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New pyrrolopyridazine derivatives as blue organic luminophors

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Abstract—New pyrrolopyridazine derivatives were synthesized as potential blue organic luminophors. Three different classes of pyrrolopyridazine derivatives were made, for example, aryl groups directly connected to the core PPY (pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester) moiety, aryl groups connected to the PPY via a vinylene linker and aryl groups connected to the PPY via an acetylene linker. Their optical and electrochemical properties were productively compared. One of the derivatives **2** showed a relative quantum yield as high as 0.9. Compound **8** in the vinyl bridged pyrrolopyridazine series has been characterized by its X-ray crystal structure analysis.

1. Introduction

Since the discovery of a thin-film organic electroluminescent device by the team at Kodak,[1a] organic light emitting diodes (OLED) have become the most promising new optoelectronic devices for practical industrial applications. Electroluminescent thin films of organic molecules have been extensively investigated because of their low operating voltage, tunable red-green-blue output colors, high brightness, mechanical flexibility and ease of fabrication.[1b] Although polymeric as well as small organic molecules are well established electroluminescent materials used in fabricating the thin film devices, smaller organic units were realized to be advantageous with facile emission color control and the easy fabrication of multilayer devices.[2] Investigations on synthesizing new blue luminous materials for applications in electroluminescent (EL) display have attracted great attention recently, but there are very few single component deep blue- and pure red-emitting dyes.[2]

Recently, Wudl et al. reported pyrrolopyridazine derivatives as a new class of blue organic luminophors. They demonstrated the possibility of tuning colors and energy levels by modifying the structures of these luminophors.[3] Herein, we report the synthesis of new pyrrolopyridazine derivatives, along with the optical properties of these new compounds. To study the relationship between optical properties and the effect of conjugation and substitution, we systematically designed and synthesized a series of luminophors containing a core pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester moiety. Three different classes of pyrrolopyridazine derivatives were synthesized, for example, aryl groups directly connected to the core PPY (pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester) moiety, aryl groups connected to the PPY via a vinylene linker and aryl groups connected to the PPY via an acetylene linker. Their comparative optical and electrochemical properties were investigated to study the effect of extended conjugation. Compound **8** in the vinyl bridged pyrrolopyridazine series has been characterized by its X-ray crystal structure analysis.

2. Results and discussion

2.1. Synthesis

For the synthesis of various pyrrolopyridazine derivatives, 3-iodopyridazine (**26**) was synthesized from 3,6-dichloropyridazine in four steps following the procedures reported elsewhere. The treatment of 3,6-dichloropyridazine with sodium iodide gave 3,6-diiodopyridazine, which was then reacted with hydrazine to give 6-iodo-3-pyridazinylhydrazine. This hydrazine was reacted with mercuric oxide to give 3-iodopyridazine.[4,5]

Keywords: Pyrrolopyridazine; Fluorescence; Luminophor; Blue luminophor; Sonogashira coupling; Blue shift; Red shift.
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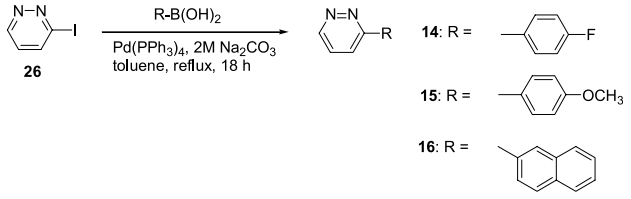
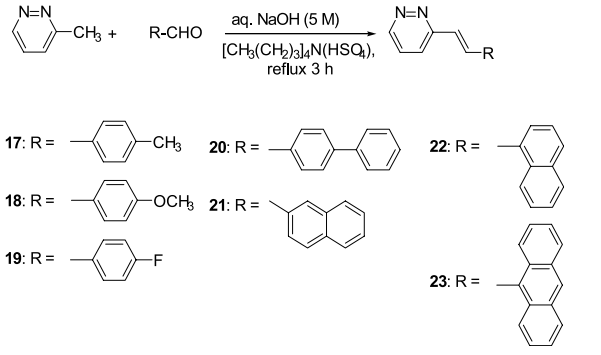
The 3-arylpyridazine derivatives (**14–16**) were synthesized as shown in Scheme 1 by modifying the literature procedures.[6] Synthesis of aryl pyridazines via Suzuki cross-coupling is a single step and more convenient than the reported method for the preparation of compound (**15**).[7] On the other hand, 3-(2-arylvinyl)pyridazine derivatives were also obtained in one step by the treatment of aromatic aldehydes with 3-methylpyridazine using the reported methodology (Scheme 2).[8a]



Scheme 1. Synthesis of 3-arylpyridazines (**14–16**) via Suzuki cross-coupling.



Scheme 2. Synthesis of 3-(2-aryl-vinyl)pyridazines (**17–23**).

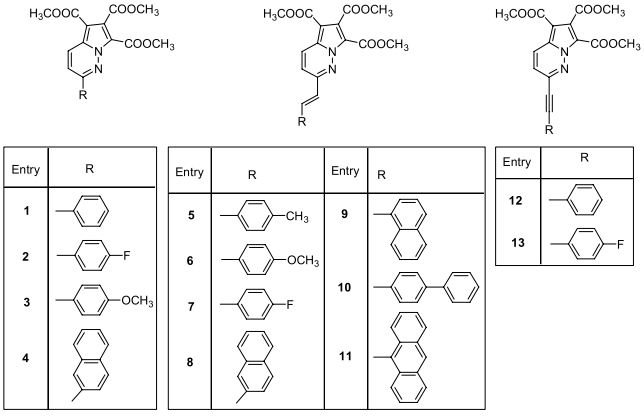
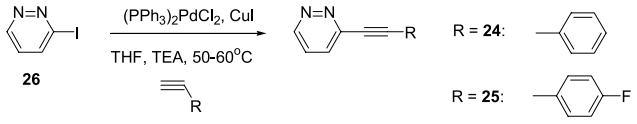


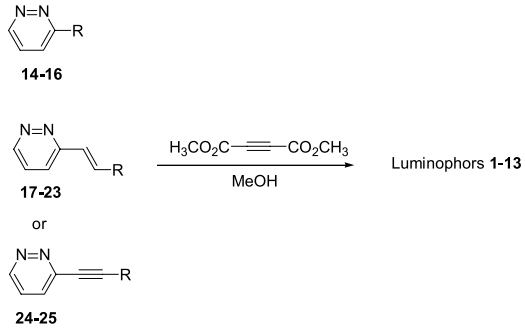
Figure 1. Luminophors synthesized (**1–13**).

The structural data of the compounds **18** and **19** were in a good agreement with the earlier reports.[8b,c] Sonogashira coupling[9] between 3-iodopyridazine and terminal alkynes in the presence of $(PPh_3)_2PdCl_2$ and CuI in basic condition yielded 3-arylethynylpyridazines (Scheme 3).

The luminescent pyrrolopyridazine derivatives (**1–13**) were prepared (Fig. 1) in one step via 1,3-dipolar cycloaddition reaction between 3-substituted pyridazines (aryl/vinylaryl/ethynylaryl) and dimethyl acetylenedicarboxylate (DMAD) in methanol at a low temperature as depicted in Scheme 4, by modifying the reported procedure.[3b]



Scheme 3. 3-Arylethynylpyridazines (**24–25**) from Sonogashira reaction.



Scheme 4. Synthesis of luminophors (**1–13**).

2.2. X-ray crystal structure

A single crystal of compound **8** was grown from a CH_2Cl_2/MeOH solution and was characterized using X-ray

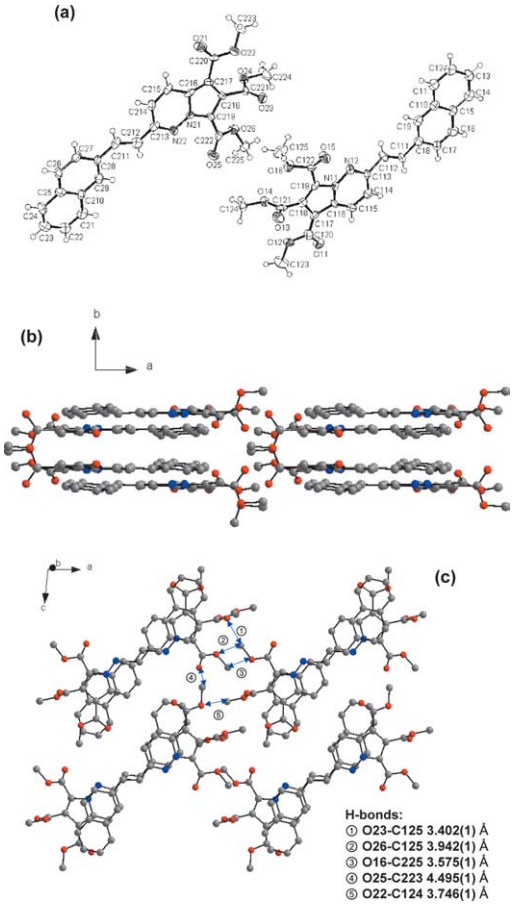


Figure 2. X-ray structure of **8** (in (b) and (c), blue: N and red: O).

crystallography. Figure 2 shows the π stacking of compound **8** in a head to tail mode. The molecules stack along the *b* axis and the average distance between the π planes was 3.66 Å (Fig. 2b). Hydrogen bonds between the oxygens and methyl group in the ester moieties were observed and the distances between these oxygens and carbons are in the range of 3.40–4.49 Å (Fig. 2c).

2.3. Optical properties

The absorption and fluorescence spectra of compounds **2**–**13** were recorded in DMSO, methanol, methylene chloride, and hexane solutions at room temperature. The relative quantum yields were determined using 9,10-diphenylanthracene in degassed hexane ($\Phi = 0.96$). The optical data for compound **1** was taken from the literature.[3]

As expected and illustrated in the cyclic voltametry data, significant red shifts were observed in UV as well as fluorescence for the compounds **6** and **7** being extended conjugation. Figure 3 exhibits that the second absorption bands of **7** (315 nm) and **6** (331 nm) are red-shifted compared with those of **2** (280 nm) and **3** (300 nm). These red shifts of compounds **6** and **7** were probably due to ground state stabilization arising from extended conjugation via vinylene linkage. The first absorption bands were assigned at around 350 nm for compound **1**, **2** and **3**. However, for compounds **5**, **6** and **7**, the absorption maximum around 320–340 nm was used as the excitation wavelength since the first absorption bands were overlapped with the second absorption bands. On the other hand, the compounds **12** and **13** bearing acetylene linkage displayed red shifts in their UV as well as fluorescence spectra (Figs 3 & 4) compared to those of **1** and **2**.

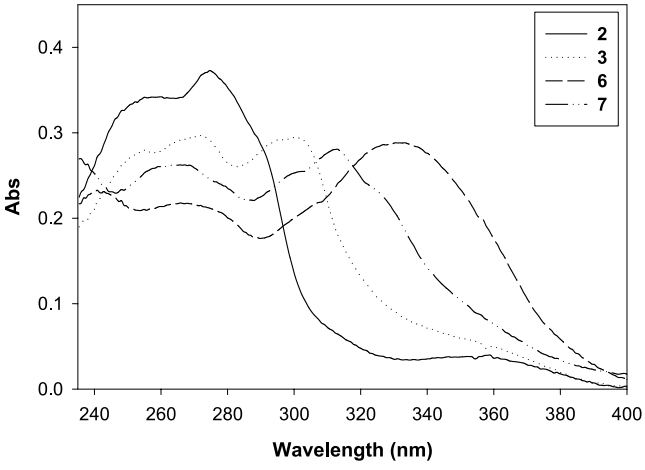


Figure 3. The UV absorption spectra of compounds **2**, **3**, **6** and **7** in dichloromethane.

Compound **2** displayed a relatively higher quantum yield values when compared to the compounds bearing extended conjugation moiety. As shown in Table 1, there was a dramatic difference in quantum yield between compounds **2** (90%) and **7** (27%). The compounds bearing aryl groups via a vinylene linkage (**5**–**11**) show relatively low fluorescent quantum yields. It is likely that the significant differences in these compounds resulted from the stronger electronic perturbation in the ground and excited states due to the extended conjugation provided by the vinylene linkage. On the other hand, the compounds **12** (44%) and **13** (52%) bearing acetylene linkage displayed better fluorescent quantum yield compared to those of compounds bearing vinylene linkage. The introduction of a fluorine atom on the aryl ring increased the fluorescent quantum yields in both cases (compound **2** vs **1** or **3**; compound **7** vs **5** or **6**; compound **13** vs **12**) (Table 1). Compounds with vinylene and acetylene spacers induced red shifts in their fluorescence λ_{max} by 5 and 18 nm, respectively. It is likely that extended conjugation enhances the intersystem crossing (ISC) rates thereby resulting in quenched emission for compounds **3**–**13**. The theory also gains significance in view that compounds **2**, **7** and **13** have relative higher quantum yield values when compared with the others in the corresponding series.

2.4. Electrochemical studies

Table 2 summarizes the cyclic voltametric data in CH_3CN containing 0.1 M tetrabutylammonium hexafluorophosphate with the scan rate of 0.1 V/s. The potential values of the first redox wave in the scan of both the positive and negative direction are included in Table 2 along with some multiple redox waves, which are known to be related to the HOMO and LUMO energy levels. Overall, as the interpretation of the electrochemical properties is similar to that reported by Wudl et al.[3a] their assignments can be applied to these compounds.

Compounds **1**–**3** show the oxidation potential at 1.89, 1.90, and 1.76 V, respectively, and the reduction potential at −1.59, −1.58, and −1.63 V, respectively, which indicates that the substituent group on the 2-phenyl group connected to PPY (pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester) affects the HOMO level slightly and the LUMO level trivially. Compounds **5**–**7** also showed a similar tendency. Compounds **1** and **4** exhibited almost the same oxidation and reduction potential, which implies that both the HOMO and LUMO level are not changed when the 2-phenyl or 2-naphthyl moiety are connected to PPY.

A relative large difference in the oxidation potential was found by a comparison of the (**2**, **7**), (**3**, **6**), and (**4**, **8**) couples, respectively. In compounds **2**, **3**, and **4**, the aromatic moieties were linked directly to position 2 of PPY while the same aromatic moieties were linked to position 2 of PPY via a vinylene linkage in compounds **7**, **6**, and **8**, respectively. Interestingly, compounds **7**, **6**, and **8** had lower oxidation potential than the corresponding compounds **2**, **3**, and **4** by 0.45, 0.37, and 0.24 V, respectively, while their reduction potentials remained similar within 0.08 V compared with their corresponding compounds. This indicates that such elongated conjugation at the position 2 in PPY mainly affects the HOMO as shown in compounds **1**–**3** and **5**–**7** (Table 2). It is likely that a vinylene linkage at position 2 affects the HOMO level but affects the LUMO level to a much lesser extent, however, no further effort to explain this phenomenon is made in this study. Figure 5 shows the cyclic voltammograms of compounds **6** and **3**, where an improvement in the reversibility in the reduction

Table 1. λ_{max} (nm) of absorption spectra, λ_{max} (nm) of fluorescence spectra, and relative efficiency (%) of compound **1–13**

Compd	Absorption (λ_{max}/nm)				Fluorescence [(λ_{max}/nm) (quantum efficiency (%))]			
	DMSO	MeOH	CH_2Cl_2	Hexane	DMSO	MeOH	CH_2Cl_2	Hexane
1	348[a]	346[a]	350[a]	351[a]	446 (81)[a]	443 (73)[a]	444 (68)[a]	442 (75)[a]
2	352	347	348	[b]	449 (90)	444 (85)	443 (79)	[b]
3	348	348	349	[b]	445 (51)	439 (43)	441 (41)	[b]
4	348	348	340	[b]	450 (39)	445 (22)	444 (31)	[b]
5	321	316	330	305	450 (9)	452 (8)	447 (7)	443 (27)
6	331	335	328	[b]	463 (5)	466 (8)	438 (9)	[b]
7	315	312	313	[b]	454 (27)	451 (25)	448 (23)	[b]
8	329	323	328	[b]	460 (9)	451 (12)	448 (8)	[b]
9	343	341	335	[b]	453 (8)	453 (11)	450 (12)	[b]
10	337	335	332	[b]	441 (6)	455 (10)	453 (8)	[b]
11	394	389	373	389	510 (5)	490 (8)	505 (13)	472 (28)
12	356	[b]	358	[b]	467 (44)	[b]	456 (41)	[b]
13	359	[b]	358	[b]	467 (52)	[b]	453 (50)	[b]

[a] Taken from Ref. 3a.
[b] Insoluble.

Table 2. Cyclic voltammetric data for **1–8**, **11**, and anthracene[a]

Compd	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**11**	Anthracene
E_{ox}[b]	1.89/…[c]	1.90/…[c]	1.76/…[c]	1.90/…[c]	1.69/…[c]	1.39/…[c]	1.46/…[c]	1.66/…[c]	1.29/…[c]	1.28/…[c]
E_{red}[b]	−1.59/ −1.67	−1.58/ −1.66	−1.63/ −1.71	−1.57/ −1.64	−1.54/ −1.61	−1.55/ −1.63	−1.54/ −1.61	−1.48/…[d]	−1.45/…[d]	−1.92/ −1.99

[a] CVs were recorded at room temperature in CH_3CN/0.1 M $TBAPF_6$.
[b] E_{ox} and E_{red} are represented as E_{pa}/E_{pc} (V vs SCE), respectively.
[c] It is hard to measure the value because of lack of reversibility.
[d] It is hard to determine the exact value due to multiple redox waves.

0/−1 couple at $E=-1.59$ V of compound **6** compared with that of **3** are easily observed at a scan rate (ν) of 0.1 V/s (Fig. 5a and b). A 5-fold increase in the scan rate leads to an enhancement in the reversibility in the reduction process of compound **3** (Fig. 5c). Judging from the i_{pc}/i_{pa} ratio depending on ν, the half-life of the anion radical of compound **3** was approximately 1 s.[10] Such kinetic stabilization phenomena of the radical anion of compound **7** and **8** in the CVs depending on ν were also observed by comparing them with compounds **2** and **4**, respectively. The estimated half-life of the anion radical of compounds **2** and **4** was >1 s and a few seconds, respectively. The above redox potential measurement data were parallel with the optical measurement data, that is, the UV λ_{max} of compounds **7** and **6** is longer than that of compounds **2** and **3** by 35 and 31 nm, respectively.

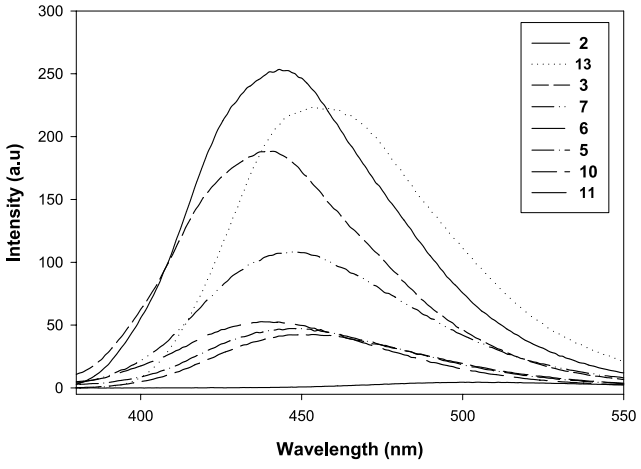


Figure 4. Fluorescence spectra of compounds **2**, **3**, **5**, **6**, **7**, **10**, **11** and **13** in dichloromethane.

Compound **11** had the lowest oxidation potential among compounds **5**, **8**, and **11**. The origin of this could be understood partially by observing the cyclic voltammograms of compound **11** and anthracene (An) in Figure 6. Anthracene itself shows an oxidation potential of $E=1.28$ V and a reduction potential of −1.95 V (Fig. 6b). The oxidation potential is retained in compound **11** (Fig. 6a). However, the reduction potential is in the similar range with the other species shown in Table 2. This suggests that the tuning of the HOMO level is possible via the covalent bonding of the substituent that has the lower oxidation potential. But it is also possible to lose some extent of the electrochemical reversibility as shown in Figure 6.

3. Conclusion

Twelve new luminescent pyrrolopyridazine pyrrolo[1,2-*b*] pyridazine-5,6,7-tricarboxylic acid trimethyl esters were synthesized from less expensive reagents and under mild reaction conditions. In this systematic investigation, three different classes of target molecules were synthesized, for example, aryl groups directly connected to the core PPY (pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester) moiety, aryl groups connected to the PPY via a vinylene linker and aryl groups connected to the PPY via an acetylene linker. Their optical and electrochemical properties were studied in detail and compared. One of these compounds was characterized by X-ray structure analysis. In particular, it was observed that, compounds bearing fluorine substituent were showing relatively higher quantum

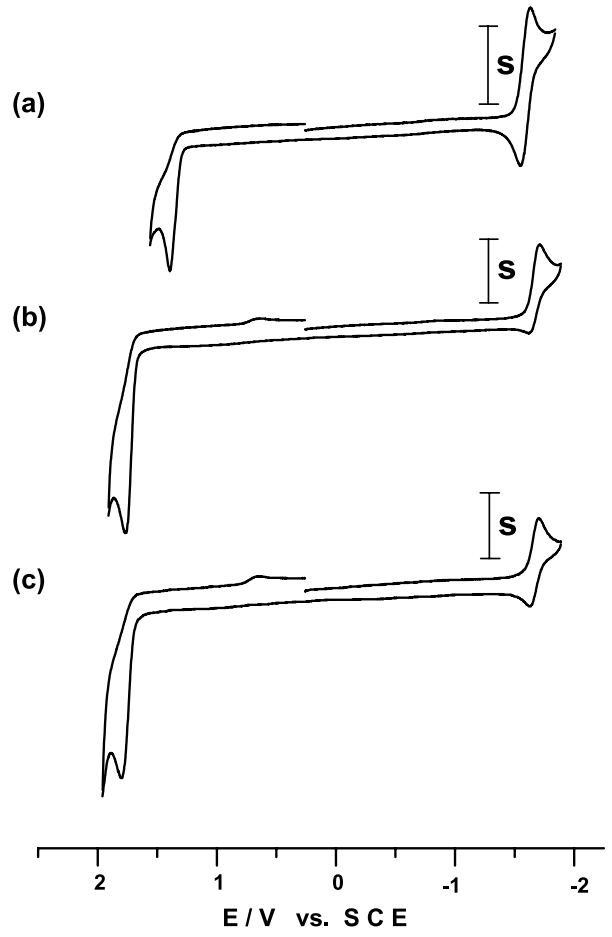


Figure 5. Cyclic voltammograms of 1 mM **6** (a) and **3** (b, c) at a glassy carbon disk electrode with negative scan direction; in CH_3CN containing 0.1 M $TBAPF_6$; $v=0.1$ V/s (a, b) or 0.5 V/s (c). The scale bar represents 20 (a, b) and 50 μA (c), respectively.

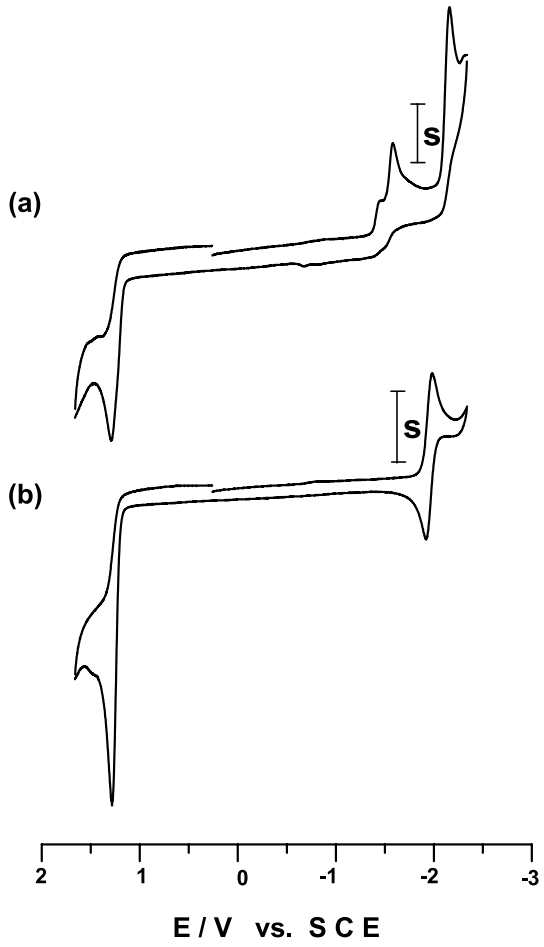


Figure 6. Cyclic voltammograms of 1 mM **11** (a) and anthracene (b) at a glassy carbon disk electrode with negative scan direction; in CH_3CN containing 0.1 M $TBAPF_6$; $v=0.1$ V/s. The scale bar represents 10 (a) and 20 μA (b), respectively.

yield values in comparison with the other substituents in that series. The possibility of tuning the colors and energy levels of these luminophors was studied by extending the π-system at the position 2 of the core PPY through a proper modification such as vinylene or acetylene linkage. We also demonstrated that pyrrolopyridazine systems bearing an aryl groups with a suitable electron donor/withdrawing groups can result in push–pull effects on the overall photochemical properties of the luminophors.

4. Experimental

4.1. General methods

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel 60 (230–400 mesh ASTM; Merck). Thin-layer chromatography (TLC) was carried out using Merck 60 F_{254} plates with a thickness of 0.25 mm. Preparative TLC was performed using Merck 60 F_{254} plates with a thickness of 1 mm.

Melting points were measured using a Büchi 530 melting point apparatus, and are uncorrected. ^{1}H NMR spectra were recorded using Bruker 250 MHz spectrometer with TMS as the internal standard. Fluorescence measurements were made on a RF-5301 PC Spectrofluorophotometer with excitation at 367 nm; both emission and excitation slit widths were 5 nm. Mass spectra were obtained using JMS-700 Mstation spectrometers.

3-Phenylpyridazine was purchased from Spec, Rijswijk, The Netherlands. Compound **1** was prepared following the published procedure.[3] Preparation of recently reported compound **15** involves four steps.[7] But in our case we could able to get the same in one step via Suzuki coupling. The vinyl derivatives such as **18** and **19** were confirmed with reported results.[8]

4.2. General procedure for the preparation of 2-arylpyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (1–4) and 2-(2-arylvinyl)pyrrolo[1,2-*b*]-pyridazine-5,6,7-tricarboxylic acid trimethyl ester (5–11)

Dimethyl acetylenedicarboxylate (DMAD) (1 mmol) was added dropwise to a stirring solution of 3-arylpyridazine/3-(2-arylvinyl)pyridazine (0.5 mmol) in anhydrous methanol (2 mL) at 0 °C. Stirring was continued at 0 °C for 1.5 h and then at ambient temperature 5 h. Solvents were

evaporated under reduced pressure and added 2 mL of methanol. Solid separated slowly on standing the solution at room temperature for 2–4 h. It was filtered, washed with small amount of methanol and dried in vacuo. The crude product was crystallized in dichloromethane/methanol. Yields were ranging from 20 to 30%.

4.2.1. 2-(4-Fluorophenyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (2). Mp 194–195 °C; ^{1}H NMR ($CDCl_3$) δ 8.66 (d, 1H, J=9.5 Hz), 8.12 (dd, 2H), 7.58 (d, 1H, J=9.5 Hz), 7.19 (m, 2H), 4.03 (s, 3H), 3.98 (s, 3H), 3.94 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.4, 165.6, 162.8, 162.4, 158.7, 152.2, 131.0, 130.9, 130.6, 129.3, 129.1, 128.8, 128.5, 117.4, 116.5, 116.1, 102.8, 53.1, 52.2, 51.9; HRMS (FAB) m/z=387.0982 $(M+H)^+$, calcd for $C_{19}H_{16}FN_2O_6$=387.0992.

4.2.2. 2-(4-Methoxyphenyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (3). Mp 157–158 °C; ^{1}H NMR ($CDCl_3$) δ 8.57 (d, 1H, J=9.6 Hz), 8.02 (d, 2H, J=8.8 Hz), 7.55 (d, 1H, J=9.6 Hz), 7.01 (d, 2H, J=2.7 Hz), 4.02 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.8, 162.8, 161.7, 158.8, 152.7, 130.6, 128.6, 128.1, 127.2, 117.3, 116.2, 114.6, 102.6, 55.4, 53.0, 52.1, 51.9; HRMS (FAB) m/z=399.1199 $(M+H)^+$, calcd for $C_{20}H_{19}N_2O_7$=399.1192. Anal. Calcd for $C_{20}H_{18}N_2O_7$: C, 60.30; H, 4.55; N, 7.03. Found: C, 60.03; H, 4.36; N, 7.26.

4.2.3. 2-Naphthalen-2-yl-pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (4). Mp 180–182 °C; ^{1}H NMR ($CDCl_3$) δ 8.58 (d, 1H, J=9.5 Hz), 8.41 (s, 1H), 8.25 (dd, 1H, J_1=8.6 Hz and J_2=1.5 Hz), 7.94 (d, 2H, J=8.3 Hz), 7.86 (m, 1H), 7.70 (d, 1H, J=9.5 Hz), 7.53 (m, 2H), 4.04 (s, 3H), 3.98 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.7, 162.8, 158.7, 152.8, 134.3, 133.1, 132.0, 130.7, 129.1, 128.8, 128.7, 128.4, 128.1, 127.8, 127.5, 127.2, 126.7, 123.9, 117.4, 116.5, 102.7, 53.0, 52.2, 51.9; HRMS (FAB) m/z=419.1243 $(M+H)^+$, calcd for $C_{23}H_{19}N_2O_6$=419.1243.

4.2.4. 2-(2-*p*-Tolylvinyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (5). Mp 240–241 °C; ^{1}H NMR ($CDCl_3$) δ 8.53 (d, 1H, J=9.6 Hz), 7.43–7.68 (m, 4H), 7.12–7.26 (m, 3H), 4.01 (s, 3H), 3.96 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.7, 162.8, 158.8, 152.8, 139.7, 136.4, 132.8, 130.9, 129.7, 128.5, 127.6, 127.4, 123.5, 117.3, 116.0, 102.9, 53.0, 52.2, 51.9, 21.4; MS (FAB) m/z=409.3 $(M+H)^+$. Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.87; H, 4.97; N, 6.74.

4.2.5. 2-[2-(4-Methoxyphenyl)vinyl]pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (6). Mp 216–217 °C; ^{1}H NMR ($CDCl_3$) δ 8.52 (d, 1H, J=9.6 Hz), 7.55 (d, 2H, J=8.8 Hz), 7.48 (d, 1H, J=9.6 Hz), 7.43 (d, 1H, J=2.7 Hz), 7.13 (d, 1H, J=16.5 Hz), 6.94 (d, 2H, J=8.8 Hz), 4.01 (s, 3H), 3.96 (s, 3H), 3.91 (s, 3H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.8, 162.8, 160.7, 158.8, 152.9, 136.0, 130.9, 128.9, 128.4, 128.3, 127.5, 122.2, 117.2, 116.0, 114.4, 102.8, 55.4, 53.0, 52.2, 51.9; MS (FAB) m/z=425.3 $(M+H)^+$. Anal. Calcd for $C_{22}H_{20}N_2O_7$: C, 62.26; H, 4.75; N, 6.60. Found: C, 62.41; H, 4.79; N, 6.59.

4.2.6. 2-[2-(4-Fluorophenyl)vinyl]pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (7). Mp 189–190 °C; ^{1}H NMR ($CDCl_3$) δ 8.58 (d, 1H, J=9.5 Hz), 7.61–7.02 (m, 8H), 4.01 (s, 3H), 3.95 (s, 3H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.7, 165.4, 162.8, 159.70, 157.4, 152.4, 135.1, 131.8, 131.4, 130.9, 127.8, 124.3, 117.3, 116.2, 115.9, 114.8, 103.0, 53.0, 52.0, 51.8; MS (FAB) m/z=413.3 $(M+H)^+$. Anal. Calcd for $C_{21}H_{17}FN_2O_6$: C, 61.16; H, 4.16; N, 6.79. Found: C, 61.01; H, 4.26; N, 6.64.

4.2.7. 2-(2-Naphthalen-2-yl-vinyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (8). Mp 191–192 °C; ^{1}H NMR ($CDCl_3$) δ 8.53 (d, 1H, J=10.0 Hz), 7.95 (s, 1H), 7.85–7.77 (m, 4H), 7.68 (d, 1H, J=17.5 Hz), 7.52–7.43 (m, 3H), 7.38 (d, 1H, J=17.5 Hz), 4.02 (s, 3H), 3.97 (s, 3H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.7, 162.7, 158.7, 152.5, 136.4, 133.8, 133.4, 133.0, 130.8, 128.7, 128.3, 127.8, 127.6, 126.8, 126.6, 124.6, 123.4, 117.3, 116.0, 102.9, 53.0, 52.2, 51.9; MS (FAB) m/z=445.3 $(M+H)^+$. Anal. Calcd for $C_{25}H_{20}N_2O_6$: C, 67.56; H, 4.54; N, 6.30. Found: C, 67.68; H, 4.46; N, 6.32.

4.2.8. 2-(2-Naphthalen-1-yl-vinyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (9). Mp 192–193 °C; ^{1}H NMR ($CDCl_3$) δ 8.57 (d, 1H, J=9.5 Hz), 8.35 (d, 1H, J=16.2 Hz), 8.22 (d, 1H, J=8.0 Hz), 7.85–7.89 (m, 3H), 7.52–7.59 (m, 4H), 7.32 (d, 1H, J=16.2 Hz), 4.03 (s, 3H), 3.97 (s, 3H), 3.93 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.7, 162.8, 158.8, 152.6, 133.7, 133.3, 132.9, 131.3, 130.9, 129.7, 128.8, 128.7, 127.7, 127.1, 126.7, 126.1, 125.7, 124.6, 123.3, 117.4, 116.2, 102.9, 53.0, 52.2, 51.9; MS (FAB) m/z=445.3 $(M+H)^+$. Anal. Calcd for $C_{25}H_{20}N_2O_6$: C, 67.56; H, 4.54; N, 6.30. Found: C, 67.45; H, 4.54; N, 6.26.

4.2.9. 2-(2-Biphenyl-4-yl-vinyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (10). Mp 236–237 °C; ^{1}H NMR ($CDCl_3$) δ 8.56 (d, 1H, J=9.5 Hz), 7.59–7.71 (m, 6H), 7.52 (d, 1H, J=6.4 Hz), 7.34–7.49 (m, 4H), 7.26 (d, 1H), 4.01 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.7, 162.8, 158.7, 152.6, 142.2, 140.3, 135.9, 134.5, 130.9, 128.9, 128.6, 127.9, 127.7, 127.6, 127.5, 127.0, 124.4, 117.3, 116.0, 102.9, 53.0, 52.2, 51.9; MS (FAB) m/z=471.3 $(M+H)^+$. Anal. Calcd for $C_{27}H_{22}N_2O_6$: C, 68.93; H, 4.71; N, 5.95. Found: C, 68.85; H, 4.78; N, 5.92.

4.2.10. 2-(2-Anthracen-9-yl-vinyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (11). Mp 209–210 °C; ^{1}H NMR ($CDCl_3$) δ 8.65 (d, 1H, J=9.5 Hz), 8.44 (d, 1H, J=16.7 Hz), 8.43 (s, 1H), 8.31 (m, 2H), 8.03 (m, 2H), 7.62 (d, 1H, J=9.6 Hz), 7.50 (m, 4H), 7.16 (d, 1H, J=16.7 Hz), 4.03 (s, 3H), 3.94 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 178.7, 177.0, 173.8, 165.7, 162.8, 158.8, 152.1, 151.5, 133.4, 132.8, 131.4, 131.0, 130.4, 129.5, 128.9, 128.8, 128.0, 127.9, 126.5, 126.2, 125.7, 125.4, 125.3, 53.1, 52.2, 51.9; HRMS (FAB) m/z=495.1531 $(M+H)^+$, calcd for $C_{29}H_{23}N_2O_6$=495.1556.

4.3. General procedure for the preparation of 2-aryl-ethynyl-pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (12–13)

Dimethyl acetylenedicarboxylate (DMAD) (1 mmol) was added dropwise to a stirring solution of 3-arylethynyl-pyridazine (0.5 mmol) in anhydrous methanol (6 mL) at 0 °C. Stirring was continued at 0 °C for 1.5 h and then at ambient temperature 24 h. Solvents were evaporated under vacuum and the residue, which contains tarry impurities was eluted on silica gel column using hexane + ethyl acetate 7:3. It was again crystallized in methanol with trace amount of dichloromethane. Yields were ranging from 15 to 20%.

4.3.1. 2-Phenylethynylpyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (12). Mp 188–189 °C; ^{1}H NMR ($CDCl_3$) δ 8.60 (d, 1H, J=9.4 Hz), 7.66–7.62 (m, 2H), 7.45–7.36 (m, 3H), 7.30 (d, 1H, J=10.00 Hz), 4.02 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.4, 162.5, 158.5, 140.8, 132.3, 130.4, 129.9, 129.0, 128.5, 127.7, 121.2, 117.6, 103.2, 93.9, 84.9, 53.0, 52.4, 52.0; HRMS (FAB) m/z=393.1098 $(M+H)^+$, calcd for $C_{21}H_{17}N_2O_6$=393.1087. Anal. Calcd for $C_{21}H_{16}N_2O_6$: C, 64.28; H, 4.11; N, 7.14. Found: C, 64.26; H, 4.14; N, 7.40.

4.3.2. 2-(4-Fluorophenylethynyl)pyrrolo[1,2-*b*]pyridazine-5,6,7-tricarboxylic acid trimethyl ester (13). Mp 167–168 °C; ^{1}H NMR ($CDCl_3$) δ 8.61 (d, 1H, J=10 Hz), 7.67–7.59 (m, 2H), 7.29 (d, 1H, J=10 Hz), 7.14–7.08 (m, 2H), 4.02 (s, 3H), 3.97 (s, 3H), 3.92 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 165.1, 162.5, 161.4, 158.5, 140.7, 134.4, 134.3, 130.4, 129.1, 127.8, 121.1, 117.6, 117.3, 117.2, 116.2, 115.8, 103.3, 92.8, 84.7, 53.1, 52.4, 52.0; HRMS (FAB) m/z=411.1007 $(M+H)^+$, calcd for $C_{21}H_{16}FN_2O_6$= 411.0992. Anal. Calcd for $C_{21}H_{15}FN_2O_6$: C, 61.47; H, 3.68; N, 6.83. Found: C, 61.62; H, 3.64; N, 7.00.

4.4. General procedure for the preparation 3-aryl-pyridazines via Suzuki cross-coupling (14–16)

These compounds were prepared according to a modified literature method.[6] A mixture of 3-iodopyridazine (2.42 mmol), arylboronic acid (3.64 mmol), $Pd(PPh_3)_4$ (0.075 mmol), toluene (20 mL) and Na_2CO_3 (2.6 mL, 2 M) was flushed with N_2 for 5 min under stirring. The reaction mixture was heated at 120 °C for 18–24 h under a N_2 atmosphere. After cooling to room temperature the solvents were evaporated to dryness under reduced pressure. EtOAc (80 mL) was added and the suspension was placed in an ultrasonic bath for 5 min. The mixture was filtered, washed the residue thoroughly with EtOAc (~40 mL) and the filtrate evaporated under reduced pressure to dryness. The residue was purified by flash column chromatography on silica gel using EtOAc.

4.4.1. 3-(4-Fluorophenyl)pyridazine (14). Mp 122–123 °C; ^{1}H NMR ($CDCl_3$) δ 9.15 (dd, 1H, J_1=4.9 Hz and J_2=1.6 Hz), 8.03–8.11 (m, 2H), 7.83 (dd, 1H, J_1=8.7 Hz and J_2=1.6 Hz), 7.54 (dd, 1H, J_1=8.6 Hz and J_2=4.8 Hz), 7.16–7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 166.4, 162.5, 158.7, 150.2, 132.8, 129.4, 129.2, 127.0, 123.8, 116.5, 116.2; HRMS (EI) m/z=174.0588 $(M)^+$, calcd for $C_{10}H_7FN_2$=174.0593.

4.4.2. 3-(4-Methoxyphenyl)pyridazine (15). Mp 107–108 °C; ^{1}H NMR ($CDCl_3$) δ 9.10 (dd, 1H, J_1=4.8 Hz and J_2=1.6 Hz), 8.03–8.08 (m, 2H), 7.80 (dd, 1H, J_1=8.7 Hz and J_2=1.6 Hz), 7.47 (dd, 1H, J_1=8.7 Hz and J_2=4.9 Hz), 7.02–7.08 (m, 2H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 161.7, 159.4, 149.9, 129.16, 129.0, 128.8, 127.1, 123.6, 114.8, 114.3, 55.8; HRMS (EI) m/z=186.0789 $(M)^+$, calcd for $C_{11}H_{10}N_2O$=186.0793. Anal. Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.0. Found: C, 70.71; H, 5.49; N, 15.18.

4.4.3. 3-Naphthalen-2-yl-pyridazine (16). Mp 173–174 °C; ^{1}H NMR ($CDCl_3$) δ 9.20 (dd, 1H, J_1=4.8 Hz and J_2=1.6 Hz), 8.58 (d, 1H, J=102 Hz), 8.24 (dd, 1H, J_1= 8.6 Hz and J_2=1.8 Hz), 8.05–7.99 (m, 4H), 7.62–7.55 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 159.4, 150.0, 134.1, 133.6, 133.4, 128.9, 128.8, 127.8, 127.2, 127.0, 126.8, 126.6, 124.2, 124.1; MS (FAB) m/z=206.2 $(M+H)^+$.

4.5. General procedure for the preparation of 3-(2-aryl-vinyl)pyridazine derivatives (17–23)

These compounds were prepared according to a modified literature method.[8a] Aromatic aldehyde (10 mmol) was slowly added over a period of 5 h to a mixture of the 3-methylpyridazine (10 mmol) and tetrabutylammonium hydrogen sulfate (1 mmol) in a hot aqueous solution (50 mL) of sodium hydroxide (5 M) under stirring. The reflux was maintained for 3 h. After cooling overnight the separated solid was filtered, washed with small amount of cold water and dried. The crude product was purified by eluting on silica gel column using ethyl acetate/hexane 1:1. Yields were ranging from 40 to 60%.

4.5.1. 3-(2-*p*-Tolyl-vinyl)pyridazine (17). Mp 121–122 °C; ^{1}H NMR ($CDCl_3$) δ 9.03 (dd, 1H, J_1=4.8 Hz and J_2= 1.6 Hz), 7.72–7.58 (m, 2H), 7.51 (s, 1H), 7.48 (s, 1H), 7.44 (dd, 1H, J_1=8.6 Hz, J_2=4.9 Hz), 7.31 (d, 1H, J=10.7 Hz), 7.19 (s, 1H), 7.14 (s, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 158.4, 149.5, 139.3, 135.1, 134.8, 133.2, 129.6, 129.2, 127.7, 127.3, 127.0, 126.3, 124.7, 123.9, 123.8, 21.4; MS (FAB) m/z=197.3 $(M+H)^+$.

4.5.2. 3-(2-Biphenyl-4-yl-vinyl)pyridazine (20). Mp 186–187 °C; ^{1}H NMR ($CDCl_3$) δ 9.05 (dd, 1H, J_1=4.8 Hz and J_2=1.5 Hz), 7.74 (d, 1H, J=16.5 Hz), 7.61–7.66 (m, 7H), 7.36–7.49 (m, 4H), 7.13 (d, 1H, J=16.5 Hz); ^{13}C NMR ($CDCl_3$) δ 158.3, 149.6, 141.8, 140.4, 134.9, 134.7, 128.9, 127.8, 127.6, 127.5, 127.3, 127.0, 126.4, 125.1, 123.9; MS (FAB) m/z=259.3 $(M+H)^+$.

4.5.3. 3-(2-Naphthalen-2-yl-vinyl)-pyridazine (21). Mp 166–167 °C; ^{1}H NMR ($CDCl_3$) δ 9.05 (dd, 1H, J_1=4.9 Hz and J_2=1.6 Hz), 7.95 (s, 1H), 7.79–7.88 (m, 5H), 7.66 (d, 1H, J=8.4 Hz), 7.42–7.51 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 158.3, 149.7, 135.2, 133.7, 133.5, 133.4, 128.6, 128.5, 128.3, 127.8, 126.7, 126.6, 126.5, 125.5, 124.0, 123.4; MS (FAB) m/z=233.3 $(M+H)^+$. Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.59; H, 5.25; N, 11.87.

4.5.4. 3-(2-Naphthalen-1-yl-vinyl)-pyridazine (22). Mp 82–83 °C; ^{1}H NMR ($CDCl_3$) δ 9.05 (dd, 1H, J_1=4.9 Hz and J_2=1.6 Hz), 8.54 (d, 1H, J=16.5 Hz), 8.29 (d, 1H, J= 7.6 Hz), 7.82–7.86 (m, 3H), 7.68 (dd, 1H, J_1=8.6 Hz and

J_2=1.6 Hz), 7.43–7.56 (m, 4H), 7.40 (d, 1H, J=16.5 Hz); ^{13}C NMR ($CDCl_3$) δ 158.2, 149.7, 133.7, 133.5, 132.2, 131.4, 129.4, 128.7, 127.7, 126.5, 126.4, 126.1, 125.6, 124.4, 124.3, 123.6; MS (FAB) m/z=233.3 $(M+H)^+$. Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.56; H, 5.27; N, 11.99.

4.5.5. 3-(2-Anthracen-9-yl-vinyl)-pyridazine (23). Mp 172–173 °C; ^{1}H NMR ($CDCl_3$) δ 9.15 (dd, 1H, J_1=4.9 Hz and J_2=1.6 Hz), 8.66 (d, 1H, J=16.5 Hz), 8.45 (s, 1H), 8.36 (m, 2H), 8.03 (m, 2H), 7.72 (dd, 1H, J_1=8.6 Hz and J_2=1.6 Hz), 7.45–7.53 (m, 5H), 7.21 (d, 1H, J=16.5 Hz); ^{13}C NMR ($CDCl_3$) δ 157.8, 150.0, 133.6, 132.2, 131.4, 131.1, 129.6, 128.8, 127.5, 126.6, 125.9, 125.5, 125.3, 124.4; MS (FAB) m/z=283.3 $(M+H)^+$. Anal. Calcd for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 84.88; H, 5.01; N, 9.73.

4.6. General procedure for the preparation of 3-(2-arylethynyl)pyridazines via Sonogashira coupling (24–25)

These compounds were prepared according to a modified literature method.[9] The suspension of iodopyridazine (2.91 mmol), $Pd(PPh_3)_2Cl_2$ (0.06 mmol) and copper(I) iodide (0.30 mmol), in dry THF (12 mL) and dry triethylamine (12 mL) was stirred at room temperature under argon atmosphere for 15 min. To this suspension the terminal alkyne (3.50 mmol), dissolved in dry THF (5 mL) was added. The reaction mixture was stirred for 5 h at 55–60 °C. The solvents were removed in vacuo, and the residue was dissolved in chloroform (50 mL) and filtered out the solids. The chloroform solution was washed with water (4×10 mL each), dried over Na_2SO_4 and evaporated the solvents in vacuo. The residue was purified on silica column using hexane+ethyl acetate 3:7 solvent mixture. Yields were ranging from 60 to 70%.

4.6.1. 3-Phenylethynylpyridazine (24). Mp 72–73 °C; ^{1}H NMR ($CDCl_3$) δ 9.14 (d, 1H, J=3.93 Hz), 7.71–7.61 (m, 3H), 7.42–7.38 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 149.3, 148.4, 132.6, 132.2, 129.5, 129.6, 128.5, 125.7, 121.5, 93.9, 85.7; HRMS (EI) m/z=180.0692 $(M)^+$, calcd for $C_{12}H_8N_2$= 180.0687. Anal. Calcd for $C_{12}H_8N_2$: C, 79.98; H, 4.47; N, 15.55. Found: C, 79.88; H, 4.38; N, 15.60.

4.6.2. 3-(4-Fluorophenylethynyl)pyridazine (25). Mp 129–130 °C; ^{1}H NMR ($CDCl_3$) δ 9.18 (s, 1H), 7.66–7.52 (m, 4H), 7.19–7.06 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 165.3, 161.3, 149.3, 134.3, 134.2, 129.5, 125.7, 117.6, 117.5, 116.1, 115.8, 92.8, 85.5; HRMS (EI) m/z=198.0611 $(M)^+$, calcd for $C_{12}H_7FN_2$=198.0593.

4.7. Cyclic voltammetry (CV) measurement

All the electrochemical measurements were carried out in acetonitrile solutions containing 1 mM electroactive compound and 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$), respectively, at room temperature using a BAS 100B electrochemical analyzer. A glassy carbon disk (diameter 3 mm) and platinum wire were used as working and counter electrodes. The reference electrode used was $Ag|AgNO_3$ (0.1 M), and all the potential values were calibrated versus the ferrocene/ferrocenium ($Fc|Fc^+$) redox couple. The potential values shown in this text were then corrected to the saturated calomel electrode (SCE) on the basis of $Fc|Fc^+$ redox potential as 0.44 V versus SCE,[3a,10–12] unless otherwise specified. The potential scan rate was varied from 0.1 to 1 V/s to check the reversibility of redox waves. E_{pa} (anodic peak potential) and E_{pc} (cathodic peak potential) were shown for redox waves.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.08.038

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