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Synthesis and optical properties of a series of pyrrolopyridazine derivatives: deep blue organic luminophors for electroluminescent devices

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We describe a systematic study of a series of eight blue light-emitting molecules which can be prepared in one step from inexpensive commercial starting materials. The relative luminescence quantum yield can be as high as 84% and the heterocycles are luminescent in the condensed state, either as solids or as oils, indicating that there is no self-quenching in this system. The last observation augurs well for these heterocycles being useful in the fabrication of deep blue light-emitting devices.

Introduction

Development of organic electroluminescence advanced in the 1970s to 1980s with the study of thin-film devices. Vincett *et al.* made devices using films of anthracene sublimed onto oxidized aluminum electrodes with thermally evaporated semi-transparent gold top electrodes. They were able to considerably reduce the driving voltages down to 12 V.[1] Tang and VanSlyke demonstrated efficient electroluminescence in two-layer devices consisting of a hole-transporting layer of an aromatic diamine and tris(quinolin-8-olato-N^1,O^8)aluminum(III) (Alq_3) as emissive materials.[2] Since then, a large number of small organic molecules have been used as charge transporting or emissive materials in light-emitting diodes (LEDs). Organic electroluminescence is moving from a simple curiosity in laboratories to the reality of commercial use.[3,4] Though the primary colors (red, green, blue, RGB) can be produced, single component deep blue- and pure red-emitting dyes are still rare.[5,6] In this paper we report on the synthesis and optical properties of a series of 'pure' blue-emitting pyrrolopyridazine (**PyPyri**) derivatives with relative quantum yields as high as 0.84.

In order to systematically investigate the relationship between the optical properties and substituent effect, a series of ester substituted pyrrolopyridazines (**PyPyri**), compounds **1** to **5** (Fig. 1) were prepared. Further, model compounds pyrrolophthalazine **6**, indolizine **7** and pyrrolopyrazine **8** (Fig. 1) were selected and prepared to examine the importance of both the position of the nitrogen heteroatom and the effective conjugation (coplanar structure) on their optical properties.

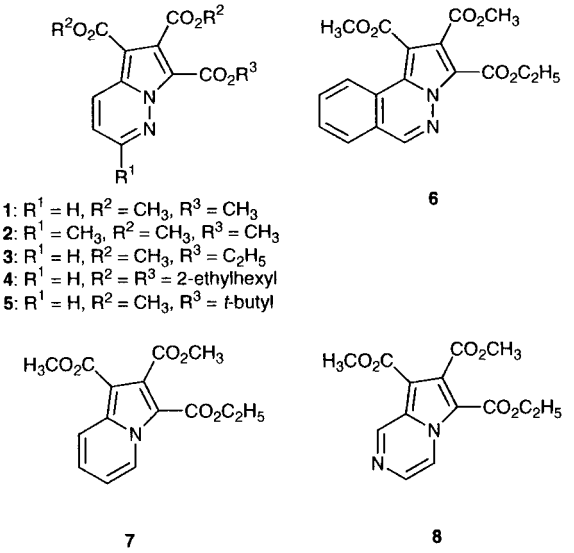
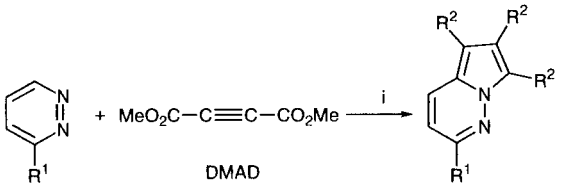


Fig. 1 Synthesized heterocyclic molecules used in this paper.



Scheme 1 *Reagents and conditions*: i, MeOH, −10 to −5 °C, 1.5 hours.

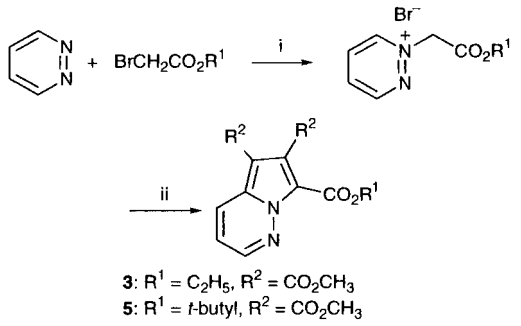
Results and discussion

Synthesis

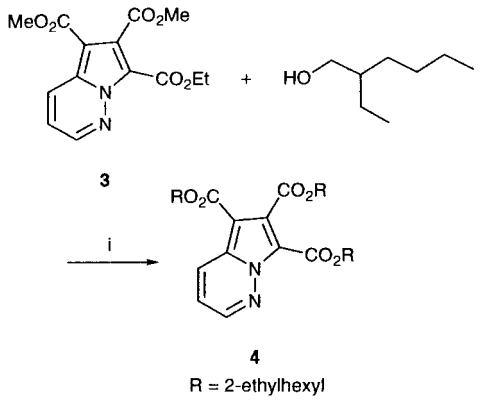
Trimethyl pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylate (**1**) and trimethyl 2-methylpyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylate (**2**) were prepared in one step as described in Scheme 1.[7,8] Pyridazine or 3-methylpyridazine was allowed to react with dimethyl acetylenedicarboxylate directly in methanol at lower temperature to afford the product in 27 and 25% yield, respectively upon recrystallization from methanol containing trace bromine. Though the yields are only moderate and have not been optimized, the products are formed in only one step from inexpensive starting materials.

Preparation of 5,6-bis(methoxycarbonyl)-7-ethoxycarbonylpyrrolo[1,2-*b*]pyridazine (**3**) and its *tert*-butyl analog, compound **5**, were carried out essentially according to the literature procedures in two steps (Scheme 2).[9] Initially, *N*-alkylation of pyridazine with the appropriate bromoacetate (ethyl or *tert*-butyl) affords a pyridazinium salt. Then, treatment of the appropriate pyridazinium salt with dimethyl acetylenedicarboxylate in the presence of triethylamine gave the pyrrolopyridazine derivatives **3** and **5** with three ester groups. Pure **3** and **5** were obtained by recrystallization from ethanol in 29 and 35% yield, respectively.

Tris(2-ethylhexyl) ester **4** was prepared *via* acid catalyzed transesterification as described in Scheme 3.[10] The neat reaction of 5,6-bis(methoxycarbonyl)-7-ethoxycarbonylpyr-



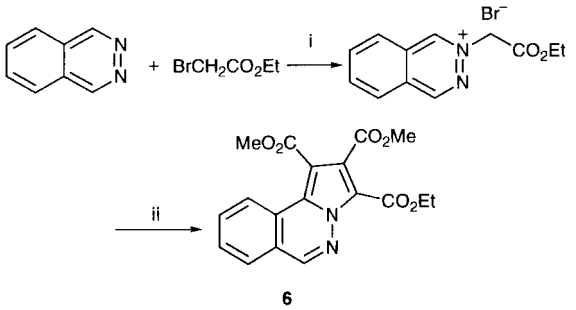
Scheme 2 *Reagents and conditions*: i, CH_2Cl_2, reflux; ii, DMAD, CH_2Cl_2, Et_3N.



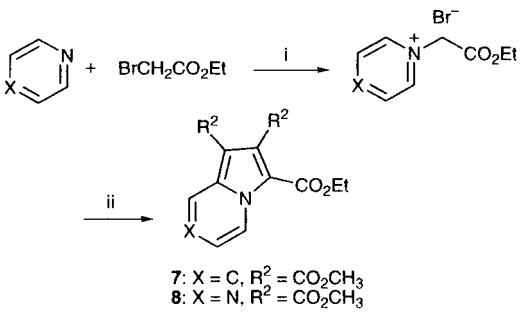
Scheme 3 *Reagents and conditions*: i, H_2SO_4, reflux.

rolo[1,2-*b*]pyridazine (**3**) with 2-ethylhexanol gave a crude reaction mixture separable by flash column chromatography.

Compounds **6** to **8** were prepared essentially according to similar procedures as for compounds **3** and **5** in two steps. Schemes 4 and 5 show these reactions. After work up, the residual 'tar' was chromatographed on silica gel, followed by recrystallization from ethanol.



Scheme 4 *Reagents and conditions*: i, CH_2Cl_2, reflux; ii, DMAD, CH_2Cl_2, Et_3N.



Scheme 5 *Reagents and conditions*: i, CH_2Cl_2, reflux; ii, DMAD, CH_2Cl_2, Et_3N.

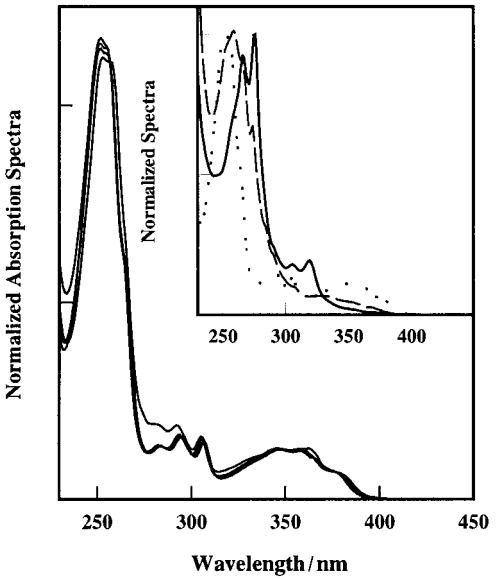


Fig. 2 Absorption spectra of compounds **1**, **3**, **4**, and **5** in hexane. Inset is the comparison of absorption spectra between compound **2** (---), **3** (···), and **6** (—) in hexane.

Optical properties

1 Electronic absorption. The absorption spectra of all the compounds were recorded in hexane at room temperature. Fig. 2 shows the absorption spectra of compounds **1**, **3**, **4**, and **5**. For comparison, the inset in Fig. 2 also lists the absorption spectra of compounds **2**, **3** and **6**. Apparently, absorption spectral profiles of the **PyPyri** series of compounds, except compounds **2** and **6**, are essentially the same, indicating that the absorption spectra of the **PyPyri** compounds are, not unexpectedly, independent of the ester alkyl groups. The absorption peak maxima occur at around 250, 300 and 350 nm in hexane. However, the absorption spectrum changes significantly for pyridazine rings bearing different substituent groups such as methyl and benzo, which is clearly demonstrated in the inset of Fig. 2. The first absorption band is blue-shifted compared with the parent **PyPyri** compound.

The absorption spectra of compounds **7** and **8** are different from that of compound **3**, as expected. The results are shown in Fig. 3 and Table 1. It is clear that the position and number of nitrogen atoms in the two-ring heterocyclic compounds play a key role in determining their electronic and optical properties, which will be further demonstrated below.

2 Emission properties. The fluorescence spectra and relative quantum yield of compounds **1** to **8** have been investigated in hexane at room temperature, employing 9,10-diphenylanthracene as fluorescence standard ($\Phi = 0.96$ in degassed hexane). The **PyPyri** series of compounds are very intense blue emitters (from 400 to 500 nm), especially compounds **1** to **5**. Their quantum yield can be as high as 84%. Also, and of greater interest, these compounds exhibit strong fluorescence in the condensed state (powders **1**–**3**, **5** and oil **4**), an important feature for LED device fabrication. Unlike the absorption behavior, the fluorescence spectra of the **PyPyri** series of compounds **1** to **6** show almost the same fluorescence spectral profile regardless of substituents on the six-membered ring or ester alkyl groups (Fig. 4 and Table 1). They basically have an emission peak maximum around 430 nm with two shoulders around 410 and 450 nm.

Remarkably, the fluorescence quantum yields of compound **1** on the one hand and compounds **2** and **5** on the other, are significantly different ($\Phi = 84$ *vs.* 66 and 68%, respectively) as listed in Table 1, showing a substantial effect by a substituent which has no through resonance electronic interaction. Even

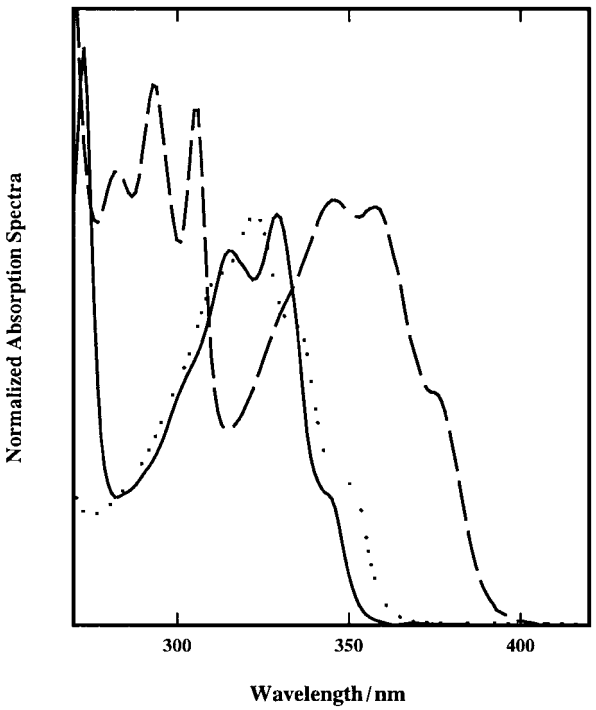


Fig. 3 Normalized absorption spectra of compounds **3** (---), **7** (—), and **8** (···) in hexane.

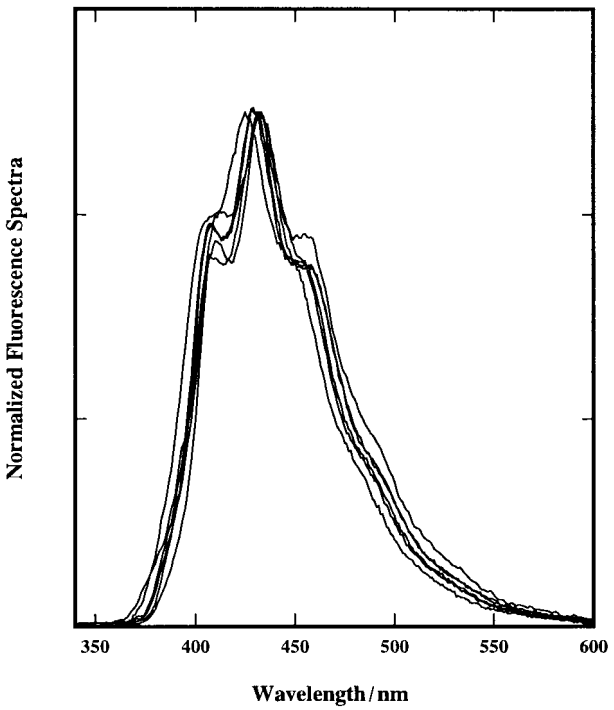


Fig. 4 Normalized fluorescence spectra of compounds **1**, **2**, **3**, **4**, **5**, and **6** in hexane.

more dramatic is the difference in quantum yield between compounds **3** (84%) and **6** (7.4%). It is likely that the significant difference of compound **6** results from the stronger electronic perturbation due to the extended conjugation provided by benzannulation of the pyrrolo[1,2-*b*]pyridazine π electronic system. A comparison of the fluorescence spectral profiles of compounds **3**, **7**, and **8** is made in Fig. 5. It can be seen that the fluorescence spectra of compounds **7** and **8** are blue-shifted and have better defined vibronic structure than compound **3**. Clearly the position and number of nitrogen atoms in these heterocycles, besides affecting their absorption spectra (Fig. 3 and Table 1), also significantly change their fluorescence spectra (Fig. 5) and quantum yields (**8** and **7** $\Phi = 41$ and 17%, respectively).

3 Effect of pH. The absorption and emission properties of compounds **2**, **3**, and **7** as a function of protonation with a trace amount of trifluoroacetic acid (TFA), revealed that protonation had a significant effect on the fluorescence quantum yields and only a minor influence on the wavelength of absorption and fluorescence of these compounds. As shown in Fig. 6, the fluorescence intensity of compound **3** decreased dramatically ($\Phi \sim 8.8\%$) with addition of a trace amount of TFA, while the absorption spectral profile of protonated compound **3** is essentially unchanged in comparison with the free base **3**. A similar behavior was observed for compounds **2** and **7** as listed in Table 1. Quenching of the fluorescence of **7** is particularly interesting since it is unlikely that protonation occurred on the nitrogen of the pyrrole ring.

In order to investigate in detail how the molecular structures of the two-ring heterocyclic compounds affect their electronic properties, especially emission, further experiments such as lifetime measurement, solvent polarity and viscosity effects, temperature effects and design of new molecules relative to

Table 1 Absorption and emission properties of compounds **1** to **8** in hexane

Compounds	UV–vis λ_{max}/nm	Fluorescence λ_{max}/nm	Fluorescence quantum yield (%)
1	346, 359	429	84
2	330	425	66
Protonated **2**	330	465	10
3	346, 459	429	84
Protonated **3**	346	442	8.8
4	348, 362	433	80
5	347, 359	433	68
6	319	432	7.4
7	315, 328	370	17
Protonated **7**	323	392	5
8	323	376	41

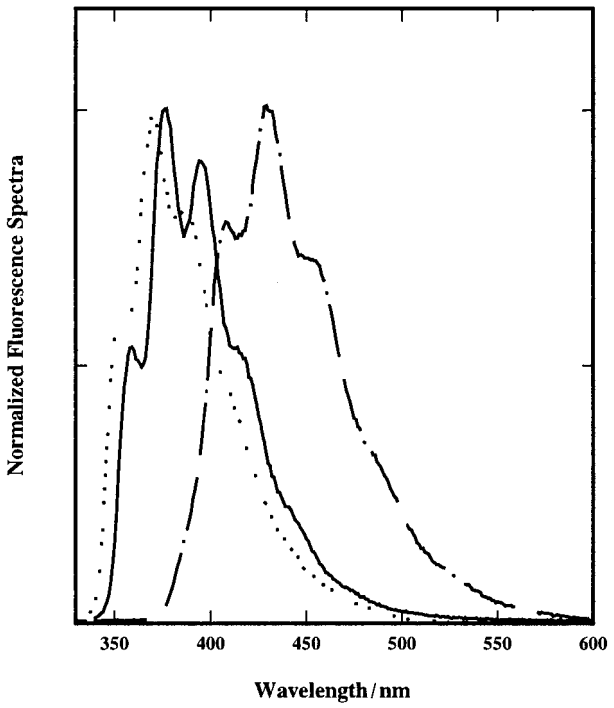


Fig. 5 Normalized fluorescence spectra of compounds **3** (–·–), **7** (···), and **8** (—) in hexane.

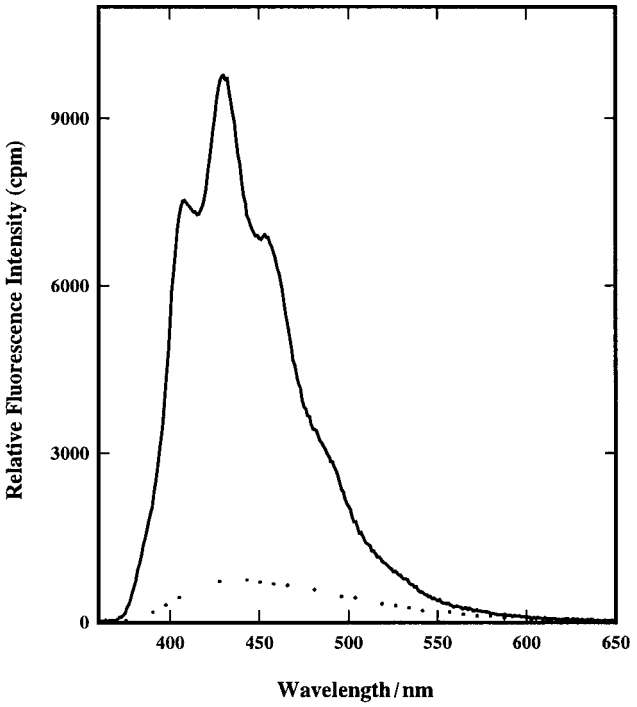


Fig. 6 Relative fluorescence intensities of compounds **3** (—) and **3** (···) with addition of a trace amount of trifluoroacetic acid (excitation was done in the same wavelength and optical density for both solutions).

the two-ring heterocyclic compounds are required and are under way in our laboratory.

Experimental

General

The 360 MHz NMR spectra were obtained on a Bruker AM-360 spectrometer, while ^{1}H NMR spectra were recorded at 360 MHz using TMS ($\delta = 0.00$ ppm) as internal reference. The ^{13}C NMR spectra were recorded at 90 MHz using $CDCl_3$ ($\delta = 77.00$ ppm) as internal reference. UV–vis spectra were recorded on a Hewlett Packard 8453 spectrophotometer in hexane (spectroscopic grade) solution. Melting points were measured using a capillary melting point apparatus and were uncorrected. Fluorescence measurements were performed on a Spex Fluorolog-3 fluorescence spectrophotometer in spectroscopic grade hexane solution. Elemental analyses were determined by Desert Analytics, Tucson, Arizona. All the solvents were purified and dried prior to use according to standard procedures.[11]

Syntheses

Reaction of pyridazine or 3-methylpyridazine with dimethyl acetylenedicarboxylate. This reaction was carried out generally following the procedures in the literature.[7,8]

Trimethyl pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylate (1). Pyridazine, 2.40 g (0.030 mol) and 15 mL of dry methanol were placed in a 50 mL round-bottomed flask equipped with a stirring bar. To this mixture, which was cooled to −5 °C, 5.2 mL of dimethyl acetylenedicarboxylate were added in several portions. The solution was stirred for 1.5 h at this temperature. The color changed to dark red and a solid began to precipitate. The mixture was placed in a freezer (−15 °C) overnight. The mixture was filtered and a yellow solid was obtained. The crude product was recrystallized from methanol containing trace bromine. Product **1**, 2.4 g (27%) was obtained as shining needles: mp 160–161 °C (lit.[7] 158–160 °C); Anal. Calcd. for ($C_{13}H_{12}N_2O_6$): C, 53.43; H, 4.14; N, 9.59; Found: C, 53.27; H, 3.95; N, 9.52%; ^{1}H NMR ($CDCl_3$) δ 8.64 (dd, $J = 1.9$ Hz, $J = 9.2$ Hz, 1H), 8.56 (dd, $J = 1.8$ Hz, $J = 4.4$ Hz, 1H), 7.16 (dd, $J = 4.4$ Hz, $J = 9.2$ Hz, 1H), 4.02 (s, 3H), 3.96 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 165.5, 162.6, 158.6, 145.0, 131.8, 128.7, 128.3, 117.6, 117.1, 102.8, 53.0, 52.2, 51.9.

Trimethyl 2-methylpyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylate (2). Dimethyl acetylenedicarboxylate, 3.7 mL and 10 mL of dry methanol were placed in a 50 mL round-bottomed flask equipped with a stirring bar. To this mixture, which was cooled to −5 °C, 4.22 g (0.045 mol) of 3-methylpyridazine was added in several portions. The solution was stirred for 1.5 h at this temperature, whereupon a solid began to precipitate. The mixture was placed in a freezer overnight, followed by filtration, affording a yellow solid. The crude product was recrystallized from methanol containing trace bromine. Product **2**, 3.4 g (25%) was obtained as shiny needles: mp 165–166 °C (lit.[7] 164.5–165 °C); Anal. Calcd. for ($C_{14}H_{14}N_2O_6$): C, 54.90; H, 4.61; N, 9.15; Found: C, 54.72; H, 4.50; N, 9.16%; ^{1}H NMR ($CDCl_3$) δ 8.49 (d, $J = 9.3$ Hz, 1H), 7.03 (d, $J = 9.3$ Hz, 1H), 4.00 (s, 3H), 3.94 (s, 3H), 3.90 (s, 3H), 2.66 (s, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 165.7, 162.7, 158.6, 154.2, 130.5, 128.0, 127.6, 119.7, 116.8, 102.4, 52.9, 52.0, 51.7, 22.2.

5,6-Bis(methoxycarbonyl)-7-ethoxycarbonylpyrrolo[1,2-*b*]pyridazine (3). This compound was prepared essentially according to the literature procedure *via* a two-step reaction.[9] First, 2.5 g (0.031 mol) of pyridazine, 5.5 g (0.033 mol) of ethyl bromoacetate and 30 mL of methylene chloride were charged in a 50 mL round-bottomed flask equipped with a stirring bar. The mixture was refluxed for about 1 h under argon and a solid precipitated. The resulting mixture was cooled to room temperature and filtered under argon. The solid was washed twice with methylene chloride or diethyl ether. *N*-(Ethoxycarbonylmethyl)pyridazinium bromide, 6.8 g (89%) was obtained as a pale yellow crystalline solid: ^{1}H NMR (CD_3OD) δ 9.97–9.96 (m, 1H), 9.63–9.62 (m, 1H), 8.81–8.77 (m, 1H), 8.71–8.68 (m, 1H), 5.89 (s, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H).

In a 50-mL three-necked flask, which was equipped with a stirring bar and a condenser capped with a drying tube, were placed 0.840 g (0.0034 mol) of *N*-(ethoxycarbonylmethyl)pyridazinium bromide (obtained from last step), 1.60 g (0.0112 mol) of dimethyl acetylenedicarboxylate and 20 mL of methylene chloride. The mixture was heated under reflux and a solution of triethylamine (1.19 g, 0.0118 mol) in methylene chloride was added dropwise over 1 h. The color of the reaction mixture changed to dark brown to black. The mixture was refluxed for an additional 4 h, followed by cooling to room temperature and dilution with methylene chloride to 50 mL. The organic phase was washed once with 12 mL of water and dried over $MgSO_4$. The CH_2Cl_2 was removed with a rotary evaporator, and a black semisolid mixture was obtained. This gummy residue was dissolved in hot ethanol, and allowed to cool slowly. Filtration yielded yellow crystals which were recrystallized from ethanol to afford 0.30 g (29%) of pure **3** as shiny needles: mp 133–134 °C (lit.[9] 133.5–134.5 °C); Anal. Calcd. for ($C_{14}H_{14}N_2O_6$): C, 54.90; H, 4.61; N, 9.15; Found: C, 54.79; H, 4.41; N, 9.01%; ^{1}H NMR ($CDCl_3$) δ 8.63 (dd, $J = 1.8$ Hz, $J = 9.2$ Hz, 1H), 8.56 (dd, $J = 1.8$ Hz, $J = 4.5$ Hz, 1H), 7.15 (dd, $J = 4.5$ Hz, $J = 9.2$ Hz, 1H), 4.41 (q, $J = 7.1$ Hz, 2H), 4.00 (s, 3H), 3.92 (s, 3H), 1.39 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 165.5, 162.7, 158.0, 145.0, 131.8, 128.4, 128.3, 117.5, 117.2, 102.7, 61.2, 52.8, 51.9, 14.1.

Tris(2-ethylhexyl) pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylate (4). A sample of 5,6-bis(methoxycarbonyl)-7-ethoxycar-

bonylpyrrolo[1,2-*b*]pyridazine (**3**), 0.50 g (1.63 mmol), 15 g of 2-ethylhexanol and 0.016 g (0.163 mmol) of sulfuric acid were charged in a 25 mL round-bottomed flask equipped with a stirring bar and a condenser capped with a drying tube. The transesterification reaction was carried out under reflux for 24 h, whereupon the mixture was cooled and diluted with CH_2Cl_2. The organic phase was washed with water twice and dried over $MgSO_4$. The CH_2Cl_2 was removed with a rotary evaporator and a viscous liquid containing an excess of 2-ethylhexanol was obtained. The 2-ethylhexanol was removed by vacuum distillation and the crude product was purified using flash column chromatography (silica gel) with ethyl acetate–hexane mixture (1 : 10) as eluent to give 0.56 g (59%) of viscous liquid product **4**: Anal. Calcd. for ($C_{34}H_{54}N_2O_6$): C, 69.59; H, 9.28; N, 4.77; Found: C, 69.91; H, 8.97; N, 4.81%; ^{1}H NMR ($CDCl_3$) δ 8.64 (dd, J=1.9 Hz, J=9.2 Hz, 1H), 8.53 (dd, J=1.9 Hz, J=4.4 Hz, 1H), 7.12 (dd, J=4.4 Hz, J=9.2 Hz, 1H), 4.30–4.23 (m, 6H), 1.71 (m, 3H), 1.47–1.25 (m, 24H), 0.95–0.88 (m, 18H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 165.1, 162.6, 158.5, 144.8, 131.8, 128.5, 128.3, 117.4, 117.3, 103.7, 69.2, 67.6, 67.1, 38.9, 38.8, 38.5, 30.3, 30.2, 30.0, 29.7, 28.9, 28.8, 23.7, 23.6, 23.4, 23.0, 22.9, 14.0, 10.9, 10.8, 10.7.

5,6-Bis(methoxycarbonyl)-7-*tert*-butyloxycarbonylpyrrolo[1,2-*b*]pyridazine (5). This adduct was prepared in the usual way (see above for compound **3**). First a pyridazinium salt was prepared from pyridazine (5.00 g, 0.062 mol) and *tert*-butyl bromoacetate (12.87 g, 0.066 mol) in CH_2Cl_2 (60 mL) to afford 15.5 g (91%) of *N*-(*tert*-butyloxycarbonylmethyl)pyridazinium bromide as a pale orange crystalline solid: ^{1}H NMR (CD_3CN) δ 10.16–10.14 (m, 1H), 9.48–9.47 (m, 1H), 8.68–8.63 (m, 1H), 8.57–8.53 (m, 1H), 5.80 (s, 2H), 1.47 (s, 9H). The 1,3-dipolar addition was carried out using the above bromide (1.87 g, 0.0068 mol), dimethyl acetylenedicarboxylate (3.2 g, 0.0224 mol) and triethylamine (2.38 g, 0.0236 mol). After work up, the gummy residue was purified using flash column chromatography (silica gel) with ethyl acetate–hexane mixture (1 : 5) as eluent. All the fluorescent fractions were combined from the column and the solvent was removed by a rotary evaporator. The crude product was recrystallized from ethanol to afford 0.79 g (35%) of product **5** as shiny needles: mp 117–118 °C; Anal. Calcd. for ($C_{13}H_{12}N_2O_6$): C, 57.48; H, 5.43; N, 8.38; Found: C, 57.21; H, 5.28; N, 8.03%; ^{1}H NMR ($CDCl_3$) δ 8.63 (dd, J=1.9 Hz, J=9.2 Hz, 1H), 8.56 (dd, J=1.9 Hz, J=4.5 Hz, 1H), 7.12 (dd, J=4.5 Hz, J=9.2 Hz, 1H), 4.00 (s, 3H), 3.92 (s, 3H), 1.60 (s, 9H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 165.4, 162.7, 157.1, 144.8, 131.5, 128.2, 127.9, 117.9, 117.2, 102.3, 82.8, 52.6, 51.8, 28.0.

1,2-Bis(methoxycarbonyl)-3-ethoxycarbonylpyrrolo[2,1-*a*]phthalazine (6). This adduct was prepared in the usual way (see above for compound **3**). The phthalazinium salt[12] was prepared from phthalazine (2.037 g, 0.015 mol) and ethyl bromoacetate (3.34 g, 0.02 mol) in CH_2Cl_2 (15 mL). Thus, 4.45 g (95%) of *N*-(ethoxycarbonylmethyl)phthalazinium bromide was obtained as light pink solid: ^{1}H NMR (CD_3CN) δ 10.49 (s, 1H), 9.88 (s, 1H), 8.71–8.38 (m, 4H), 5.78 (s, 2H), 4.32 (q, J=7.2 Hz, 2H), 1.30 (t, J=7.0 Hz, 3H). The 1,3-dipolar addition was carried out using this *N*-(ethoxycarbonylmethyl)phthalazinium bromide (1.01 g, 0.0034 mol), dimethyl acetylenedicarboxylate (1.6 g, 0.0112 mol), and triethylamine (1.19 g, 0.0118 mol). After work up, the gummy residue was purified using flash column chromatography (silica gel) with ethyl acetate–hexane mixture (1 : 5) as eluent. All the blue fluorescent fractions were combined and the solvent was removed by a rotary evaporator. The crude product was recrystallized from ethanol to afford 0.36 g (30%) of product **6** as a white crystalline solid: mp 125–126 °C; Anal. Calcd. for ($C_{18}H_{16}N_2O_6$): C, 60.67; H, 4.53; N, 7.86; Found: C, 60.45; H, 4.39; N, 7.67%; ^{1}H NMR ($CDCl_3$) δ 9.48 (d, J=8.8 Hz, 1H), 8.78 (s, 1H), 7.91–7.87 (m, 2H), 7.77–7.73 (m, 1H), 4.44 (q, J=7.1 Hz, 2H), 3.98 (s, 3H), 3.95 (s, 3H), 1.40 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 165.8, 163.9, 158.5, 147.2, 133.2, 129.8, 128.1, 127.8, 126.6, 126.5, 126.4, 121.7, 118.5, 106.1, 61.4, 52.6, 52.3, 14.1.

1,2-Bis(methoxycarbonyl)-3-ethoxycarbonylindolizine (7). This adduct was prepared in the usual way (see above for compound **3**). The pyridinium salt was prepared from pyridine (2.47 g, 0.031 mol) and ethyl bromoacetate (5.5 g, 0.033 mol) in CH_2Cl_2 (30 mL). The mixture was refluxed for about 4 h under argon, and cooled to room temperature. The solvent was evaporated to 1/3 of the original volume. The solid which precipitated was filtered under argon and was washed twice with diethyl ether, providing 7.1g (92%) of *N*-(ethoxycarbonylmethyl)pyridinium bromide as a white crystalline solid: ^{1}H NMR ($CDCl_3$) δ 9.57 (d, J=6.0 Hz, 2H), 8.61 (t, J=7.8 Hz, 1H), 8.14 (t, J=7.0 Hz, 2H), 6.36 (s, 2H), 4.29 (q, J=7.1 Hz, 2H), 1.31 (t, J=7.2 Hz, 3H). The 1,3-dipolar addition was carried out using this *N*-(ethoxycarbonylmethyl)pyridinium bromide (0.837 g, 0.0034 mol), dimethyl acetylenedicarboxylate (1.60 g, 0.0112 mol), and triethylamine (1.19 g, 0.0118 mol) to yield 0.36 g (35%) of product **7** as a white crystalline solid: mp 119–120 °C; Anal. Calcd. for ($C_{15}H_{15}NO_6$): C, 59.01; H, 4.95; N, 4.59; Found: C, 58.66; H, 4.68; N, 4.41%; ^{1}H NMR ($CDCl_3$) δ 9.55–9.53 (m, 1H), 8.35–8.33 (m, 1H), 7.40–7.36 (m, 1H), 7.07–7.03 (m, 1H), 4.37 (q, J=7.1 Hz, 2H), 4.00 (s, 3H), 3.91 (s, 3H), 1.38 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 166.3, 163.3, 160.0, 137.8, 130.4, 127.9, 126.7, 119.9, 115.3, 112.0, 102.9, 60.9, 52.7, 51.6, 14.1.

6-Ethoxycarbonyl-7,8-bis(methoxycarbonyl)pyrrolo[1,2-*a*]pyrazine (8). This adduct was prepared in the usual way (see above for compound **3**). The pyrazinium salt was prepared from pyrazine (5.01 g, 0.062 mol) and ethyl bromoacetate (13.36 g, 0.08 mol) in CH_2Cl_2 (50 mL). The mixture was refluxed for about 5 h under argon, cooled to room temperature and the solvent was evaporated to 1/2 of the original volume to provide a solid which was filtered under argon. The solid was washed twice with diethyl ether to afford 1.17 g (8%) of *N*-(ethoxycarbonylmethyl)pyrazinium bromide as a brown solid: ^{1}H NMR (CD_3CN) δ 9.49 (br, 2H), 9.02 (br, 2H), 5.71 (s, 2H), 4.29 (q, J=7.1 Hz, 2H), 1.28 (t, J=7.1 Hz, 3H). The 1,3-dipolar addition was carried out using this *N*-(ethoxycarbonylmethyl)pyrazinium bromide (0.84 g, 0.0034 mol), dimethyl acetylenedicarboxylate (1.6 g, 0.0112 mol) and triethylamine (1.19 g, 0.0118 mol). After work up, the gummy residue was purified using flash column chromatography (silica gel) with ethyl acetate–hexane mixture (1 : 5) as eluent. All the fluorescent fractions were combined off the column and the solvent was removed by a rotary evaporator. The crude product was recrystallized from methanol to afford 70 mg (7%) of product **8** as a white crystalline solid: mp 138–139 °C; Anal. Calcd. for ($C_{14}H_{14}N_2O_6$): C, 54.90; H, 4.61; N, 9.15; Found: C, 55.12; H, 4.38; N, 9.01%; ^{1}H NMR ($CDCl_3$) δ 9.69 (d, J=1.3 Hz, 1H), 9.31 (dd, J=1.4 Hz, J=4.8 Hz, 1H), 8.12 (d, J=4.8 Hz, 1H), 4.41 (q, J=7.1 Hz, 2H), 4.01 (s, 3H), 3.97 (s, 3H), 1.40 (t, J=7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) (^{1}H decoupled) δ 165.1, 162.2, 159.4, 146.0, 132.4, 130.2, 130.0, 119.5, 113.5, 106.1, 61.5, 52.8, 52.0, 13.9.

Conclusions

A series of ester-substituted pyrrolopyridazines, a pyrrolophthalazine, an indolizine and a pyrrolopyrazine were prepared and their optical properties, both absorption and emission, were studied. These heterocyclic compounds are strongly fluo-

rescent, particularly the triester derivatives of pyrrolopyridazines which show a fluorescence quantum yield up to 84%. More to the point, these heterocycles are strongly fluorescent in the **condensed** state, making them good candidates for organic LED devices. Preliminary results in collaboration with M. Thompson[13] showed that, indeed, efficient blue OLED's can be manufactured. Further research, including incorporation into polymers, is in progress.

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