Synthesis of 9-(Trifluoromethyl)pyrido[1',2':1,2]-imidazo[4,5-*b*]quinoxalines

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9-(Trifluoromethyl)pyrido[1',2':1,2]imidazo[4,5-*b*]quinoxalines (9-CF_3-PIQs) were obtained from the cyclization of 2-amino-3-chloro-6-(trifluoromethyl)quinoxaline (**1a**) with some substituted pyridines. 3-[2-(4-Pyridyl)ethenyl]-9-CF_3-PIQ, one of thus obtained 9-CF_3-PIQs, cyclized with another molecule of **1a** to produce the dihydro bis-PIQ-ethene derivative.

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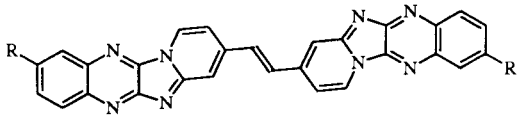
Previously we reported the synthesis of pyrido-[1',2':1,2]imidazo[4,5-*b*]quinoxalines (PIQs) by the cyclizations of 2,3-dichloro- and 2-amino-3-chloroquinoxalines with 2-aminopyridines and pyridines, respectively [1,2]. Most of PIQs revealed interesting fluorescent and electroluminescent properties. In a continuing research on the relationship between the PIQ-substituents and photo function, it is of interest to investigate the optical properties of PIQs with the elongated π-conjugation system such as bis-PIQ-ethene (Chart 1). In the synthesis of PIQ derivatives, one of the biggest problems is rather low solubility in the usual organic solvents and this difficult handling has restricted the synthetic strategy. On the other hand, perfluoroalkyl groups such as trifluoromethyl (CF_3) group are well known to increase the lipophilicity remarkably [3]. Therefore it seems profitable to introduce a CF_3-group into the PIQ ring. In this paper we wish to report the synthesis and the optical properties of the CF_3-PIQ series.



bis-PIQ-ethene

Chart 1

2,3-Dichloro-6-(trifluoromethyl)quinoxaline (**2**), which was prepared from 1,2-diamino-4-(trifluoromethyl)-benzene by the reported method [4,5], was treated with ammonium carbonate in DMF to give two regioisomeric monoaminoquinoxalines in the ratio of 78/22 (Scheme 1). The substituted position of the amino group was confirmed by X-ray crystal structure analysis (Figure 1) [6], and the major product was determined to be 2-amino-3-chloro-6-(trifluoromethyl)quinoxaline (**1a**) and the minor product to be 3-amino-2-chloro-6-(trifluoromethyl)quinoxaline (**1b**). By the way, the amination of 2,3-dichloro-6-nitroquinoxaline (**3**) gave 2-amino-3-chloro-6-nitroquinoxaline exclusively, as reported in our previous paper [1]. The appreciable formation of 3-aminoquinoxaline **1b** in the nucleophilic amination of **2** is explained by a comparison between the estimated LUMO coefficients of the dichloroquinoxalines **2** and **3**. As shown in Figure 2, the PM3 estimated LUMO coefficient of 2-position of **3** is *ca.* five times greater than that of 3-position [7]. It supports the exclusive amination at 2-position and giving the sole product. In contrast, decrease of difference in the LUMO coefficients of 2- and 3-positions of **2** supports the amination at both 2- and 3-positions, giving two regioisomers, **1a** and **1b**.

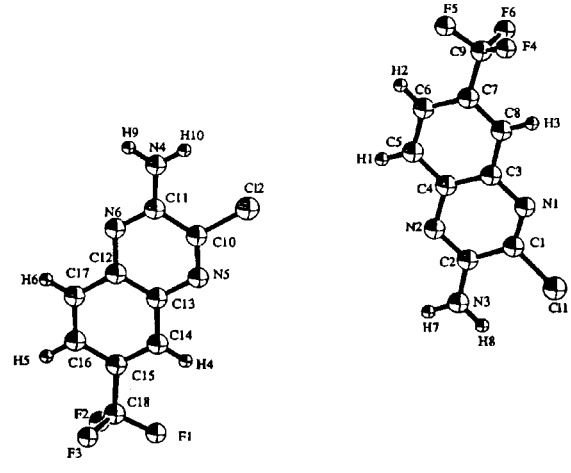
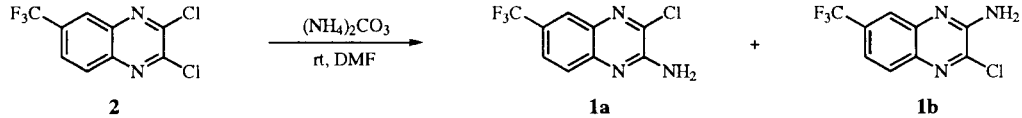
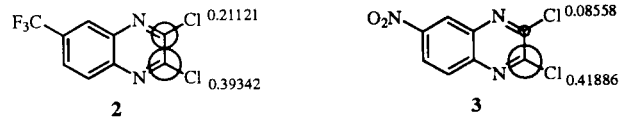


Figure 1. X-ray Structure of **1a**.

Scheme 1



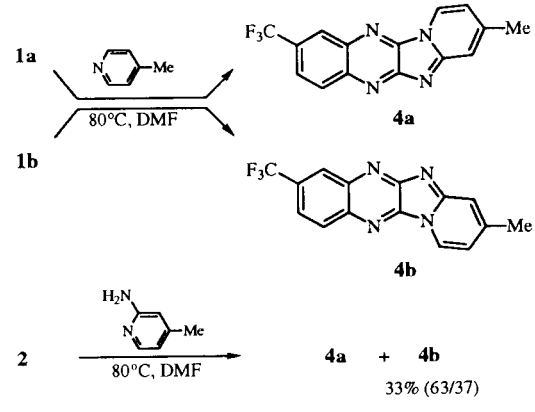


2 3

Figure 2. Estimated LUMO Coefficients of Dichloroquinoxalines.

Aminochloroquinoxalines **1a** and **1b** were both reacted with 4-methylpyridine in DMF at 80° to give 3-methyl-9-(trifluoromethyl)- and 3-methyl-8-(trifluoromethyl)-pyrido[1',2':1,2]imidazo[4,5-*b*]quinoxalines (**4a** and **4b**) in 62 and 61% yields, respectively (Scheme 2). The cyclizations of **1a** and **1b** have similar reactivities and products **4a** and **4b** have almost the same spectral and optical properties (Table 1). Furthermore, another route *via* the cyclization of dichloroquinoxaline **2** with 2-amino-4-methylpyridine gave a mixture of **4a** and **4b** in the ratio of 63/37. This product ratio is also expected by the difference in the estimated LUMO coefficients of **2**. As was anticipated, an introduction of CF_3 group to the PIQ ring increased the solubility. For example, **4a** dissolves completely in chloroform and, however, 9-nitro analogue is hardly soluble even in dimethyl sulfoxide.

Scheme 2



Aminochloroquinoxaline **1a** reacted with 4-phenylpyridine and 4,4'-bipyridine to give the corresponding 3-phenyl- and 3-(4-pyridyl)-9-(trifluoromethyl)pyrido-[1',2':1,2]imidazo[4,5-*b*]quinoxalines (**5** and **6**) in 70 and 46% yields, respectively (Scheme 3). It should be noted that the pyridyl group of **6** had so little activity as to form another PIQ ring.

Scheme 3

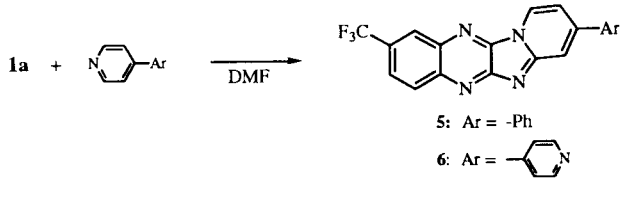
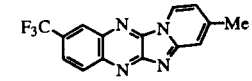
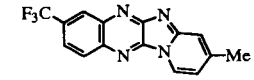
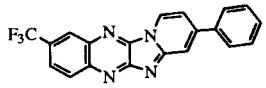
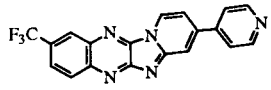
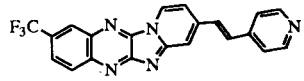
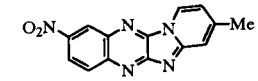
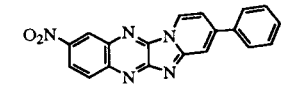
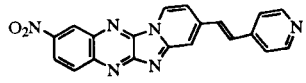


Table 1

Optical Properties of Pyridoimidazoquinoxalines

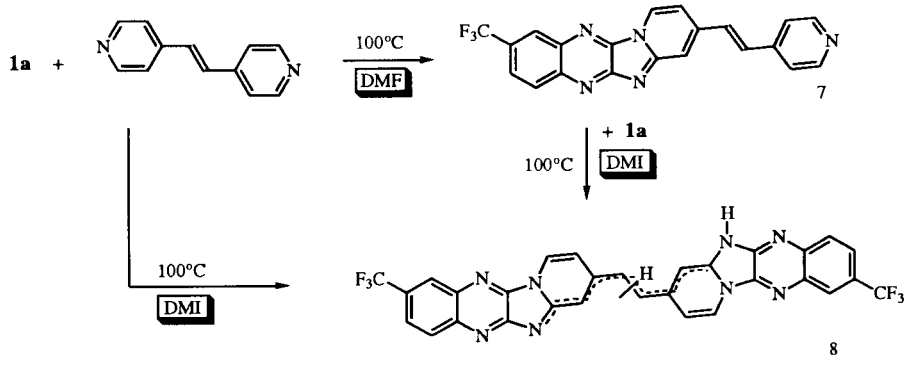
PIQ		Absorption λ_{max} /nm	Emission λ_F/nm	Stokes' Shift $\Delta\lambda$/nm
	**4a**	455	507	52
	**4b**	453	506	53
	**5**	472	525	53
	**6**	473	528	55
	**7**	483	530	47
	[a]	468	501	33
	[a]	485	530	45
	[b]	495	517	22

[a] For the synthesis of this pyridoimidazoquinoxaline, consult lit [1]. [b] Our unpublished results.

The reaction of **1a** and *trans*-1,2-di-4-pyridylethene gave an interesting result (Scheme 4). When they were reacted in DMF at 100 °, 3-[2-(4-pyridyl)ethenyl]-9-(trifluoromethyl)pyrido[1',2':1,2]imidazo[4,5-*b*]quinoxaline (**7**) was obtained in 24% yield. When 1,3-dimethyl-2-imidazolidinone (DMI) was used as a solvent instead of DMF, the pyridyl group of **7** cyclized with another molecule of **1a** at 100 °, giving the sole product **8** in fairly good yield. The analytical data for **8** such as ir (3400 cm^{-1} for NH), ms (602 for M^+ and 301 for $M^+/2$), and elemental analysis support the structure of **8** to be the dihydro bis-PIQ-ethene, as depicted in Scheme 4, although the position of one hydrogen atom could not be specified since the nmr spectra could not be measured because of its poor solubility. An one-pot synthesis of **8** was performed by the reaction of *trans*-1,2-di-4-pyridylethene with 2 equivalent of **1a**, giving **8** in 60% yield. The dehydrogenation of **8** was tried by several oxidation methods, but unfortunately bis-PIQ-ethene (R = CF_3) was not isolated.

The optical properties of these CF_3-PIQs are summarized in Table 1 together with those of some comparable PIQs. Both λ_{max} of absorption and λ_F of emission are red-shifted with the elongation of π-conjugation. For an intro-

Scheme 4



duction of CF_3 group, λ_{max} of absorption is blue-shifted, in comparison with those of the corresponding NO_2-PIQs. The Stokes' shifts $\Delta\lambda$ (λ_{max}-λ_F) of CF_3-PIQs are observed to be larger than those of NO_2-PIQs.

In conclusion, the amination of dichloroquinoxaline **2** gave 2-amino-3-chloro- and 3-amino-2-chloroquinoxalines **1a** and **1b**, and the product ratio being explained by the estimated LUMO coefficients of **2**. CF_3-PIQs have

Table 2

Atomic Coordinates and B_{iso}/B_{eq}

atom	x (x10⁴)	y (x10⁴)	z (x10⁴)	B_{eq}
Cl(1)	8784(1)	2740(9)	1243(1)	5.73(5)
Cl(2)	6461(1)	2790(2)	1519(1)	5.20(4)
F(1)	6132(3)	6173(1)	3068(3)	6.5(1)
F(2)	5450(3)	6217(2)	4224(3)	6.5(1)
F(3)	6941(3)	6247(2)	4832(3)	6.6(1)
F(4)	9426(3)	6150(2)	3106(4)	9.2(2)
F(5)	9009(4)	6303(2)	4420(3)	9.3(1)
F(6)	8021(3)	6210(2)	2817(4)	11.2(1)
N(1)	8789(3)	3840(2)	2126(3)	3.8(1)
N(2)	8630(3)	3333(2)	4079(3)	3.3(1)
N(3)	8654(4)	2335(2)	3375(3)	5.0(1)
N(4)	6336(4)	2327(2)	3757(3)	5.0(1)
N(5)	6166(3)	3870(2)	2484(3)	3.4(1)
N(6)	6351(3)	3311(2)	4540(3)	3.6(1)
C(1)	8752(4)	3249(3)	2282(4)	3.4(1)
C(2)	8680(4)	2966(3)	3279(4)	3.5(2)
C(3)	8757(4)	4231(2)	2972(4)	3.1(1)
C(4)	8671(4)	3980(2)	3934(4)	2.9(1)
C(5)	8641(4)	4396(3)	4768(4)	3.4(1)
C(6)	8684(4)	5039(2)	4641(4)	3.4(1)
C(7)	8763(4)	5284(3)	3676(4)	3.1(1)
C(8)	8799(4)	4889(3)	2857(4)	3.5(2)
C(9)	8795(5)	5976(3)	3518(5)	4.4(2)
C(10)	6214(4)	3268(3)	2627(4)	3.5(1)
C(11)	6296(4)	2957(3)	3666(4)	3.4(1)
C(12)	6308(4)	3951(3)	4415(4)	3.1(1)
C(13)	6212(4)	4243(2)	3389(4)	3.0(1)
C(14)	6179(4)	4900(2)	3273(4)	3.4(1)
C(15)	6223(4)	5266(3)	4165(4)	3.0(1)
C(16)	6323(5)	4994(3)	5194(4)	3.8(1)
C(17)	6361(4)	4353(3)	5311(4)	3.8(2)
C(18)	6202(5)	5961(3)	4076(5)	4.1(2)
H(1)	8582	4222	5434	3.8237
H(2)	8661	5327	5219	3.7612
H(3)	8857	5059	2189	3.9817
H(4)	6108	5091	2568	3.6689
H(5)	6358	5265	5822	4.4875
H(6)	6427	4160	6023	4.3238

Table 2 (continued)

atom	x (x10⁴)	y (x10⁴)	z (x10⁴)	B_{eq}
H(7)	8603	2143	4024	5.4676
H(8)	8685	2061	2797	5.4676
H(9)	6389	2119	4441	5.4894
H(10)	6298	2063	3133	4.3238

$B_{eq} = \frac{8}{3}\pi^2 \{U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha\}$

Table 3

Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
Cl(1)	C(1)	1.737(6)	Cl(2)	C(10)	1.731(6)
F(4)	C(9)	1.312(8)	F(1)	C(18)	1.337(7)
F(5)	C(9)	1.303(7)	F(2)	C(18)	1.335(8)
F(6)	C(9)	1.276(8)	F(3)	C(18)	1.318(8)
N(1)	C(1)	1.267(7)	N(5)	C(10)	1.276(8)
N(1)	C(3)	1.374(7)	N(5)	C(13)	1.381(7)
N(2)	C(2)	1.331(7)	N(6)	C(11)	1.321(7)
N(2)	C(4)	1.389(7)	N(6)	C(12)	1.369(7)
N(3)	C(2)	1.338(7)	N(4)	C(11)	1.346(7)
N(3)	H(7)	0.96	N(4)	H(9)	0.96
N(3)	H(8)	0.96	N(4)	H(10)	0.96
C(1)	C(2)	1.458(8)	C(10)	C(11)	1.464(8)
C(3)	C(4)	1.405(7)	C(13)	C(12)	1.400(7)
C(3)	C(8)	1.415(8)	C(13)	C(14)	1.391(7)
C(4)	C(5)	1.391(8)	C(12)	C(17)	1.420(8)
C(5)	C(6)	1.386(8)	C(17)	C(16)	1.360(8)
C(6)	C(7)	1.394(8)	C(16)	C(15)	1.399(8)
C(7)	C(8)	1.370(8)	C(15)	C(14)	1.382(8)
C(7)	C(9)	1.489(8)	C(15)	C(18)	1.496(8)
C(5)	H(1)	0.97	C(17)	H(6)	0.96
C(6)	H(2)	0.97	C(16)	H(5)	0 99
C(8)	H(3)	0.96	C(14)	H(4)	0.96

Table 4
Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	N(1)	C(3)	116.0(5)	C(10)	N(5)	C(13)	117.0(5)
C(2)	N(2)	C(4)	116.8(5)	C(11)	N(6)	C(12)	117.6(5)
C(2)	N(3)	H(7)	121.4	C(11)	N(4)	H(9)	120.7
C(2)	N(3)	H(8)	120.9	C(11)	N(4)	H(10)	121.2
H(7)	N(3)	H(8)	117.7	H(9)	N(4)	H(10)	118.1
Cl(1)	C(1)	N(1)	118.0(4)	Cl(2)	C(10)	N(5)	118.9(4)
Cl(1)	C(1)	C(2)	117.2(5)	Cl(2)	C(10)	C(11)	117.1(5)
N(1)	C(1)	C(2)	124.8(5)	N(5)	C(10)	C(11)	124.0(5)
N(2)	C(2)	N(3)	119.6(5)	N(6)	C(11)	N(4)	120.1(5)
N(2)	C(2)	C(1)	119.7(5)	N(6)	C(11)	C(10)	119.1(5)
N(3)	C(2)	C(1)	120.7(6)	N(4)	C(11)	C(10)	120.8(5)
N(1)	C(3)	C(4)	122.2(5)	N(5)	C(13)	C(12)	120.4(5)
N(1)	C(3)	C(8)	119.0(5)	N(5)	C(13)	C(14)	118.1(5)
C(4)	C(3)	C(8)	118.8(5)	C(12)	C(13)	C(14)	121.5(5)
N(2)	C(4)	C(3)	120.5(5)	N(6)	C(12)	C(13)	121.9(5)
N(2)	C(4)	C(5)	120.3(5)	N(6)	C(12)	C(17)	119.5(5)
C(3)	C(4)	C(5)	120.2(5)	C(13)	C(12)	C(17)	118.5(5)
C(4)	C(5)	C(6)	120.3(5)	C(12)	C(17)	C(16)	119.7(5)
C(4)	C(5)	H(1)	119.6	C(12)	C(17)	H(6)	119.5
C(6)	C(5)	H(1)	120.0	C(16)	C(17)	H(6)	120.7
C(5)	C(6)	C(7)	119.6(5)	C(17)	C(16)	C(15)	120.8(5)
C(5)	C(6)	H(2)	120.1	C(17)	C(16)	H(5)	119.9
C(7)	C(6)	H(2)	120.2	C(15)	C(16)	H(5)	119.3
C(6)	C(7)	C(8)	121.1(5)	C(16)	C(15)	C(14)	120.9(5)
C(6)	C(7)	C(9)	120.8(5)	C(16)	C(15)	C(18)	118.3(5)
C(8)	C(7)	C(9)	118.2(5)	C(14)	C(15)	C(18)	120.8(5)
C(3)	C(8)	C(7)	120.0(5)	C(13)	C(14)	C(15)	118.5(5)
C(3)	C(8)	H(3)	119.1	C(13)	C(14)	H(4)	121.9
C(7)	C(8)	H(3)	120.9	C(15)	C(14)	H(4)	119.7
F(4)	C(9)	F(5)	103.9(6)	F(1)	C(18)	F(2)	104.8(6)
F(4)	C(9)	F(6)	104.7(6)	F(1)	C(18)	F(3)	107.6(5)
F(4)	C(9)	C(7)	113.4(5)	F(1)	C(18)	C(15)	112.3(5)
F(5)	C(9)	F(6)	106.6(6)	F(2)	C(18)	F(3)	105.8(5)
F(5)	C(9)	C(7)	112.5(5)	F(2)	C(18)	C(15)	112.4(5)
F(6)	C(9)	C(7)	114.8(6)	F(3)	C(18)	C(15)	113.3(6)

fairly good solubility and this ease of handling made possible the synthesis of dihydro bis-PIQ-ethene **8**. Both λ_{max} of absorption and λ_F of emission are noticed to be red-shifted with the elongation of π-conjugation.

EXPERIMENTAL

Melting points are uncorrected. The ir spectra were recorded on a JASCO Report-100 spectrophotometer and samples were run as potassium bromide pellets. The uv spectra were measured with a JASCO Ubest-50 spectrophotometer in dichloromethane solution. The fluorescence spectra were obtained on a HITACHI 650-40 spectrophotometer in dichloromethane solution (λ ex = 290 nm). The ^{1}H-nmr spectra were taken on a JEOL JNM-GX270 (270 MHz) spectrometer by using TMS as an internal standard. The chemical shifts (δ) were given in deuteriochloroform unless otherwise noted. The mass spectra were taken on a HITACHI M-2500 spectrometer operating at 70 eV. The elemental analyses were measured with a YANACO MT-3 equipment.

X-Ray Crystal Structural Analysis of **1a**.

An orange plate crystal of **1a** ($C_9H_5N_3F_3Cl$) having approximate dimensions of 0.60 x 0.20 x 0.80 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5S diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å) .

Crystal constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 33.66 < 2θ < 34.91° corresponded to a primitive monoclinic cell with dimensions: a = 15.24(2), b = 21.108(8), c = 12.91(1) Å, β = 112.3(1)°, V = 3840(7) Å^3. For Z = 16, F.W. = 247.61 and F_{000} = 1984.00, the calculated density is 1.71 g/ml. Based in the systematic absence of: hkl: h + k ≠ 2n, h01: 1 ≠ 2n packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of structure, the space group was determined to be C2/c.

The data were collected at a temperature of 23 ±1° using the ω-2θ scan technique to a maximum 2θ value of 60.0°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.28° with a take-off angle of 6.0°. Scans of (1.68 + 0.30 tan θ)° were made at a speed of 8.0°/minute (in omega). The weak reflections (F < 10.0 σ(F)) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting satistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 1.0 mm, the crystal to detector distance was 285 mm, and the detector aperture was 6.0 x 6.0 mm (horizontal x vertical).

Of the 11661 reflections which were collected, 5751 were unique (R_{int} = 0.096): equivalent reflections were merged. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied.

The linear absorption coefficient, μ, Mo-Kα radiation is 4.0 cm^{-1}. Azimuthal scans of several reflections indicated no need for absorption correction. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficent = 1.78982 x 10^{-08}).

The structure was solved by direct methods [8] and expanded using Fourier techniques [9]. The non-hydrogen atoms are refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement (function minimized: $\sum w(|F_o|-|F_c|)^2$) was based on 1609 observed reflections (I > 3.00 σ (I)) and 290 variable parameters and converged which unweighted and weighted agreement factors of R = 0.048 and R_w = 0.032, respectively. The atom coordinates are listed in Table 2 and bond lengths and angles are given in Tables 3 and 4, respectively.

Synthesis of 2,3-Dichloro-6-(trifluoromethyl)quinoxaline (**2**).

1,2-Diamino-4-(trifluoromethyl)benzene (20.0 g, 0.11 mole) was reacted with oxalic acid dihydrate (31.5 g, 0.25 mole) at 130° for 3 hours. The formed solid was collected on a filter and washed with 1*M* hydrochloric acid and cold ethanol. The solid was recrystallized from ethanol to give 22.8 g (87%) of 6-trifluoromethyl-1,4-dihydro-2,3-quinoxalinedione as a white powder, mp 337.0-339.0°; ir: 3450 (NH), 1720 (C=O), 1170, 1120 cm^{-1} (CF_3).

Anal. Calcd. for $C_9H_5N_2O_2F_3$: C, 46.95; H, 2.19; N, 12.17. Found: C, 46.85; H, 2.30; N, 12.31.

The dihydroquinoxalinedione obtained (22.8 g, 0.10 mole) was stirred at 100° for 1.5 hours in a thionyl chloride (36 ml) solution containing 4 ml of DMF. After removal of excess thionyl chloride, the residue was extracted with ethyl acetate. The extracts were washed with water and brine, dried over magnesium sulfate, and evaporated. The residue was recrystallized from hexane to give 15.3 g (58%) of **2** as a red-violet powder, mp 77.0-77.5°; ^{1}H-nmr: δ = 7.99 (1H, dd, J = 8.8 and 1.8 Hz), 8.18 (1H, d, J = 8.8 Hz), 8.35 (1H, d, J = 1.8 Hz); ir: 1180, 1130 cm^{-1} (CF_3).

Anal. Calcd. for $C_9H_3N_2Cl_2F_3$: C, 40.61; H, 1.14; N, 10.53. Found: C, 40.39; H, 1.14; N, 10.69.

Amination of **2**.

Dichloroquinoxaline **2** (5.00 g, 0.019 mole) and ammonium carbonate (4.50 g, 0.050 mole) were stirred in DMF (10 ml) at room temperature for 6 hours. The reaction mixture was extracted with ethyl acetate and the extracts were washed with water and brine, dried over magnesium sulfate, and evaporated. The residue was chromatographed (silica gel, hexane:ether = 2:1) to give two fractions. The first fraction, 0.82 g (17%) of 3-amino-2-chloro-6-(trifluoromethyl)quinoxaline (**1b**) as ivory needles, mp 224.0-225.0° (recrystallized from hexane-ethyl acetate); ^{1}H-nmr: δ = 5.50 (2H, br s), 7.65 (1H, d, J = 9.5 Hz), 7.95 (1H, d, J = 9.5 Hz), 7.97 (1H, s); ir: 3500 (NH), 1140, 1120 cm^{-1} (CF_3).

Anal. Calcd. for $C_9H_5N_3ClF_3$: C, 43.72; H, 2.04; N, 17.01. Found: C, 43.81; H, 1.97; N, 17.18.

The second fraction, 2.81 g (60%) of 2-amino-3-chloro-6-(trifluoromethyl)quinoxaline (**1a**) as orange needles, mp 160.0-161.0° (recrystallized from hexane-ethyl acetate); ^{1}H-nmr: δ = 5.70 (2H, br s), 7.79 (1H, d, J = 8.6 Hz), 7.97 (1H, d, J =8.6 Hz), 8.13 (1H, s); ir: 3500 (NH), 1140 cm^{-1} (CF_3).

Anal. Calcd. for $C_9H_5N_3ClF_3$: C, 43.72; H, 2.04; N, 17.01. Found: C, 43.89; H, 2.04; N, 17.30.

Synthesis of 3-Methyl-9-(trifluoromethyl)pyrido[1',2':1,2]imidazo[4,5-*b*]quinoxaline (**4a**).

Aminochloroquinoxaline **1a** (0.50 g, 2.0 mmoles) was reacted with 4-methylpyridine (0.66 g, 7.0 mmoles) in DMF (5 ml) at 80° for 40 hours. After cooling the reaction mixture, the resulting precipitate was filtered and washed with hot water and ether. The precipitate was recrystallized from ethyl acetate-methanol to give 0.44 g (73%) of **4a** as yellow fine plates, mp 295.0-297.0°; ^{1}H-nmr: δ = 2.60 (3H, s), 6.93 (1H, dd, J = 7.3 and 1.5 Hz), 7.58 (1H, d, J = 1.5 Hz), 7.98 (1H, dd, J = 9.0 and 2.3 Hz), 8.44 (1H, d, J = 9.0 Hz), 8.55 (1H, d, J = 2.3 Hz), 8.79 (1H, d, J = 7.3 Hz); ir: 1120 cm^{-1} (CF_3).

Anal. Calcd. for $C_{15}H_9N_4F_3$: C, 59.59; H, 3.00; N, 18.54. Found: C, 59.98; H, 3.02; N, 18.14.

Synthesis of 3-Methyl-8-(trifluoromethyl)pyrido[1',2':1,2]imidazo[4,5-*b*]quinoxaline (**4b**).

Aminochloroquinoxaline **1b** (0.40 g, 1.6 mmoles) was reacted with 4-methylpyridine (0.45 g, 4.9 mmoles) in DMF (4 ml) at 80° for 40 hours. A similar workup to the above afforded a yellow powder, **4b** (0.31 g, 64%), mp 259.5-261.0°; ^{1}H-nmr: δ = 2.60 (3H, s), 6.91 (1H, dd, J = 7.1 and 1.8 Hz), 7.57 (1H, d, J = 1.8 Hz), 7.91 (1H, dd, J = 8.5 and 1.5 Hz), 8.34 (1H, d, J = 8.5 Hz), 8.65 (1H, d, J = 1.5 Hz), 8.78 (lH, d, J = 7.1 Hz); ir: 1120 cm^{-1} (CF_3).

Anal. Calcd. for $C_{15}H_9N_4F_3$: C, 59.59; H, 3.00; N, 18.54. Found: C, 59.81; H, 3.34; N, 18.16.

Synthesis of 3-Phenyl-9-(trifluoromethyl)pyrido[1,2':1,2]imidazo[4,5-*b*]quinoxaline (**5**).

Aminochloroquinoxaline **1a** (0.40 g, 1.6 mmoles) was reacted with 4-phenylpyridine (0.38 g, 2.5 mmoles) in DMF (4 ml) at 80° for 46 hours. A similar workup afforded an orange powder, **5** (0.41 g, 70%), mp 344.0-344.5° dec; ^{1}H-nmr (dimethyl sulfoxide-d_6-deuteriochloroform): δ 7.42 (1H, d, J = 7.1 Hz), 7.59 (3H, m), 7.82 (2H, d, J = 8.2 Hz), 8.02 (1H, d, J = 9.5 Hz), 8.04 (1H, s), 8.46 (1H, d, J = 9.5 Hz), 8.60 (1H, br s), 8.89 (1H, d, J = 7.1 Hz); ir: 1140 cm^{-1} (CF_3).

Anal. Calcd. for $C_{20}H_{11}N_4F_3$: C, 65.93; H, 3.04; N, 15.38. Found: C, 65.91; H, 2.93; N, 15.58.

Synthesis of 3-(4-Pyridyl)-9-(trifluoromethyl)pyrido[1',2':1,2]-imidazo[4,5-*b*]quinoxaline (**6**).

Aminochloroquinoxaline **1a** (0.30 g, 1.2 mmoles) was reacted with 4,4'-bipyridine (0.19 g, 1.2 mmoles) in DMF (4 ml) at 80° for 120 hours. A similar workup afforded an orange powder, **6** (0.20 g, 46%), mp 282.0-283.0° dec; ^{1}H-nmr (dimethyl sulfoxide-d_6-deuteriochloroform): δ = 7.70 (1H, d, J = 9.8 Hz), 8.06 (1H, d, J = 10.1 Hz), 8.17 (1H, d, J = 10.1 Hz), 8.44 (1H, s), 8.47 (2H, d, J = 5.4 Hz), 8.66 (1H, br s), 8.81 (2H, d, J = 5.4 Hz), 9.29 (1H, d, J = 9.8 Hz); ir: 1140 cm^{-1} (CF_3).

Anal. Calcd. for $C_{19}H_{10}N_5F_3$: C, 62.45; H, 2.76; N, 19.18. Found: C, 62.09; H, 2.93; N, 19.40.

Synthesis of 3-[2-(4-Pyridyl)ethenyl]-9-(trifluoromethyl)pyrido-[1',2':1,2]imidazo[4,5-*b*]quinoxaline (**7**) .

Aminochloroquinoxaline **1a** (0.53 g, 2.1 mmoles) was reacted with *trans*-1,2-di-4-pyridylethene (0.39 g, 2.1 mmoles) in DMF (5 ml) at 100° for 96 hours. A similar workup afforded an orange powder, **7** (0.20 g, 24%), mp 331.0-332.0°; ^{1}H-nmr (dimethyl sulfoxide-d_6-deuteriochloroform): δ = 7.37 (1H, d, J = 7.3 Hz), 7.41 (2H, d, J = 3.4 Hz), 7.49 (2H, d, J = 4.5 Hz), 7.83 (1H, s), 7.99 (1H, d, J = 8.9 Hz), 8.43 (1H, d, J = 8.9 Hz), 8.56 (1H, s), 8.69 (2H, d, J = 4.5 Hz), 8.91 (lH, d, J = 7.3 Hz); ir: 1170, 1120 cm^{-1} (CF_3).

Anal. Calcd. for $C_{21}H_{12}N_5F_3$: C, 64.43; H, 3.09; N, 17.90. Found: C, 64.06; H, 3.30; N, 18.02.

Synthesis of Dihydro bis-PIQ-ethene (**8**).

Pyridoimidazoquinoxaline **7** (0.28 g, 0.72 mmole) was reacted with aminochloroquinoxaline **1a** (0.18 g, 0.73 mmole) in DMI (5 ml) at 100° for 96 hours. A similar workup afforded an orange powder, **8** (0.24 g, 55%), mp >400° (recrystallized from DMAc); ir: 3400 (NH), 1140 cm^{-1} (CF_3); uv: λ max = 455 nm; emission: λ_F = 517 nm; ms m/z (relative intensity): 602 (85), 301 (100); hrms: m/z calcd. for $C_{30}H_{16}N_8F_6$: 602.1402, Found 602.1409.

Anal. Calcd for $C_{30}H_{16}N_8F_6$: C, 59.79; H, 2.68; N, 18.60. Found: C, 59.65; H, 2.93; N, 18.50.

One-pot Synthesis of Dihydro bis-PIQ-ethene (**8**).

Aminochloroquinoxaline **1a** (0.70 g, 2.9 mmoles) was reacted with *trans*-1,2-di-4-pyridylethene (0.26 g, 1.4 mmoles) in DMI (6 ml) at 100° for 96 hours. A similar workup afforded an orange powder, **8** (0.51 g, 60%).

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