.*, **111**, 409 (1981).

9) P. V. Tagdiwala and D. W. Rangnekar, *Indian J. Chem., Sect. B*, **25B**, 1057 (1986).

10) H. Tomoda, S. Saito, M. Ohishi, and S. Shiraishi, *Nippon Kagaku Kaishi*, **1989**, 2059.

11) K. Köller, *Appl. Fluorescence Technol.*, **1**, 1 (1989); I. Aoki, T. Harada, T. Sakaki, Y. Kawahara, and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, **1992**, 1341; M. Inoue, T. Miyake, M. Frusyo, and H. Nakazumi, *J. Am. Chem. Soc.*, **117**, 12416 (1995); T. Mutai, Y. Abe, and K. Araki, *J. Chem. Soc., Perkin Trans. 2*, **1997**, 1805.

12) C. W. Tang and S. A. Vanslyke, *Appl. Phys. Lett.*, **51**, 913 (1987).

13) R. A. Hann, *Mol. Cryst. Liq. Cryst.*, **236**, 65 (1993).

14) K. Araki, T. Mutai, Y. Shigemitsu, M. Yamada, T. Nakajima, S. Kuroda, and I. Shimao, *J. Chem. Soc., Perkin Trans. 2*, **1996**, 613.

15) H. Tomoda, K. Kawahara, N. Ishida, M. Muroi, S. Saito, K. Araki, and S. Shiraishi, "61st National Meeting of the Chemical Society of Japan," Tokyo, March 1991, Abstr., No. 1G514.

16) a) Lit, 7) mp 279—280 °C, IR 3000 cm^{-1} (NH_2); ^{1}H NMR $\delta = 1.55$ (s-NH_2), 7.50 (d-1H), 8.34 (d-1H), 8.56 (s-1H); b) Lit, 7) mp 260—263 °C, IR 3400 cm^{-1} (NH_2); ^{1}H NMR $\delta = 1.55$ (s-NH_2), 7.63—7.85 (d-1H), 8.24 (d-1H), 8.27 (d-1H), 8.30 (s-1H); c) Lit, 7) mp 138—140 °C, IR 3400 cm^{-1} (NH_2); ^{1}H NMR $\delta = 1.55$ (s-NH_2), 7.75 (d-1H), 7.98 (d-1H), 8.02 (s-1H).

17) Lit, 8) mp 295 °C, greenish-brown; ^{1}H NMR (DMSO-d_6) $\delta = 1.55$ (s-NH_2), 7.50 (d-1H), 8.34 (d-1H), 8.56 (s-1H); Lit, 9) mp 265 °C, dark brown.

18) A. N. Diaz, *J. Photochem. Photobiol. A*, **53**, 141 (1990).

19) K. Araki, M. Fuse, N. Kishii, and S. Shiraishi, *Bull. Chem. Soc. Jpn.*, **65**, 1220 (1992).