Substituent-Dependence of Photophysical Properties of *trans*-2-Styrylpyridazin-3(2*H*)-ones

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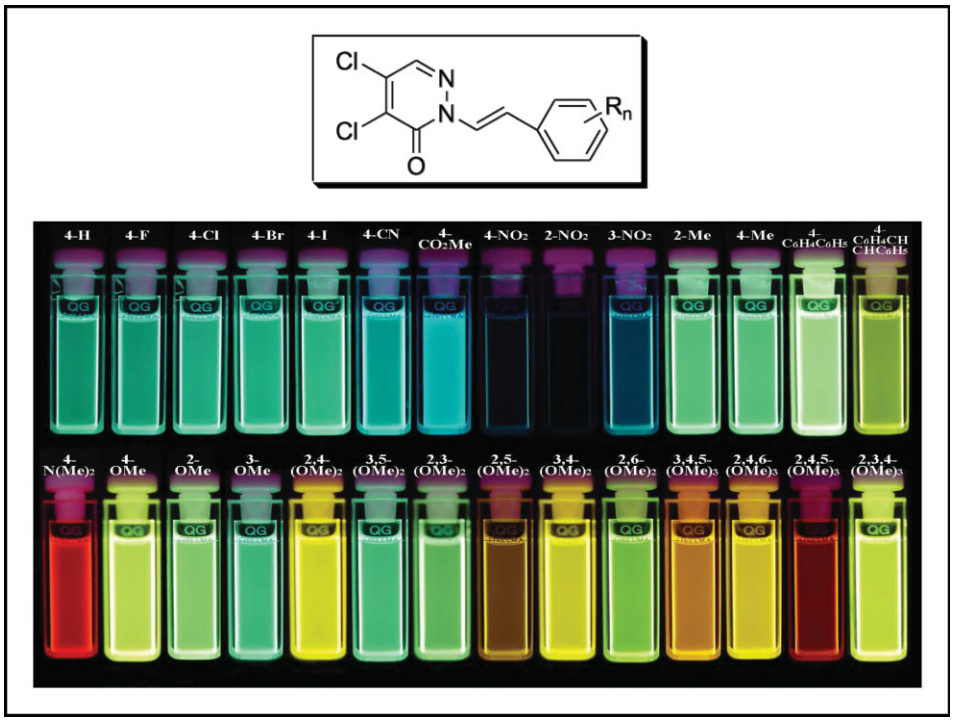

The photophysical behavior of *trans*-2-styrylpyridazin-3(2*H*)-ones **3** strongly depend on the number and the position of substituents in the phenyl ring in THF, methylene chloride, acetonitrile and methanol. The absorption spectra of **3** containing the electron-donating substituents at the *para*-position show the red-shift, whereas the spectra of **3** containing the electron-withdrawing substituents show the blue-shift. For the *trans*-2-(*p*-substituted-styryl)pyridazin-3(2*H*)-ones **3b–3h** and **3k–3o**, the magnitude of the solvatochromic shifts and the shape of the fluorescence spectra depend on the number and/or the position of substituents in benzene ring. The emission maximum of *trans*-2-styrylpyridazin-3(2*H*)-ones involving the electron-donating group is larger than one of *trans*-2-styrylpyridazin-3(2*H*)-ones involving the electron-withdrawing group in the phenyl ring. The magnitude of the emission maximum is roughly parallel to the relative electron-withdrawing ability of the substituents of the phenyl ring.

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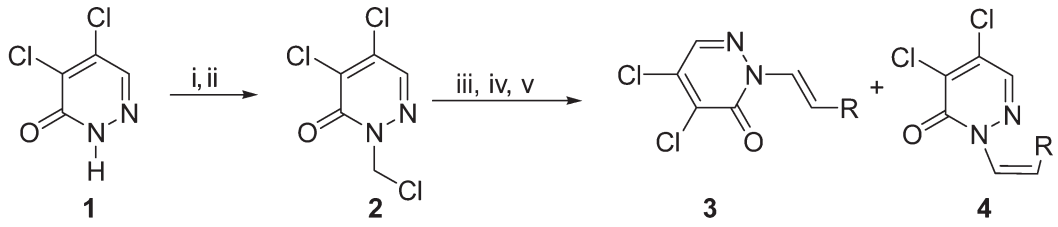
INTRODUCTION

The creation of luminescent molecules is an active field of research in supramolecular chemistry [1–8]. The chemosensors also have the advantages of possessing high sensitivity and selectivity, as well as providing on-line and real time analysis [9–25]. However, the development of a useful fluorescent probes is difficult because of the lack of flexible design strategies. The design also is largely empirical at present. Thus, the tuning of the photophysical properties introducing the substituent is very useful in this field.

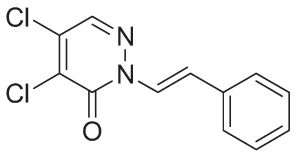
Organic molecules that contain styryl moiety are an important fluorescent class and show a number of attractive photophysical and electro-optical properties

Scheme 1



[20,26–36]. The substitution of phenyl ring in stilbene with a heterocyclic acceptor (pyridine) significantly affected the photophysical and photochemical behavior, because of the involvement of the (nπ^*) state [28,37]. According to the literature [26,28,38–40], the photophysical behavior and the torsional barrier of *trans*-stilbene derivatives depend on the nature of substituents and/or solvent polarity. Therefore, the fluorescent property could be tunable by the introduction of a suitable substituent on the phenyl ring in stilbene.

Recently, we reported the synthesis the photophysical properties and the potentiality for the application as spectroscopic or fluorescent probes for some *N*-styrylazinones containing Het-N═CH═CH─Ar (Het = hetetocycle) moiety [41]. The heterocycle-dependent photophysical behavior of *trans*-2-(2-arylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones was also reported [42]. Because of the utility of C─Cl bond in 4,5-dichloropyridazin-3(2*H*)-one ring for the derivatization, we selected *trans*-4,5-dichloro-2-styrylpyridazin-3(2*H*)-one as parent fluorescence molecules, and studied on the dependence on the substituents of the phenyl ring about the photophysical properties of **3**. Here we report on the synthesis and tuning of the photophysical properties of some *trans*-2-styrylpyridazin-3(2*H*)-ones **3**.



trans-4,5-Dichloro-2-styrylpyridazin-3(2*H*)-one

RESULTS AND DISCUSSION

Synthesis. Various *trans*-2-(substituted-styryl)pyridazin-3(2*H*)-ones **3** were prepared according to the literature [41] using the synthetic sequence outlined in Scheme 1. Compound **2** [43] was reacted with benzaldehyde after treating potassium iodide and then triphenylphosphine to give *trans*-isomers **3** as the major product. Although *cis*-isomers **4** were formed as the minor product, it was not isolated since the *cis*-isomer changed slowly to *trans*-isomer at room temperature during the workup. The structures of **3** were established by NMR, IR and elemental analyses.

Absorption spectra. All the *trans*-2-styrylpyridazin-3(2*H*)-ones **3a**–**3aa** displays a single intense long wavelength absorption band in methylene chloride, tetrahydrofuran, acetonitrile and methanol. The absorption maxima are reported in Table 2. In general, the absorption maximum of **3** depends on substituent of *para*-position in benzene ring; that is, the electron-donating group shows the red-shift (e.g., **3o** vs. **3a**), whereas the electron-withdrawing group shows the blue-shift (e.g., **3f** vs. **3a**).

The substituted position also affects about absorption maximum of nitrophenyl derivatives, that is, the 4-nitro: the red-shift (**3h** *vs*. **3a**); the 2-nitro or 3-nitro group: the blue-shift (**3i/3j** *vs*. **3a**). The **3b** show the blue-shift in the absorption maximum due to the 4-fluoro group.

On the other hand, we investigated the dependence of an absorption spectrum on the position and the number of methoxy group. All methoxy compounds showed the red-shift compared with **3a** in the absorption spectrum. The magnitude of the bathochromic effect of 2-methoxy and 4-methoxy compounds (**3o** and **3p**) is larger than that of 3-methoxy derivative (**3q**) (Table 2 entries 15–17). For the dimethoxy derivatives, the bathochromic effect of 2,4-, 2,5-, 2,6-, and 3,4-dimethoxy compounds (**3r**, **3u**, **3w**, **3v**) is also larger than one of 3,5-and 2,3-dimethoxy derivatives (**3s, 3t**) (Table 2 entries 18–23). All four trimethoxy derivatives (**3x–3aa**) show much larger the bathochromic effect than mono- and dimethoxy derivatives. Among four trimethoxy derivatives, the magnitude of the bathochromic shift for 2,4,5- and 2,4,6-trimethoxy compounds (**3y** and **3z**) is especially large (Table 2 entries 25 and 26).

Table 1

Synthesis of *trans*-**3** from **2**.

Entry		**3,** R	Yield (%)[a]	Entry		**3,** R	Yield (%)[a]
1	**a**	C_6H_5—	47	15	**o**	4-$MeOC_6H_4$—	46
2	**b**	4-FC_6H_4—	45	16	**p**	2-$MeOC_6H_4$—	45
3	**c**	4-ClC_6H_4—	44	17	**q**	3-$MeOC_6H_4$—	43
4	**d**	4-BrC_6H_4—	51	18	**r**	2,4-$(MeO)_2C_6H_3$	43
5	**e**	4-IC_6H_4—	42	19	**s**	3,5-$(MeO)_2C_6H_3$—	44
6	**f**	4-NCC_6H_4—	41	20	**t**	2,3-$(MeO)_2C_6H_3$—	41
7	**g**	4-$(MeO_2C)C_6H_4$—	49	21	**u**	2,5-$(MeO)_2C_6H_3$—	42
8	**h**	4-$NO_2C_6H_4$—	58	22	**v**	3,4-$(MeO)_2C_6H_3$—	41
9	**i**	2-$NO_2C_6H_4$—	49	23	**w**	2,6-$(MeO)_2C_6H_3$—	47
10	**j**	3-$NO_2C_6H_4$—	54	24	**x**	3,4,5-$(MeO)_3C_6H_3$—	45
11	**k**	4-MeC_6H_4—	65	25	**y**	2,4,6-$(MeO)_3C_6H_2$—	42
12	**l**	4-$(C_6H_5)C_6H_4$—	43	26	**z**	2,4,5-$(MeO)_3C_6H_2$—	38
13	**m**	4-$(C_6H_5CHCH)C_6H_4$—	41	27	**aa**	2,3,4-$(MeO)_3C_6H_2$—	39
14	**n**	4-$(Me)_2NC_6H_5$—	51				

[a] Isolated yield.

In addition, the absorption spectra of **3** show hypsochromic and hyperchromic effects (exception for **3l**, **3m**, **3o**, **3s**, **3u**, **3w**, and **3y-3aa**) in acetonitrile comparing with the spectra in methylene chloride. The absorption spectra of **3** show hypsochromic and hyperchromic effects (exception for **3b**, **3d**, **3g-3l**, **3n, 3r**, and **3z**) in methanol comparing with the spectra in methylene chloride. The absorption spectra of **3** show bathochromic effect (exception for **3h**, **3k**, **3m**, **3p**, **3r**, **3u**, **3v**, **3z**, and **3aa**) and hyperchromic effect (exception for **3c**, **3e**, **3o**,

Table 2

The absorption maxima (nm) for *trans*-2-(substituted-styryl)pyridazin-3(2*H*)-ones **3** at room temperature.[a]

		λ_{max} (ε)			
Entry	**3**	CH_2Cl_2	THF	CH_3CN	MeOH
1	**3a**	371 (8657)	371 (8799)	365 (10410)	366 (8254)
2	**3b**	370 (7935)	371 (8017)	361 (10117)	364 (8172)
3	**3c**	371 (8090)	371 (7236)	363 (10104)	365 (7429)
4	**3d**	370 (6919)	370 (8596)	365 (9874)	365 (8780)
5	**3e**	370 (8837)	373 (8763)	367 (10110)	367 (8629)
6	**3f**	362 (7941)	364 (8009)	359 (8587)	357 (7030)
7	**3g**	369 (9209)	370 (9954)	363 (9349)	363 (8511)
8	**3h**	373 (7004)	372 (9546)	370 (9369)	378 (7310)
9	**3i**	362 (7358)	365 (8901)	358 (7952)	358 (7612)
10	**3j**	356 (7036)	361 (8750)	356 (8813)	353 (9042)
11	**3k**	379 (9820)	379 (8010)	373 (8350)	374 (8570)
12	**3l**	384 (9594)	382 (4797)	374 (5285)	376 (6154)
13	**3m**	396 (8898)	390 (9427)	387 (7948)	390 (7055)
14	**3n**	373 (6264)	439 (8509)	432 (8589)	437 (8272)
15	**3o**	389 (8684)	389 (8314)	382 (7115)	382 (8610)
16	**3p**	383 (8382)	382 (8755)	373 (8920)	366 (8254)
17	**3q**	373 (8699)	374 (8232)	367 (9164)	366 (8649)
18	**3r**	401 (8670)	401 (8794)	394 (8844)	397 (8748)
19	**3s**	373 (8857)	374 (8653)	368 (8499)	369 (7211)
20	**3t**	373 (7366)	376 (8024)	367 (9517)	368 (7556)
21	**3u**	395 (8435)	394 (7464)	386 (8096)	387 (8172)
22	**3v**	399 (8775)	397 (8842)	388 (8833)	390 (8970)
23	**3w**	392 (9180)	393 (8327)	385 (7635)	387 (8717)
24	**3x**	386 (7788)	387 (8118)	378 (8655)	378 (7310)
25	**3y**	411 (9237)	414 (8056)	405 (8620)	410 (8728)
26	**3z**	415 (8930)	413 (8357)	407 (6915)	408 (8213)
27	**3aa**	393 (8844)	394 (9618)	384 (8396)	387 (8992)

[a] Data were collected from sample solution prepared under atmosphere without degassing or inert gas bubbling.

Table 3

Maxima of fluorescence (λ_f), fluorescence band half-width ($\Delta\nu_{1/2}$), 0,0 transition ($\lambda_{0,0}$), Stokes shifts ($\Delta\nu_{st}$), and quantum yields of 2-styryl-pyridazin-3(2*H*)-ones **3** in tetrahydrofuran, methylene chloride, methanol, and acetonitrile.[a]

Compound	Solvent	λ_f[b](nm)	$\Delta\nu_{st}$ (cm^{-1})[c]	$\lambda_{0,0}$ (nm)[d]	$\Delta\nu_{1/2}$ (cm^{-1})	Quantum yield (Φ)[e]
3a	THF	492(513)	6629	435	3451	0.18
	CH_2Cl_2	492	6608	434	3407	0.41
	MeOH	494	7096	431	3432	0.18
	CH_3CN	496 (519)	7335	431	3383	0.12
3b	THF	492 (501)	6645	435	3355	0.18
	CH_2Cl_2	491	6697	434	3396	0.27
	MeOH	496	7329	431	3431	0.20
	CH_3CN	494	7233	431	3375	0.11
3c	THF	496 (517)	6773	435	3384	0.33
	CH_2Cl_2	491	6603	435	3401	0.18
	MeOH	492 (516)	7051	431	3487	0.09
	CH_3CN	495 (517)	7223	431	3404	0.09
3d	THF	493	6650	436	3404	0.05
	CH_2Cl_2	487	6472	434	3416	0.08
	MeOH	495	7175	433	3496	0.02
	CH_3CN	495	7203	431	3378	0.01
3e	THF	491	6423	440	3335	0.24
	CH_2Cl_2	491	6640	438	3324	0.19
	MeOH	499	7225	436	3335	0.04
	CH_3CN	496 (513)	7053	434	3271	0.06
3f	THF	482	6726	427	3648	0.18
	CH_2Cl_2	475	6588	423	3751	0.41
	MeOH	476	7003	443	3717	0.18
	CH_3CN	485	7092	421	3787	0.12
3g	THF	485	6387	431	3594	0.18
	CH_2Cl_2	476	6310	431	3567	0.27
	MeOH	484	6866	426	3661	0.20
	CH_3CN	486	6951	428	3575	0.11
3h	THF	479	6019	429	3718	0.33
	CH_2Cl_2	467	5409	425	3591	0.18
	MeOH	482	6554	424	3932	0.09
	CH_3CN	471	5821	423	3747	0.09
3i	THF	478	6455	421	3844	0.05
	CH_2Cl_2	472	6454	417	3889	0.08
	MeOH	471	6702	415	3837	0.02
	CH_3CN	480	7023	412	4098	0.01
3j	THF	463	6141	416	4072	0.24
	CH_2Cl_2	471	6875	417	3774	0.19
	MeOH	485	7689	418	3816	0.04
	CH_3CN	477	7111	416	3865	0.06
3k	THF	502	6480	444	3122	0.55
	CH_2Cl_2	502	6320	446	3177	0.42
	MeOH	504	6913	442	3148	0.51
	CH_3CN	505	7044	441	3710	0.35
3l	THF	514	6757	453	2883	0.83
	CH_2Cl_2	514	6568	457	2862	0.46
	MeOH	519	7309	479	2854	0.83
	CH_3CN	521	7474	449	2820	0.84
3m	THF	529	6720	477	2425	0.32
	CH_2Cl_2	531	6420	476	2408	0.27
	MeOH	536	6984	508	3002	0.16
	CH_3CN	535	7320	470	2741	0.33
3n	THF	619	6624	545	2121	0.11
	CH_2Cl_2	618	10664	532	2168	0.13
	MeOH	621	6793	572	2665	–
	CH_3CN	641	7753	535	16816	0.01
3o	THF	526	6711	466	2431	0.75
	CH_2Cl_2	527	6747	466	2492	0.83
	MeOH	532	7415	467	2503	0.74
	CH_3CN	531	7373	462	2543	0.69

(*Continued*)

Table 3
(*Continued*)

Compound	Solvent	λ_f[b](nm)	$\Delta\nu_{st}$ (cm^{-1})[c]	$\lambda_{0,0}$ (nm)[d]	$\Delta\nu_{1/2}$ (cm^{-1})	Quantum yield (Φ)[e]
3p	THF	519	6910	455	2842	0.73
	CH_2Cl_2	519	6842	455	2457	0.78
	MeOH	523	7725	453	2797	0.81
	CH_3CN	523	7480	449	2742	0.64
3q	THF	500	6774	441	3220	0.46
	CH_2Cl_2	498	6745	440	3222	0.67
	MeOH	508	7544	438	3308	0.31
	CH_3CN	504	7423	436	3187	0.25
3r	THF	535	6260	484	2348	0.62
	CH_2Cl_2	537	6316	483	2400	0.85
	MeOH	540	6653	485	2816	0.30
	CH_3CN	541	7070	479	2755	0.52
3s	THF	505	6972	444	3189	0.39
	CH_2Cl_2	500	6847	442	3214	0.55
	MeOH	506	7374	438	3227	0.29
	CH_3CN	507	7541	437	4084	0.10
3t	THF	511	7043	444	3165	0.62
	CH_2Cl_2	513 (516)	7298	443	3148	0.77
	MeOH	507	7468	436	3386	0.04
	CH_3CN	514	7689	433	3307	0.02
3u	THF	536	6739	475	2716	0.21
	CH_2Cl_2	538	6729	476	2864	0.12
	MeOH	473	4709	438	4249	0.02
	CH_3CN	534	7332	433	6092	0.01
3v	THF	537	6581	482	2521	0.76
	CH_2Cl_2	536	6438	479	2491	0.78
	MeOH	544	7292	479	3082	0.17
	CH_3CN	541	7337	475	3047	0.24
3w	THF	524	6361	465	2602	0.95
	CH_2Cl_2	524	6441	467	2611	0.50
	MeOH	526	6862	465	2615	0.66
	CH_3CN	528	6991	461	2541	0.58
3x	THF	540	7355	475	3020	0.35
	CH_2Cl_2	546	7609	473	3091	0.35
	MeOH	573	9038	460	3614	0.03
	CH_3CN	574	8914	467	3409	0.15
3y	THF	537	5562	494	2390	0.69
	CH_2Cl_2	539	5808	495	2488	0.40
	MeOH	555	6372	497	2881	0.33
	CH_3CN	547	6863	490	2835	0.43
3z	THF	585	7104	509	2760	0.24
	CH_2Cl_2	585	7031	508	2857	0.16
	MeOH	538	5922	477	4155	–
	CH_3CN	601	8150	478	3878	0.01
3aa	THF	530	6513	472	2453	0.64
	CH_2Cl_2	532	6663	472	2426	0.91
	MeOH	535	7148	471	2614	0.18
	CH_3CN	535	7320	468	2623	0.55

[a] Fluorescence data were obtained from corrected spectra.
[b] The second vibronic band is given in parentheses.
[c] $\Delta\nu_{st} = \nu_{abs-} \nu_{f.}$
[d] The value of $\lambda_{0,0}$ was obtained from the intersection of normalized absorption and fluorescence spectra.
[e] Quantum yield of the emission is evaluated at 25°C, the quantum yield values is that relative to 9,10-diphenylanthracene (1.00×10^{-4} *M*) in acetonitrile (from 352 nm excitation wavelength, $\Phi = 0.95$).

3q, **3s**, **3u**, **3w**, and **3y**-**3aa**) in tetrahydrofuran comparing with the spectra in methylene chloride. However, the solvatochromic effect of these compounds is rather small, which indicate a small difference between the dipole moment of the Franck-Condon excited state and the ground state [44].

Emission spectra. The fluorescence maxima (λ_f), the half-bandwidth ($\Delta\nu_{1/2}$), the 0,0 transitions ($\lambda_{0,0}$), the

Stokes shift ($\Delta\nu_{st}$), and the fluorescence quantum yield (Φ) of all compounds **3** are reported in four solvents in Table 3. For the *trans*-2-(*p*-substituted-styryl)pyridazin-3(2*H*)-ones **3b–3h** and **3k–3o**, the magnitude of the solvatochromic shifts and the shape of the fluorescence spectra depend on the substituents in four solvents. In general, the emission maximum of **3** involving an electron-donating substituent is larger than one of **3** involving an electron-withdrawing. Among all *p*-substituted derivatives, compound **3n** shows the largest emission maximum and the lowest fluorescence efficiency in four solvents.

The magnitude of the emission maximum for *p*-substituted derivatives **3a–3h** and **3k–3o** is in the order **3n** (4-Me_2N) >**3m** (4-C_6H_5CHCH) >**3o** (4-MeO) >**3l** (4-C_6H) >**3k** (4-Me) >**3a** (4-H) >**3b** (4-F), **3c** (4-Cl), **3e** (4-I) >**3d** (4-Br) >**3g** (4-CO_2Me) >**3f** (4-CN) >**3h** (4-NO_2) in methylene chloride, **3n** (4-Me_2N) >**3m** (4-C_6H_5CHCH) >**3o** (4-MeO) >**3l** (4-C_6H_5) >**3k** (4-Me) >**3a** (4-H), **3e** (4-I) >**3d** (4-Br), **3c** (4-Cl) >**3b** (4-F) >**3g** (4-CO_2Me) >**3f** (4-CN) >**3h** (4-NO_2) in acetonitrile,**3n** (4-Me_2N) >**3m** (4-C_6H_5CHCH) >**3o** (4-MeO) >**3l** (4-C_6H_5) >**3k** (4-Me) >**3e** (4-I) >**3b** (4-F) >**3d** (4-Br) >**3a** (4-H) >**3c** (4-Cl) >**3g** (4-CO_2Me) >**3h** (4-NO_2) >**3f** (4-CN) in methanol and **3n** (4-Me_2N) >**3m** (4-C_6H_5CHCH) >**3o** (4-MeO) >**3l** (4-C_6H_5) >**3k** (4-Me) >**3c** (4-Cl) >**3d** (4-Br) >**3a** (4-H), **3b** (4-F) >**3e** (4-I) >**3g** (4-CO_2Me) >**3f** (4-CN) >**3h** (4-NO_2) in Tetrahydrofuran. The magnitude of the emission maximum for *p*-substituted derivatives is roughly parallel with the relative electron-withdrawing ability of the substitutents. According to the 0-0 transition energies (Table 3), the planar ^{1}t* (ICT) state of **3a** (4-H) is stabilized by the electron-donating substituents (e.g., **3k**, **3n**, and **3o**) but destabilized by the electron-withdrawing substituents (e.g., **3b**, **3f**, **3g**, and **3h**) [26,38]. The number and the position of the substituents on the phenyl ring and/or the solvents affected about the magnitude of fluorescence band half-width ($\Delta\nu_{1/2}$) of all derivatives. Fluorescence band half-width increases due to the electron-withdrawing groups, whereas one of derivatives containing the electron-donating groups decreases. All derivatives are strongly fluorescent in methylene chloride, but the values of Φ_f decrease in more polar solvents. It depends on the substituents of the phenyl ring. The quantum yields of **3f–3j** decrease due to the strong electron-withdrawing substituents, whereas one of **3b–3e** and **3k–3aa** increases due to halogen at the para-position (for **3b–3e**) and the electron-donating substituents (for **3k–3aa**).

According to the literatures [26,45], the energies of the fluorescence maxima of benzene derivatives correlate better with the Hammett σ^+ than with the σ constants. The relationship of the energies of the fluorescence maxima for **3** and the Hammett σ^+ shows in the Figure 2. In four solvents, a nice linear relationship can be observed for *p*-substituted derivatives **3e–3h, 3k**, and **3o** except for **3l**.

For the **3h** (4-NO_2), **3i** (2-NO_2), and **3j** (3-NO_2), the magnitude of the solvatochromic shifts and the shape of the fluorescence spectra (Fig. 1) depend on the substituted position. The magnitude of the emission maximum for **3h–3j** is in the order **3i** (2-NO_2) >**3j** (3-NO_2) >**3h** (4-NO_2) in methylene chloride and acetonitrile, **3j** (3-NO_2) >**3h** (4-NO_2) >**3i** (2-NO_2) in methanol and **3h** (4-NO_2) >**3i** (2-NO_2) >**3j** (3-NO_2) in THF. The magnitude of the quantum yields for **3h**, **3i**, and **3j** is in the order **3h** (4-NO_2) >**3j** (3-NO_2) >**3i** (2-NO_2). According 0-0 transition energies (Table 3), the stability of the planar ^{1}t* (ICT) state in the excited state for *trans*-2-(nitrostyryl)pyridazin-3(2*H*)-ones **3h-3j** depends on the substituted position of the nitro group and/or slightly the solvent. Among the *trans*-2-(*p*-substituted-styryl)pyridazin-3(2*H*)-ones, *p*-methoxy derivative **3o** shows the largest value of the emission maximum and the 0-0 transition energy in four solvents. Therefore, we have been investigated the dependence of the fluorescence spectra for mono-, di- and trimethoxystyryl derivatives on the position and the numbers of the methoxy group. Among the three monomethoxy derivatives, *p*-substituted derivative **3o** shows excellent emission maximum and the high fluorescence intensity in four solvents except for **3p** in methanol.

For the *trans*-2-(dimethoxystyryl)pyridazin-3(2*H*)-ones **3r-3w**, the emission maximum and the quantum yield depend very highly on the solvent and the substituted position (Table 3). Among six dimethoxy derivatives, compound **3v** [3,4-$(MeO)_2$] shows the highest quantum yield in tetrahydrofuran. For the *trans*-2-(trimethoxystyryl)pyridazin-3(2*H*)-ones **3x-3aa**, the number and the position of the methoxy group and/or the solvent affected about the magnitude of the solvatochromic shifts, the shape of the fluorescence spectra and the quantum yield.

In case of the *trans*-2-(methoxystyryl)pyridazin-3(2*H*)-ones **3o-3aa**, the magnitude of the solvatochromic shifts and the shape of the fluorescence spectra depend on the number and the substituted position of the methoxy group. These effects for the di- and trimethoxy derivatives **3r–3w, 3x–3aa** are larger than the monomethoxy derivatives **3p** and **3q** in polar solvents such as acetonitrile and methanol. Among the methoxy derivatives, the magnitude of the solvatochromic shifts and the shape of the fluorescence spectra for 2,5-dimethoxy derivative (**3u**) change dramatically in polar solvent such as methanol and acetonitrile. The magnitude of the fluorescence maxima for the trimethoxy derivatives **3x–3z** is larger than the magnitude of the mono- or dimethoxyphenyl derivatives **3p–3w** except for **3r**. In the case of

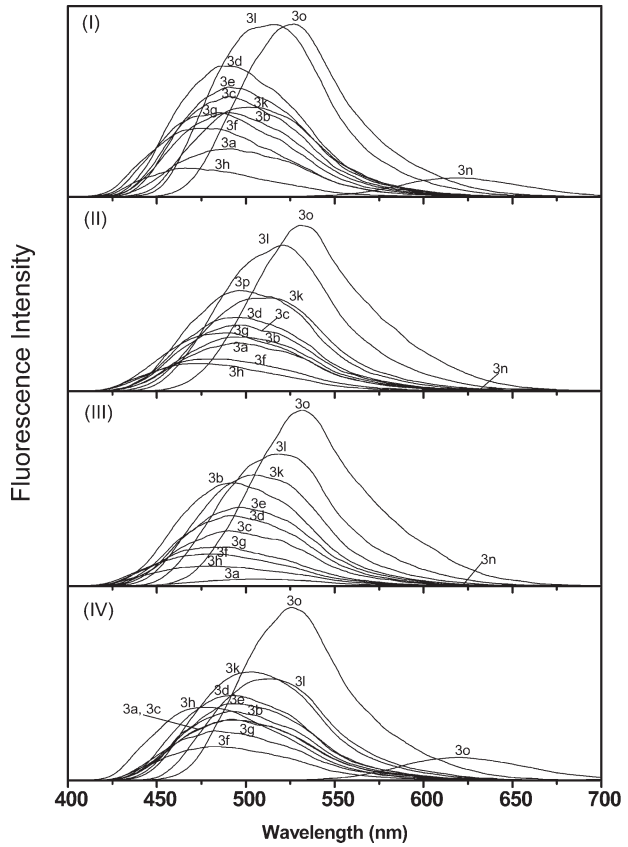


Figure 1. Normalized fluorescence spectra of *p*-substituted-2-styrylpyridazin-3(2*H*)-ones **3a-3h** and **3k-3o** in methylene chloride (I), acetonitrile (II), methanol (III), and tetrahydrofuran (IV).

dimethoxy derivatives **3r–3w**, the emission maximum strongly depends on the substitution position and the solvent. According to the 0-0 transition energies (Table 3), the stability of the planar ^{1}t* (ICT) state for all methoxy compounds **3o–3aa** depends also on the substituted position and the number of the methoxy group and slightly the solvent. Especially, the methoxy group at the *para*-position should be more stabilized, whereas the methoxy group at the *meta*-position should be more destabilized.

CONCLUSIONS

The substituent-dependent photophysical behavior of the 28 *trans*-2-styryl-4,5-dichloropyridazin-3(2*H*)-ones **3** as novel fluorescent molecules has been elucidated. According to our observation, the absorption maximum of compounds **3** depends on the substituent, the substituted position of the benzene ring and the solvent polarity. In addition, the intensity of absorption spectra for compounds **3** depends on the solvent polarity.

The magnitude of the solvatochromic shifts and the shape of the fluorescence spectra for **3** depend on the substituents. In general, the emission maxima of *trans*-2-styrylpyridazin-3(2*H*)-ones involving the electron-donating group is larger than that of *trans*-2-styrylpyridazin-3(2*H*)-ones involving the electron-withdrawing group. The magnitude of the emission maximum is roughly parallel with the relative electron-withdrawing ability of the substitutents. According to the 0-0 transition energies (Table 3), the planar ^{1}t* (ICT) state of the *trans*-2-(*p*-substituted-styryl)pyridazin-3(2*H*)-ones is stabilized by electron donating substituents but destabilized by electron withdrawing substituents. The number and the position of the substituents on the phenyl ring and/or the solvents also affected about the magnitude of fluorescence band half-width ($\Delta\nu_{1/2}$) of all derivatives. The quantum yield and fluorescent intensity of all compounds **3** depend on the number, the kind and the position of substituent in the phenyl ring and the solvent.

By introducing the suitable substituent in the phenyl ring of styryl moiety, *trans*-2-styrylpyridazin-3(2*H*)-ones **3** may use as a platform for fluorescence probes. These results may be a guide-line for the tuning of novel fluorescence molecules containing styryl moiety.

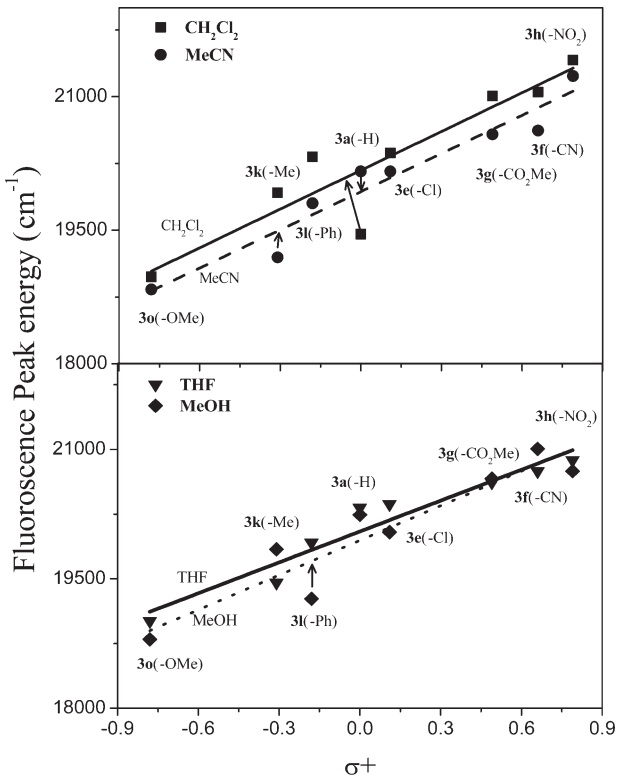


Figure 2. Correlation diagram of the energies of the fluorescence maxima against the Hammett σ^+ constants for *p*-substituted derivatives **3e-3h**, **3k**, **3l,** and **3o** in methylene chloride, tetrahydrofuran, methanol and acetonitrile.

Further dynamic, theoretical and application studies on these and the related systems would complement the current results and provide more insights into the photophysical behaviors of *trans-N*-styryl-nitrogen-heterocycles.

EXPERIMENTAL

General comments. Melting points were determined with a capillary apparatus and uncorrected. ^{1}H and ^{13} NMR spectra were recorded on a 300 MHz spectrometer with chemical shift values reported in δ units (ppm) relative to an internal standard TMS. IR spectra were obtained on an IR spectrophotometer. Elemental analyses were performed with a Perkin Elmer 240 C. Open-bed chromatography was carried out on silica gel (70–230 mesh, Merck) using gravity flow. The column was packed as slurries with the elution solvent.

Typical process of 4,5-dichloro-2-chloromethylpyridazin-3(2*H*)-one (2). A mixture of 4,5-dichloropyridazin-3(2*H*)-one (**1**, 60 g, 364 mmol) and distilled water (350 mL) was stirred for 10 min at room temperature. After adding formaldehyde solution (36%, 70 mL), the solution was refluxed for 1.5 h. After cooling to 5–10°C, the resulting precipitate was filtered, washed with cold water (0–5°C, 200 mL) and dried in air to give *N*-hydroxymethyl-4,5-dichloropyridazin-3(2*H*)-one. A solution of thionyl chloride (357 mmol) and dimethylformamide (360 mmol) in methylene chloride (50 mL) was added slowly to the mixture of *N*-hydroxymethyl-4,5-dichloropyridazin-3(2*H*)-one and methylene chloride (550 mL) for 30 min at room temperature with stirring. The resulting mixture was stirred for 2 h at room temperature. After cooling to 0°C, water (200 mL) was added slowly. The solution was neutralized to pH 6.7–7.4 by using saturated solution of $NaHCO_3$. The organic layer was separated and then dried over anhydrous magnesium sulfate. The resulting organic solution was evaporated under reduced pressure. The residue was washed with *n*-hexane (100 mL) to give 4,5-dichloro-2-chloromethylpyridazin-3(2*H*)-one (**2**, 71.2 g, 92%) as white color. White crystal (diethyl ether/*n*-hexane = 1:5, v/v). mp 69–70°C (lit. 43 mp 70–71°C). TLC (CH_2Cl_2) R_f = 0.65. IR (KBr) 3046, 2984, 1670, 1292, 1122, 964 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.83 (s, 2H), 7.88 ppm (s, 1H); ^{13}C NMR ($CDCl_3$) δ 58.40, 134.87, 137.23, 137.34, 155.58 ppm. Elemental analysis calcd. for $C_5H_3Cl_3N_2O$: C 28.13, H 1.42, N 13.12; found: C 28.10, H 1.41, N 13.09.

Typical process of synthesis for trans-4,5-dichloro-2-styrylpyridazin-3(2*H*)-one 3. A mixture of 2-chloromethyl-4,5-dichloropyridazin-3(2*H*)-one (**2**, 3 g, 14.055 mmol), sodium iodide (2.45 g, 14.76 mmol) and acetonitrile (50 mL) was refluxed for 10 h. After cooling to 30–40°C, triphenylphosphine (4.07 g, 15.51 mmol) was added to the reaction solution. The mixture was then refluxed for 6 h. After cooling to room temperature, the mixture was filtered by using Celite 545 and washed with methylene chloride (50 mL). The organic layer was concentrated under reduced pressure. After adding dichloromethane (100 mL) to the resulting mixture, the solution was stirred for 20 min. The solution was filtered and then concentrated under reduced pressure. After cooling to room temperature, the resulting precipitate was filtered, washed with excess diethyl ether and dried to give the product as thin yellow crystals. The product was used without further purification.

To a solution of crude ((4,5-dichloro-6-oxopyridazin-1(6*H*)-yl)methyl)triphenyl phosphonium iodide (8 g, 14.10 mmol) in acetonitrile (50 mL) was added benzaldehyde (1.5 g, 14.10 mmol) at 0–10°C. After stirring for 30 min, potassium *t*-butoxide (2.05 g, 95%, 17.21 mmol) was added. The resulting mixture was stirred for 2 h. The solution was concentrated under reduced pressure. After adding dichloromethane (100 mL) and then water (50 mL), the solution was stirred for 10 min, and neutralized to pH 6.7–7.4 by using saturated solution of $NaHCO_3$. The organic layer was separated and then dried over anhydrous magnesium sulfate. The resulting organic solution was evaporated under reduced pressure. The resulting residue was applied to the top of an open-bed silica gel. The column was eluted with methylene chloride/*n*-hexane (1:4, v/v). Fractions containing *trans*-isomer **3** were combined and evaporated to give pure *trans*-isomer **3**, respectively. The yields of all compounds **3** showed in Table 1.

(E)-4,5-Dichloro-2-styrylpyridazin-3(2H)-one (3a). Pale yellow crystal (diethyl ether:*n*-hexane = 1:2, v/v). mp 161–162°C. IR (KBr) 3108, 1664, 1592, 1300, 1238, 1134, 958, 898, 742, 696 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ 7.25 ∼ 7.38 (m, 4H), 7.47 ∼ 7.50 (m, 2H), 7.86 (s, 1H), 8.10 (d, J = 14.35 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 122.21, 124.13, 127.02, 128.49, 128.88, 134.49, 134.56, 135.94, 136.04, 154.68. Anal. Calcd. for $C_{12}H_8Cl_2N_2O$: C, 53.96; H, 3.02; N, 10.49. Found: C, 53.94; H, 3.01; N, 10.51.

(E)-4,5-Dichloro-2-(4-fluorostyryl)pyridazin-3(2H)-one (3b). Pale yellow crystal (methylene chloride). mp 158–159°C. IR (KBr) 3096, 1664, 1596, 1520, 1240, 1138, 960, 858, 748 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ 7.01 ∼ 7.09 (m, 2H), 7.24 (d, J = 14.58 Hz, 1H), 7.43 ∼ 7.48 (m, 2H), 7.87 (s, 1H), 8.04 (d, J = 14.34 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 115.78 (C—F), 116.07 (C—F), 121.02, 123.79 (C—F), 123.82 (C—F), 128.58 (C—F), 128.69 (C—F), 130.65 (C—F), 130.69 (C—F), 134.49, 136.00 (C—F), 136.11 (C—F), 154.66, 161.12, 164.42. Anal. Calcd. for $C_{12}H_7Cl_2FN_2O$: C, 50.55; H, 2.47; N, 9.83. Found: C, 50.56; H, 2.49; N, 9.84.

(E)-4,5-Dichloro-2-(4-chlorostyryl)pyridazin-3(2H)-one (3c). Light yellow crystal (methylene chloride). mp 177–178°C. IR (KBr) 3086, 1664, 1582, 1494, 1290, 960, 818 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ 7.21 (d, J = 14.36 Hz, 1H), 7.27 ∼ 7.34 (m, 2H), 7.38 ∼ 7.43 (m, 2H), 7.87 (s, 1H), 8.08 (d, J = 14.35 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 120.80, 124.37, 128.14, 129.06, 133.03, 134.16, 134.52, 136.06, 136.20, 154.63. Anal. Calcd. for $C_{12}H_7Cl_3N_2O$: C, 47.79; H, 2.34; N, 9.29. Found: C, 47.78; H, 2.33; N, 9.25.

(E)-2-(4-Bromostyryl)-4,5-dichloropyridazin-3(2H)-one (3d). Light yellow crystal (methylene chloride). mp 183–184°C. IR (KBr) 3100, 1676, 1594, 1496, 1300, 1138, 963, 902, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$); δ 7.20 (d, J = 14.35 Hz, 1H), 7.32 ∼ 7.36 (m, 2H), 7.46 ∼ 7.50 (m, 2H), 7.87 (s, 1H), 8.09 (d, J = 14.32 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 120.91, 122.37, 124.55, 128.43, 132.04, 133.55, 134.58, 136.05, 136.19, 154.63. Anal. Calcd. for $C_{12}H_7BrCl_2N_2O$: C, 41.65; H, 2.04; N, 8.10. Found: C, 41.66; H, 2.03; N, 8.08.

(E)-4,5-Dichloro-2-(4-iodostyryl)pyridazin-3(2H)-one (3e). Light yellow crystal (methylene chloride). mp 194–195°C. IR (KBr) 3122, 1680, 1596, 1298, 1234, 970, 900, 806, 760

cm^{-1}. ^1H NMR ($CDCl_3$); δ 7.17 ∼ 7.24 (m, 3H), 7.69 (d, J = 8.42 Hz, 2H), 7.88 (s, 1H), 8.12 (d, J = 14.37 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 99.94, 121.01, 124.54, 128.61, 134.09, 134.59, 136.09, 136.25, 137.99, 154.66. Anal. Calcd. for $C_{12}H_7ICl_2N_2O$: C, 36.67; H, 1.80; N, 7.13. Found: C, 36.65; H, 1.79; N, 7.10.

(E)-2-(4-Cyanostyryl)-4,5-dichloropyridazin-3(2H)-one (3f). Light yellow crystal (methylene chloride). mp 226–227°C. IR (KBr) 3092, 2998, 2226, 1665, 1584, 1294, 1136, 962, 947, 895, 864, 824, 556 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.81 (s, $2OCH_3$), 6.40 ∼ 6.42 (t, J = 2.19 Hz, 1H), 6.62 (d, J = 2.21 Hz, 2H), 7.27 (d, J = 14.37 Hz, 1H), 7.56–7.59 (m, 2H), 7.64 ∼ 7.67 (m, 2H), 7.91 (s, 1H), 8.19 (d, J = 14.38 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 111.57, 118.67, 119.97, 126.65, 127.38, 132.66, 134.83, 136.40, 136.62, 139.28, 154.73 ppm. Anal. Calcd. for $C_{13}H_7Cl_2N_3O$: C, 53.45; H, 2.42; N, 14.38. Found: C, 53.44; H, 2.42; N, 14.35.

(E)-4,5-Dichloro-2-(4-methoxycarbonylstyryl)pyridazin-3(2H)-one (3g). Light yellow crystal (methylene chloride). mp 212–214°C. IR(KBr) 3086, 3053, 3005, 2954, 1711, 1670, 1589, 1436, 1277, 1182, 112, 954 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.91 (s, OCH_3), 7.30 (d, J = 14.37 Hz, 1H), 7.54 ∼ 7.57 (m, 2H), 7.90 (s, 1H), 8.02 ∼ 8.05 (m, 2H), 8.20 (d, J = 14.35 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 52.17, 120.91, 125.82, 126.85, 129.77, 130.17, 134.70, 136.21, 136.38, 139.12, 154.72, 166.62 ppm. Anal. Calcd. for $C_{14}H_{10}Cl_2N_2O_3$: C, 51.72; H, 3.10; N, 8.62. Found: C, 51.71; H, 3.11; N, 8.60.

δ 7.32 (d, J = 14.38 Hz, 1H), 7.61 ∼ 7.65 (m, 2H), 7.92 (s, 1H), 8.20 ∼ 8.27 (m, 3H). ^{13}C NMR ($CDCl_3$); δ 119.47, 124.25, 127.19, 127.44, 134.86, 136.44, 136.69, 141.26, 147.32, 154.72. Anal. Calcd. for $C_{12}H_7Cl_2N_3O_3$: C, 46.18; H, 2.26; N, 13.46. Found: C, 46.16; H, 2.23; N, 13.47.

(E)-4,5-dichloro-2-(2-nitrostyryl)pyridazin-3(2H)-one (3i). Light yellow crystal (methylene chloride). mp 180–181°C. IR (KBr) 3108, 3068, 1668, 1596, 1520, 1340, 1300, 1280, 1146, 1122, 964, 950, 898, 738 cm^{-1}. ^1H NMR ($CDCl_3$); δ 7.45 ∼ 7.50 (m, 1H), 7.61 ∼ 7.66 (m, 1H), 7.70 ∼ 7.73 (m, 1H), 7.80 (d, J = 14.15 Hz, 1H), 7.93 (s, 1H), 8.00 ∼ 8.04 (m, 1H), 8.08 (d, J = 14.12 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 117.55, 125.07, 127.30, 128.59, 128.92, 130.38, 133.46, 134.72, 136.50, 136.64, 148.24, 154.79. Anal. Calcd. for $C_{12}H_7Cl_2N_3O_3$: C, 46.18; H, 2.26; N, 13.46. Found: C, 46.15; H, 2.24; N, 13.45.

δ 7.38 (d, J = 14.26 Hz, 1H), 7.59 ∼ 7.64 (m, 1H), 7.88 ∼ 7.91 (m, 1H), 8.08 ∼ 8.15 (m, 2H), 8.23 (d, J = 14.38 Hz, 1H), 8.34 (s, 1H). ^{13}C NMR ($CDCl_3$); δ 119.34, 121.89, 123.06, 127.12, 130.78, 133.35, 134.01, 136.36, 136.92, 137.69, 148.83, 154.75. Anal. Calcd. for $C_{12}H_7Cl_2N_3O_3$: C, 46.18; H, 2.26; N, 13.46. Found: C, 46.13; H, 2.23; N, 13.42.

(E)-4,5-dichloro-2-(4-methylstyryl)pyridazin-3(2H)-one (3k). Light yellow crystal (methylene chloride). mp 179–180°C. IR (KBr) 3150, 2976, 1688, 1610, 1322, 1158, 980, 920, 832, 758 cm^{-1}. ^1H NMR ($CDCl_3$); δ 2.35 (s, CH_3), 7.15 (d, J = 7.97 Hz, 2H), 7.25 (d, J = 14.34 Hz, 1H), 7.38 (d, J = 8.08 Hz, 2H), 7.85 (s, 1H), 8.08 (d, J = 14.32 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 21.28, 122.22, 123.37, 126.94, 129.57, 131.69, 134.37, 135.80, 135.91, 138.59. Anal. Calcd. for $C_{13}H_{10}Cl_2N_2O$: C, 55.54; H, 3.59; N, 9.96. Found: C, 55.51; H, 3.58; N, 9.93.

(E)-2-(2-(biphenyl-4-yl)vinyl)-4,5-dichloropyridazin-3(2H)-one (3l). Light yellow crystal (methylene chloride). mp 212–213°C. IR (KBr) 3088, 1680, 1614, 1140, 972, 838, 760 cm^{-1}. ^1H NMR ($CDCl_3$); δ 7.31 ∼ 7.38 (m, 2H), 7.42 ∼ 7.47 (m, 2H), 7.55 ∼ 7.63 (m, 6H), 7.92 (s, 1H), 8.16 (d, J = 14.31 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 121.99, 123.92, 126.84, 126.96, 127.43, 127.49, 128.77, 133.47, 134.34, 136.09, 136.26, 140.29, 141.25, 154.84. Anal. Calcd. for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; N, 8.16. Found: C, 62.98; H, 3.49; N, 8.15.

4,5-Dichloro-2-((E)-4-(E)-styrylstyryl)pyridazin-3(2H)-one (3m). Yellow crystal (methylene chloride). mp 224–225°C. IR (KBr) 3106, 1670, 1600, 1520, 1306, 1142, 968, 906, 820, 768, 698 cm^{-1}. ^1H NMR ($CDCl_3$); δ 7.12 (d, J = 4.01 Hz, 2H), 7.24 ∼ 7.29 (m, 2H), 7.32 ∼ 7.39 (m, 25H), 7.47 ∼ 7.54 (m, 6H), 7.89 (s, 1H), 8.15 (d, J = 14.32 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 121.87, 123.93, 126.58, 126.98, 127.39, 127.81, 128.02, 128.71, 129.28, 133.86, 134.38, 136.07, 137.18, 137.67. Anal. Calcd. for $C_{20}H_{14}Cl_2N_2O$: C, 65.06; H, 3.82; N, 7.59. Found: C, 65.05; H, 3.81; N, 7.57.

(E)-4,5-dichloro-2-(4-(dimethylamino)styryl)pyridazin-3(2H)-one (3n). Deep red crystal (methylene chloride). mp 130–132°C. IR (KBr) 3134, 2962, 1678, 1620, 1540, 1522, 1380, 1200, 1248, 1236, 964, 914 cm^{-1}. ^1H NMR ($CDCl_3$); δ 2.99 (s, 6H), 6.68 (d, J = 8.86 Hz, 2H), 7.22 (d, J = 14.26 Hz, 1H), 7.39 (d, J = 8.84 Hz, 2H), 7.85 (s, 1H), 7.98 (d, J = 14.24 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 40.30, 112.25, 120.51, 122.36, 122.75, 128.27, 133.89, 135.33, 135.60, 150.59, 154.52. Anal. Calcd. for $C_{14}H_{13}Cl_2N_3O$: C, 54.21; H, 4.22; N, 13.55. Found: C, 54.19; H, 4.20; N, 13.52.

(E)-4,5-dichloro-2-(4-methoxystyryl)pyridazin-3(2H)-one (3o). Yellow crystal (methylene chloride). mp 177–178°C. IR (KBr) 3062, 2944, 1666, 1614, 1590, 1522, 1308, 1258, 1196, 1140, 1038, 960, 906, 812, 744 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.83 (s, OCH_3), 6.87 ∼ 6.92 (m, 2H), 7.23 (d, J = 14.32 Hz, 1H), 7.41 ∼ 7.4 5 (m, 2H), 7.86 (s, 1H), 8.01 (d, J = 14.29 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.34, 114.32, 121.95, 122.36, 127.09, 128.37, 134.25, 135.74, 135.88, 154.62, 159.95. Anal. Calcd. for $C_{13}H_{10}Cl_2N_2O_2$: C, 52.55; H, 3.39; N, 9.43. Found: C, 52.52; H, 3.38; N, 9.40.

(E)-4,5-dichloro-2-(2-methoxystyryl)pyridazin-3(2H)-one (3p). Light yellow crystal (methylene chloride). mp 133–135°C. IR (KBr) 3132, 2987, 1684, 1600, 1500, 1478, 1300, 1260, 1140, 1042, 966, 760 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.91 (s, OCH_3), 6.91 ∼ 6.99 (m, 2H), 7.26 ∼ 7.31 (m, 1H), 7.48 ∼ 7.51 (m, 1H), 7.53 (d, J = 14.02 Hz, 1H), 7.89 (s, 1H), 8.87 (d, J = 14.32 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.50, 110.96, 118.06, 120.82, 123.42, 124.89, 128.31, 129.58, 134.33, 135.81, 135.90, 154.73, 157.45. Anal. Calcd. for $C_{13}H_{10}Cl_2N_2O_2$: C, 52.55; H, 3.39; N, 9.43. Found: C, 52.53; H, 3.37; N, 9.42.

(E)-4,5-dichloro-2-(3-methoxystyryl)pyridazin-3(2H)-one (3q). Pale yellow crystal (methylene chloride). mp 143–145°C. IR (KBr) 3126, 2988, 1676, 1602, 1504, 1478, 1264, 1134, 1046, 960, 900, 796, 740 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.84 (s, OCH_3), 6.84 ∼ 6.88 (m, 1H), 7.01 ∼ 7.02 (m, 1H), 7.08 ∼ 7.11 (m, 1H), 7.24 ∼ 7.31 (m, 2H), 7.89 (s, 1H), 8.12 (d, J = 14.32 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.33, 112.12, 114.34, 119.73, 122.15, 124.30, 129.88, 134.52, 135.92, 136.00, 136.12, 154.72, 159.95. Anal. Calcd. for $C_{13}H_{10}Cl_2N_2O_2$: C, 52.55; H, 3.39; N, 9.43. Found: C, 52.51; H, 3.38; N, 9.43.

(E)-4,5-dichloro-2-(2,4-dimethoxystyryl)pyridazin-3(2H)-one (3r). Yellow crystal (methylene chloride). mp 169–170°C. IR (KBr) 3066, 2982, 1660, 1620, 1592, 1516, 1460, 1298, 1280,

1216, 1156, 1134, 1040, 966, 898, 834 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.83 (s, OCH_3), 3.88 (s, OCH_3), 6.47 ~ 6.52 (m, 2H), 7.39 ~ 7.46 (m, 3H), 7.86 (s, 1H), 8.17 (d, J = 14.36 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.42, 55.51, 98.64, 105.08, 116.50, 118.10, 123.21, 129.30, 134.08, 135.52, 135.65, 154.62, 158.71, 161.23. Anal. Calcd. for $C_{14}H_{12}Cl_2N_2O_3$: C, 51.40; H, 3.70; N, 8.56. Found: C, 51.38; H, 3.70; N, 8.55.

δ 3.81 (s, 2OCH_3), 6.40 ~ 6.42 (t, J = 2.19 Hz, 1H), 6.62 (d, J = 2.21 Hz, 2H), 7.20 (d, J = 14.30 Hz, 1H), 7.86 (s, 1H), 8.09 (d, J = 14.29 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.43, 100.85, 104.99, 122.16, 124.40, 134.47, 135.98, 136.12, 136.41, 154.66, 161.03. Anal. Calcd. for $C_{14}H_{12}Cl_2N_2O_3$: C, 51.40; H, 3.70; N, 8.56. Found: C, 51.36; H, 3.69; N, 8.53.

(E)-4,5-dichloro-2-(2,3-dimethoxystyryl)pyridazin-3(2H)-one (3t). Yellow crystal (methylene chloride). mp 149–150°C. IR (KBr) 3066, 2962, 1674, 1592, 1482, 1276, 1076, 966 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.86 (s, OCH_3), 3.88 (s, OCH_3), 6.87 (dd, J = 1.28, 8.06 Hz, 1H), 7.05 (t, J = 7.96 Hz, 1H), 7.15 (dd, J = 1.27, 7.90 Hz, 1H), 7.54 (d, J = 14.46 Hz, 1H), 7.89 (s, 1H), 8.20 (d, J = 14.44 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.85, 60.96, 112.34, 117.20, 118.82, 124.27, 125.26, 128.72, 134.38, 135.95, 136.03, 147.46, 153.12, 154.75. Anal. Calcd. for $C_{14}H_{12}Cl_2N_2O_3$: C, 51.40; H, 3.70; N, 8.56. Found: C, 51.39; H, 3.68; N, 8.55.

(E)-4,5-dichloro-2-(2,5-dimethoxystyryl)pyridazin-3(2H)-one (3u). Yellow crystal (methylene chloride). mp 158–159°C. IR (KBr) 3068, 2974, 1664, 1594, 1506, 1300, 1228, 1046, 972, 896, 814, 742 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.80 (s, OCH_3), 3.85 (s, OCH_3), 6.83 (s, 2H), 7.02 (d, J = 1.93 Hz, 1H), 7.47 (d, J = 14.40 Hz, 1H), 7.86 (s, 1H), 8.23 (d, J = 14.38 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.80, 56.10, 112.20, 113.06, 114.83, 117.78, 124.10, 125.05, 134.29, 135.79, 135.90, 151.92, 153.63, 154.66. Anal. Calcd. for $C_{14}H_{12}Cl_2N_2O_3$: C, 51.40; H, 3.70; N, 8.56. Found: C, 51.38; H, 3.67; N, 8.53.

(E)-4,5-dichloro-2-(3,4-dimethoxystyryl)pyridazin-3(2H)-one (3v). Yellow crystal (methylene chloride). mp 163–164°C. IR (KBr) 3076, 2966, 1674, 1600, 1530, 1272, 1156, 1036, 958, 908, 814 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.90 (s, OCH_3), 3.93 (s, OCH_3), 6.84 (d, J = 7.97 Hz, 1H), 7.01 ~ 7.04 (m, 2H), 7.22 (d, J = 14.30 Hz, 1H), 7.85 (s, 1H), 8.01 (d, J = 14.28 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.94, 55.97, 109.01, 111.27, 120.81, 122.20, 122.48, 127.41, 134.25, 135.74, 135.90, 149.26, 149.67, 154.59. Anal. Calcd. for $C_{14}H_{12}Cl_2N_2O_3$: C, 51.40; H, 3.70; N, 8.56. Found: C, 51.39; H, 3.68; N, 8.55.

(E)-4,5-dichloro-2-(2,6-dimethoxystyryl)pyridazin-3(2H)-one (3w). Light yellow crystal (methylene chloride). mp 190°C. IR (KBr) 3060, 2964, 1660, 1590, 1480, 1258, 1136, 1106, 962, 776, 720 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.90 (s, 2OCH_3), 6.56 (d, J = 8.39 Hz, 2H), 7.19 (t, J = 8.37 Hz, 1H), 7.66 (d, J = 14.42 Hz, 1H), 7.86 (s, 1H), 8.63 (d, J = 14.42 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.84, 103.75, 111.99, 113.20, 126.91, 12916, 134.06, 135.53, 135.62, 154.73, 158.81. Anal. Calcd. for $C_{14}H_{12}Cl_2N_2O_3$: C, 51.40; H, 3.70; N, 8.56. Found: C, 51.37; H, 3.66; N, 8.54.

(E)-4,5-dichloro-2-(3,4,5-trimethoxystyryl)pyridazin-3(2H)-one (3x). Yellow crystal (methylene chloride). mp 149–150°C. IR (KBr) 3120, 2962, 1678, 1590, 1516, 1460, 1428, 1360, 1300, 1246, 1136, 1014, 952, 900 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.87 (s, OCH_3), 3.90 (s, 2OCH_3), 6.71 (s, 2H), 7.22 (d, J = 14.28 Hz, 1H), 7.88 (s, 1H), 8.04 (d, J = 14.26 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 56.22, 60.97, 104.18, 122.32, 123.55, 130.12, 134.46, 135.95, 136.11, 138.69, 153.52, 154.68. Anal. Calcd. for $C_{15}H_{14}Cl_2N_2O_4$: C, 50.44; H, 3.95; N, 7.84. Found: C, 50.43; H, 3.93; N, 7.82.

(E)-4,5-dichloro-2-(2,4,6-trimethoxystyryl)pyridazin-3(2H)-one (3y). Orange crystal (methylene chloride). mp 209–210°C. IR (KBr) 3058, 2950, 1650, 1600, 1580, 1458, 1334, 1232, 1196, 1120, 956 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.84 (s, OCH_3), 3.90 (s, 2OCH_3), 6.16 (s, 2H), 7.62 (d, J = 14.37 Hz, 1H), 7.88 (s, 1H), 8.51 (d, J = 14.37 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 55.36, 55.80, 90.62, 105.36, 113.45, 124.96, 133.86, 135.30, 135.45, 154.70, 159.78, 161.20. Anal. Calcd. for $C_{15}H_{14}Cl_2N_2O_4$: C, 50.44; H, 3.95; N, 7.84. Found: C, 50.41; H, 3.93; N, 7.83.

δ 3.89 (s, 2 OCH_3), 3.92 (s, OCH_3), 6.53 (s, 1H), 6.99 (d, J = 2.66 Hz, 1H), 7.47 (d, J = 14.38 Hz, 1H), 7.87 (s, 1H), 8.14 (d, J = 14.37 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 56.10, 56.45, 56.61, 97.40, 110.86, 115.04, 117.73, 123.03, 134.09, 135.59, 135.75, 143.38, 150.41, 152.41, 152.52, 154.64. Anal. Calcd. for $C_{15}H_{14}Cl_2N_2O_4$: C, 50.44; H, 3.95; N, 7.84. Found: C, 50.40; H, 3.93; N, 7.84.

(E)-4,5-dichloro-2-(2,3,4-trimethoxystyryl)pyridazin-3(2H)-one (3aa). Yellow crystal (methylene chloride). mp 127–128°C. IR (KBr) 3106, 2964, 1670, 1598, 1500, 1472, 1420, 1306, 1114, 1100, 970, 896 cm^{-1}. ^1H NMR ($CDCl_3$); δ 3.89 (s, 2 OCH_3), 3.93 (s, OCH_3), 6.69 (d, J = 8.77 Hz, 1H), 7.22 (d, J = 8.74 Hz, 1H), 7.426 (d, J = 14.43 Hz, 1H), 7.88 (s, 1H), 8.14 (d, J = 14.39 Hz, 1H). ^{13}C NMR ($CDCl_3$); δ 56.06, 60.88, 61.12, 107.76, 117.54, 121.48, 122.12, 123.66, 134.19, 135.73, 135.85, 142.51, 152.25, 154.07, 154.66. Anal. Calcd. for $C_{15}H_{14}Cl_2N_2O_4$: C, 50.44; H, 3.95; N, 7.84. Found: C, 50.43; H, 3.94; N, 7.85.

Absorption spectra, fluorescence spectra and quantum yield. UV spectra were measured on a Shimadzu PC-2401 double beam spectrophotometer. Absorption spectra were collected from sample solution prepared under atmosphere without degassing or inert gas bubbling. The concentration of the sample solution is 1.0×10^{-4} M. [b](M^{-1} cm^{-1}).

Fluorescence spectra were recorded on a PerkinElmer LS50B spectrofluorometer at room temperature. Quantum yield of the emission is evaluated in acetonitrile at 25°C, the quantum yield values are that relative to 9,10-diphenylanthrancene (1.00×10^{-4} M) in acetonitrile (from 352 nm extraction, Φ = 0.95).

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