Synthesis and Photochemical Properties of *trans*-2-(2-Aryl- or heteroarylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones

Heung-Seop Yim,[a] Mi-Ra Kim,[b] Gi-Hyeon Sung,[a] Hyun-A Chung,[a] Jin-Kook Lee,[c]* Sang-Gyeong Lee[a] and Yong-Jin Yoon[a]*

[a]Department of Chemistry &Research Institute of Natural Science, Graduate School for Molecular Materials and Nanochemistry, Gyeongsang National University, Jinju 660-701, Korea
[b]Center for Plastic Information of System, Pusan National University, Busan 609-735, Korea
[c]Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea
yjyoon@gnu.ac.kr

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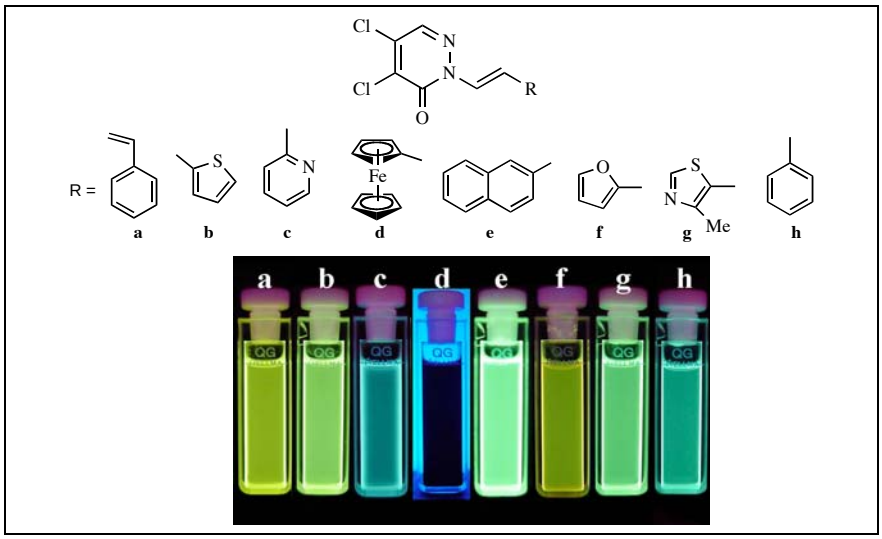

trans-2-(2-Aryl- or heteroarylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3** were synthesized from 4,5-dichloropyridazin-3(2*H*)-one *via* 2 step. The photochemical behavior of **3** in THF, methylene chloride, acetonitrile and methanol is dependent on the kind of aryl or heterocyclic ring and the solvent polarity

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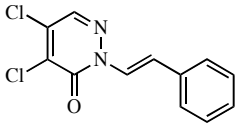
INTRODUCTION

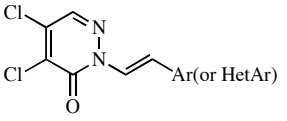
The development of luminescent molecules is an active field of research in supramolecular chemistry [1-8]. An important area within this field is the development of novel luminescent chemosensors [6-8] because those sensors have the advantage of possessing high sensitivity and selectivity, as well as providing on-line and real time analysis revolutionizing the field of chemical analysis [9-25].

In connection with our research program for the novel chemosensors, we studied the fluorescence molecule involving the (nπ*) state. Recently, we reported the synthesis and the photophysical properties of some *N*-styrylazinones containing Het-N-CH=CH-Ar moiety [26].

According to our previous results [26], *trans*-4,5-dichloro-2-styrylpyridazin-3(2*H*)-one showed the potential for applications as a spectroscopic or fluorescent probe. Therefore, we attempted the evaluation of the photophysical properties for some *trans*-2-(2-ary- or heteroarylvinyl)-4,5-dichloropyridazin-3(2*H*)-one as a fluorescence molecules. Here we report on their photophysical properties.



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



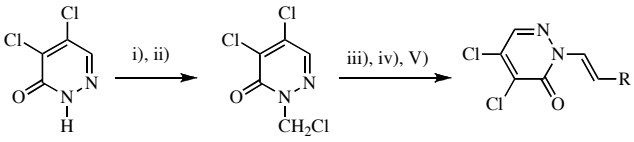
trans-2-(2-Aryl or heteroarylvinyl) -4,5-dichloropyridazin-3(2*H*)-one

RESULTS AND DISCUSSION

Some *trans*-2-(2-aryl or heteroarylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3** were prepared from 4,5-dichloropyridazin-3(2*H*)-one *via* two steps according to the literature method [26] (Scheme 1). The results were shown in Table 1. After compound **2** [27] was reacted with potassium iodide followed by triphenylphosphine, the resulting mixture was treated with heterocyclic aldehyde in the presence of potassium *tert*-butoxide in refluxing acetonitrile to give *trans*-isomer **3** as the major product and *cis*-isomer as the minor product. However, we isolated only *trans*-isomers **3** for our examination. The proposed structures of **3** were established by NMR, IR, HRMS and elemental analyses.

Absorption spectra. All the *trans*-2-(2-arylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3** except for **3d** in methylene chloride, tetrahydrofuran, acetonitrile and methanol display a single intense long-wavelength absorption band. The corresponding absorption maxima are reported in Table 2, and their normalized spectra are presented in Figure 1 for **3a** – **3h**. The absorption maxima of **3** depend on the heterocycles and the solvents. Comparing with **3h,** compounds **3a, 3b** and **3d - 3g** show the red-shift effect in the four solvents. Although **3c** shows the red-shift in methylene chloride, it shows the blue-shift in THF, methanol and acetonitrile. The magnitude of the absorption maximum for **3** in each solvent is in the order **3c > 3a > 3f > 3b > 3e > 3g > 3h > 3d** in methylene chloride, **3a > 3f > 3b > 3e > 3g > 3d > 3h > 3c** in THF, **3a > 3f > 3b > 3e > 3g > 3d > 3h > 3c** in acetonitrile, and **3a > 3f > 3b > 3e > 3g > 3d > 3c** in methanol. Compound **3d** have an absorption maximum and a second absorption band from *d-d* transition [28] at longer wavelengths in four solvents.

Scheme 1.



i) CH_2O,. ii) $SOCl_2$. iii) KI, CH_3CN, rf.
iv) PPh_3, CH_3CN, rf.
v) RCHO, *t*-BuOK, CH_3CN, rf

R = Phenyl, naphthyl or Heterocycles

Emission spectra. The fluorescence spectra of *trans*-2-(2-arylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3** except for **3d** are structured in THF, methylene chloride, methanol and acetonitrile. 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 quantum yield (Φ) of *trans*-2-(2-aryl or heteroarylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3a** – **3c** and **3e** - **3h** in four solvents are reported in Table 3. The size of the solvatochromic shifts and the shape of the fluorescence spectra depend on the kind of aryl or heterocyclic ring. As shown in Figure 3, the fluorescence spectra are in a normal Gaussian shape, but they are not available for **3d** in four solvents. Therefore, compound **3d** cannot be used as the fluorescence probe. Among eight compounds, the emission maximum of **3a** is the largest in methanol and acetonitrile, while the emission maximum of **3c** is the smallest in four solvents. The quantum yield of compound **3e** in methylene chloride is the highest. The 0,0 transition values of **3a**–**3c** and **3e** -**3g** are larger than that of **3h** involving the phenyl ring in four solvents.

The photophysical properties of **3** like *N*-styrylazinone affect on the deconjugation that twisted the C-N bond between the azinone and the styryl group [26]. The fluorescence of *trans*-stilbene depends on the double bond torsional barrier. Substituents in stilbene can, in principle affect on the torsional barrier [29,30]. Therefore, the photophysical properties of **3** may regarded to depend on the deconjugation and the kind of ring attached at vinyl group.

Table 1

Yields of **3**

Entry		**3,** R	Yield (%)[a]	Entry		**3,** R	Yield (%)[a]
1	**a**	C_6H_5CHCH-	62	5	**e**	Naphth-2-yl	63
2	**b**	2-Thiophenyl	66	6	**f**	2-Furyl	66
3	**c**	Pyridin-2-yl	58	7	**g**	4-(Me)thiazol-5-yl	64
4	**d**	Ferrocen-1-yl	61	8	**h**	C_6H_5	67

[a]Isolated yield

Table 2

The Absorption maxima (nm) for *trans*-2-(2-aryl or heteroarylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3**.

Entry	**3**	λ_{max}[a] (ε)[b]			
		CH_2Cl_2	THF	CH_3CN	MeOH
1	**3a**	393(8452)	393(8815)	387(7758)	387(9217)
2	**3b**	391(8118)	387(8163)	380(8903)	383(8913)
3	**3c**	394(7247)	366(7441)	360(8529)	356(8015)
4	**3d**	370(7830) [508][c]	372(7673) [501][c]	367(6741) [496][c]	366(9326) [502][c]
5	**3e**	385(7782)	382(8771)	376(8794)	374(9170)
6	**3f**	392(8541)	391(7909)	385(7948)	386(8978)
7	**3g**	381(7905)	380(8737)	376(8635)	372(8925)
8	**3h**	371(8657)	371(8799)	365(10410)	366(8254)

[a]1.0 x 10^{-4} M. [b]($M^{-1}cm^{-1}$). [c]The second absorption band is given in brackets.

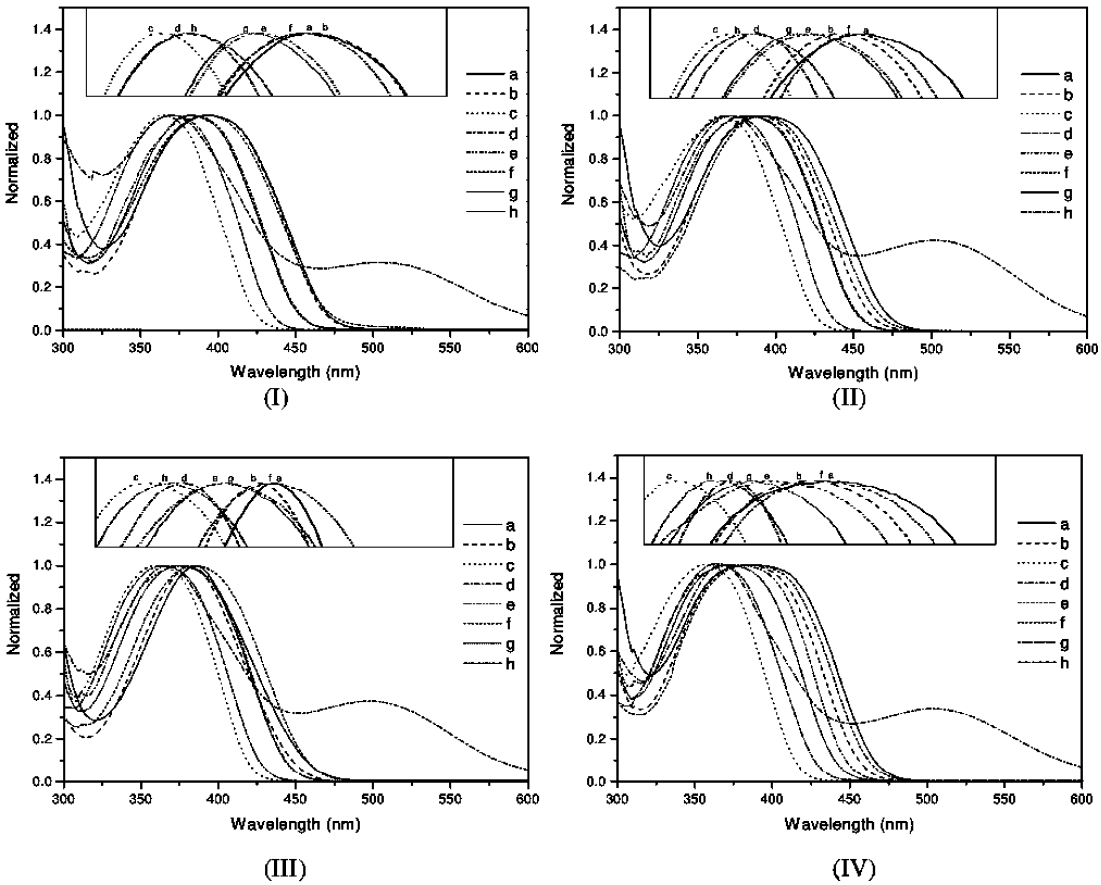


Figure 1. Normalized UV-vis absorption spectra for **3a** – **3h** in methylene chloride (I), THF (II), acetonitrile (III) and methanol (IV).

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 **3** in tetrahydrofuran, methylene chloride, methanol and acetonitrile [a]

Entry	**3**	Solvent	λ_f (nm)	$\Delta\nu_{st}$ (cm^{-1})[b]	$\lambda_{0,0}$ (nm)[c]	$\Delta\nu_{1/2}$ (cm^{-1})	Quantum Yield(Φ)[d]
1	**3a**	THF	526	6466	471	2518	0.30
2		CH_2Cl_2	524	7060	470	2545	0.17
3		MeOH	531	7041	494	2580	0.18
4		CH_3CN	531	7116	465	2548	0.24
5	**3b**	THF	524	6738	462	2663	0.43
6		CH_2Cl_2	519	6308	464	2685	0.63
7		MeOH	527	7116	487	2629	0.32
8		CH_3CN	527	7212	457	2613	0.38
9	**3c**	THF	482	6554	424	3720	0.34
10		CH_2Cl_2	482	6726	423	3774	0.28
11		MeOH	481	7340	441	3839	0.50
12		CH_3CN	484	11237	414	3787	0.14
13	**3e**	THF	514	6723	543	2931	0.72
14		CH_2Cl_2	514	6534	453	2945	0.83
15		MeOH	517	7377	478	2881	0.59
16		CH_3CN	520	7370	448	2820	0.70
17	**3f**	THF	527	6615	467	2528	0.36
18		CH_2Cl_2	525	6444	468	2550	0.34
19		MeOH	527	6931	496	2460	0.28
20		CH_3CN	530	7126	464	2495	0.29
21	**3g**	THF	517	7008	452	2960	0.44
22		CH_2Cl_2	502	5635	450	3023	0.56
23		MeOH	517	7576	471	3063	0.49
24		CH_3CN	519	7381	448	2921	0.32

Table 3. (continued)

Entry	**3**	Solvent	λ_f (nm)	$\Delta\nu_{st}$ (cm^{-1})[b]	$\lambda_{0,0}$ (nm)[c]	$\Delta\nu_{1/2}$ (cm^{-1})	Quantum Yield(Φ)[d]
25	**3h**	THF	492	6629	435	3451	0.29
26		CH_2Cl_2	492	6608	434	3407	0.26
27		MeOH	494	7096	431	3432	0.02
28		CH_3CN	496	7335	431	3383	0.15

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

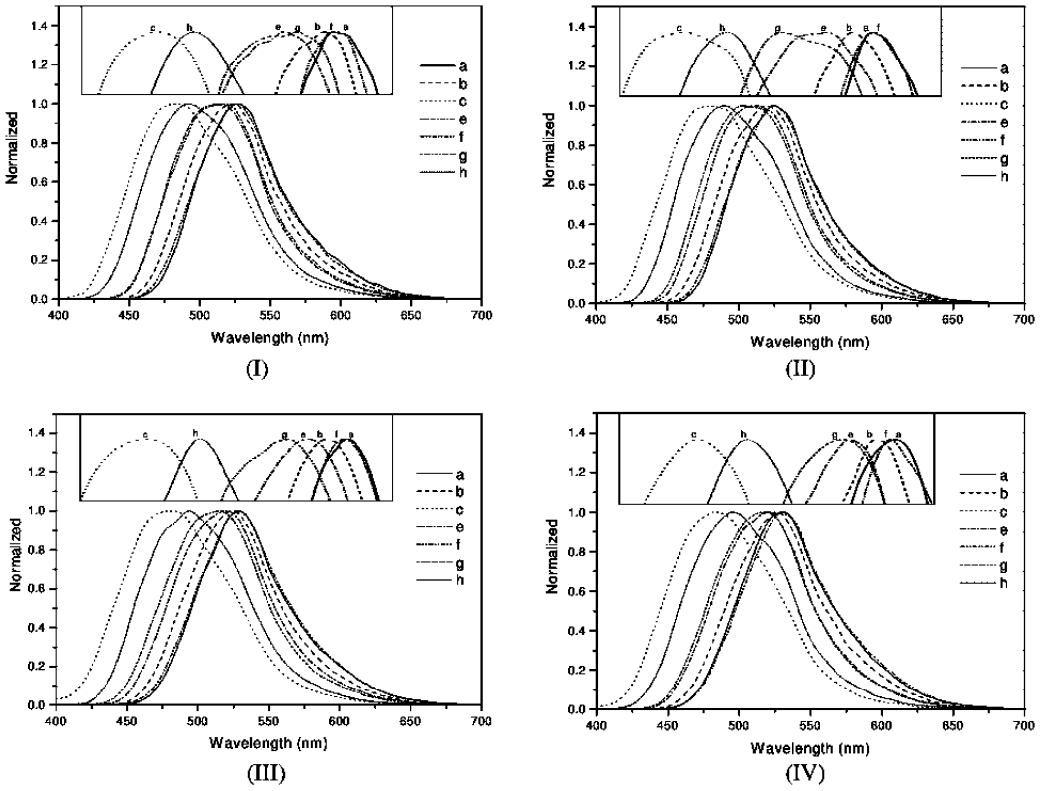


Figure 2. Normalized fluorescence spectra of **3a** – **3c** and **3e** – **3h** in THF (I), methylene chloride (II), methanol (III) and acetonitrile (IV).

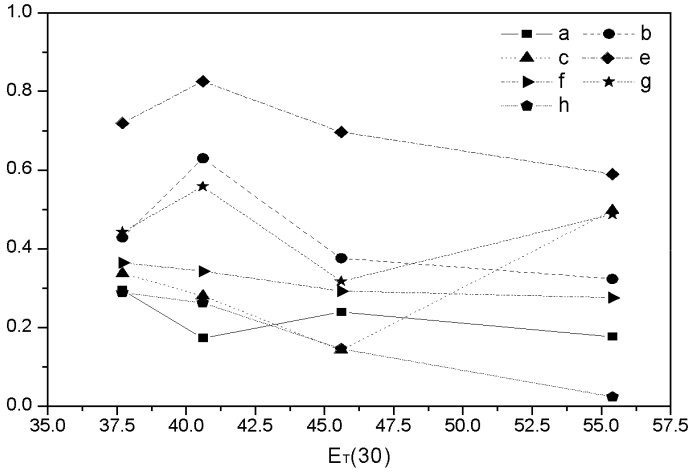


Figure 3. The plot of Φ_f against the solvent parameter [E_T(30)] for **3a – 3g**. The solvents [E_T (30)] are (from left to right) THF (37.4), methylene chloride (40.7), acetonitrile (45.6), and methanol.

In general, the photophysical behaviors also depend on the solvent polarity. Therefore, we studied the relationship of quantum yield and the microscopic solvent polarity parameter for compounds **3**. The plots of Φ against the microscopic solvent polarity parameter, $E_T(30)$ [31], are shown in Figure 3 for **3a** – **3c** and **3e** – **3h**. Nice linear relationship can be observed for **3f** and **3h**, although others show the large deviation in methylene chloride.

CONCLUSION

In conclusion, the heterocycle-dependent photophysical behavior of the some *trans*-2-(2-arylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3** as novel fluorescent molecules has been elucidated. By examining the photophysical properties of these new *trans*-2-(2-arylvinyl)-4,5-dichloropyridazin-3(2*H*)-ones **3**, the size of solvatochromic shifts and the shape of the fluorescence spectra in four solvents depend on the kind of heterocycles and the solvent polarity. By introducing suitable recognition site on the pyridazinone, **3e** may use a platform for fluorescence probes.

EXPERIMENTAL

General. 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.

4.2. Typical process of 4,5-dichloro-2-chloromethyl-pyridazin-3(2*H*)-one (2) [27]. A mixture of 4,5-dichloropyridazin-3(2*H*)-one (**1**, 60g, 364mmol) and distilled water (350 mL) was stirred for 10 minutes at room temperature. After adding formaldehyde solution (36%, 70 mL), the solution was refluxed for 1.5 hours. 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 minutes at room temperature with stirring. The resulting mixture was stirred for 2 hours at room temperature. After cooling to 0°C, water (200 mL) was added slowly. And 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**, 71.2g, 92%). White crystal (diethyl ether/*n*-hexane = 1:5, v/v). mp 69 - 70 °C (lit.[27] 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. *Anal*. calcd. for $C_5H_3Cl_3N_3O$: C 28.13, H 1.42, N 13.12;Found: C 28.10, H 1.41, N 13.09.

Typical process of [(4,5-dichloro-6-oxopyridazin-1(6*H*)-yl)methyl]triphenyl phosphonium iodide. 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 hours. After cooling to 30 – 40 °C, triphenylphosphine (4.07 g, 15.51 mmol) was added to the reaction solution. And the mixture was then refluxed for 6 hours. 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 minutes. The solution was filtered and than concentrated under reduced pressure. After cooling to room temperature, the resulting precipitate was filtered, washed with excess diethyl ether and dried to the product as thin yellow crystals. The product was used without purified further more.

Typical process of *trans*-2-(2-arylvinyl)-4,5-dichloropyridazin-3(2*H*)-one 3. To a solution of crude [(4,5-dichloro-6-oxopyridazin-1(6*H*)-yl)methyl]triphenyl phosphon-ium iodide (8 g, 14.10 mmol) in acetonitrile (50 mL) was added arylaldehyde (14.10 mmol) at 0 – 10°C. After stirring for 30 minites, potassium *t*-butoxide (2.05 g, 95%, 17.21 mmol) was added. The resulting mixture was stirred for 2 hours. The solution was concentrated under reduced pressure. After adding dichloromethane (100mL) and than water (50 mL), the solution was stirred for 10 minites, 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.

4,5-Dichloro-2-((1*E*,3*E*)-4-phenylbuta-1,3-diphenyl)pyridazin-3(2*H*)-one (3a). mp 182 - 184°C. IR (KBr) 3100, 1678, 1594, 1296, 1150, 1110, 982, 968, 898, 752, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.75 (d, *J* = 15.37Hz, 1H), 6.93 (dd, *J* = 10.97. 15.32Hz, 1H), 7.11 (dd, *J* = 10.94, 13.52Hz, 1H), 7.23 ~ 7.29 (m, 1H), 7.32 ~ 7.37 (m, 2H), 7.42 ~ 7.4 (m, 2H), 7.75 (d, *J* = 13.50Hz, 1H), 7.86 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 122.74, 125.34, 126.58, 126.68, 128.17, 128.75, 134.30, 135.68, 135.80, 136.13, 136.74, 154.46. *Anal*. calcd for $C_{14}H_{10}Cl_2N_2O$: C, 57.36; H, 3.44; N, 9.56. Found: C, 57.35; H, 3.43; N, 9.54. HRMS(EI) calcd. for $C_{14}H_{10}Cl_2N_2O$ 292.0170, Found : m/z 292.0164.

***trans*-4,5-Dichloro-2-(2-(thiophen-2-yl)vinyl)pyridazin-3(2*H*)-one (3b)**. mp 183 - 184 °C. IR (KBr) 3122, 1680, 1598, 1302, 1240, 1126, 950, 796, 732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.99 (dd, *J* = 3.61, 5.06Hz, 1H), 7.13 (d, *J* = 3.47Hz, 1H), 7.24 (d, *J* = 6.13Hz, 1H), 7.42 (d, *J* = 14.13Hz, 1H), 7.85 (s, 1H), 8.00 (d, *J* = 14.13Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 115.78, 123.39, 125.70, 127.78, 134.40, 134.68, 135.82, 136.10, 138.91, 154.46. *Anal*. calcd for $C_{10}H_6Cl_2N_2OS$: C, 43.97; H, 2.21; N, 10.26. Found: C, 43.95; H, 2.21; N, 10.23. HRMS(EI) calcd. for $C_{10}H_6Cl_2N_2OS$ 271.9578, Found : m/z 271.9580.

***trans*-4,5-Dichloro-2-(2-(pyridin-3-yl)vinyl)pyridazin-3(2*H*)-one (3c)**. mp 234 - 235 °C. IR (KBr) 3074, 1680, 1604, 1496, 1460, 1206, 1138, 976, 952, 854, 768 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.14 ~ 7.19 (m, 1H), 7.32 (d, *J* = 14.00Hz, 1H), 7.34 ~ 7.37 (m, 1H), 7.61 ~ 7.68 (m, 1H), 7.88(s, 1H), 8.55 ~ 8.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 121.29, 122.68, 123.69, 128.10, 134.72,

136.10, 136.32, 136.58, 149.91, 153.73, 154.74. *Anal.* calcd for $C_{11}H_7Cl_2N_2O_3$: C, 49.28; H, 2.63; N, 15.67. Found: C, 49.28; H, 2.60; N, 15.66. HRMS(EI) calcd. for $C_{11}H_7Cl_2N_3O$ 266.9966, Found : m/z 266.9922.

***trans*-4,5-Dichloro-2-(2-ferrocenyl)pyridazin-3(2*H*)-one (3d).** mp 250> °C. IR (KBr) 3105, 3082, 1662, 1580, 1504, 1286, 1232, 1184, 1126, 943, 891, 820, 711, 490 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.15 (s, 5H), 4.34 (t, *J* = 1.84Hz, 2H), 4.48 (t, *J* = 1.83Hz, 2H), 7.06 (d, *J* = 14.13Hz, 1H), 7.74 (d, *J* = 14.13Hz, 1H), 7.87 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 67.48, 69.43, 69.72, 79.88, 121.13, 121.45, 134.23, 135.48, 135.80, 154.27. *Anal.* calcd for $C_{16}H_{12}Cl_2FeN_2O$: C, 51.24; H, 3.23; N, 7.47. Found: C, 51.22; H, 3.21; N, 7.46. HRMS(EI) calcd. for $C_{16}H_{12}Cl_2N_2OFe$ 373.9676, Found : m/z 373.9671.

***trans*-4,5-Dichloro-2-(2-(naphthalen-2-yl)vinyl)pyridazin-3(2*H*)-one (3e)**. mp 194 - 195 °C. IR (KBr) 3098, 1682, 1606, 1140, 972, 838, 760 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz); 7.41 ~ 7.49(m, 3H), 7.65 ~ 7.68(dd, *J* = 1.72, 8.64Hz, 1H), 7.80 ~ 7.87(m, 5H), 8.23(d, *J* = 14.31Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz); 122.34, 123.51, 124.32, 126.44, 126.58, 127.65, 127.77, 128.08, 128.65, 132.10, 133.36, 133.58, 134.48, 135.94, 136.07, 154.69. *Anal.* calcd for $C_{16}H_{10}Cl_2N_2O$: C, 60.59; H, 3.18; N, 8.83. Found: C, 60.57; H, 3.17; N, 8.80. HRMS(EI) calcd. for $C_{16}H_{10}Cl_2N_2O$ 316.0170, Found : m/z 316.0169.

***trans*-4,5-Dichloro-2-(2-(furan-2-yl)vinyl)pyridazin-3(2*H*)-one (3f)**. mp 138 - 140 °C. IR (KBr) 3122, 1680, 1598, 1302, 1240, 1126, 950, 796, 732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.43 (d, *J* = 0.61Hz, 2H), 7.10 (d, *J* = 14.10Hz, 1H), 7.42 (s, 1H), 7.86 (s, 1H), 8.07 (d, *J* = 14.10Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 110.37, 110.98, 111.84, 123.01, 134.37, 135.74, 136.06, 142.96, 150.49, 154.48. *Anal.* calcd for $C_{10}H_6Cl_2N_2O_2$: C, 46.72; H, 2.35; N, 10.90. Found: C, 46.71; H, 2.33; N, 10.88. HRMS(EI)calcd. for $C_{10}H_6Cl_2N_2O_2$ 255.9806, Found : m/z 255.9802.

***trans*-4,5-Dichloro-2-(2-(4-methylthiazol-5-yl)vinyl)pyridazin-3(2*H*)-one (3g)**. mp 216 - 217 °C. IR (KBr) 3108, 1660, 1598, 1308, 1260, 1158, 1138, 976, 946, 898 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.51 (s, 3H), 7.41 (d, *J* = 14.04Hz, 1H), 7.82 (d, J=14.05Hz, 1H), 8.08 (s, 1H), 8.72 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 15.30, 112.00, 124.91, 127.01, 133.36, 135.93, 136.54, 150.66, 152.46, 154.10. *Anal.* calcd for $C_{10}H_7Cl_2N_3OS$: C, 41.68; H, 2.45; N, 14.58. Found: C, 41.66; H, 2.44; N, 14.54. HRMS(EI) calcd. for $C_{10}H_7Cl_2N_3OS$ 286.9687, Found : m/z 286.9689.

***trans*-4,5-Dichloro-2-styrylpyridazin-3(2*H*)-one (3h).** mp 161 - 162°C. IR (KBr) 3108, 1664, 1592, 1300, 1238, 1134, 958, 898, 742, 696 cm^{-1}; ^1H 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. HRMS(EI) calcd. for $C_{12}H_8Cl_2N_2O$ 266.0014, Found : m/z 266.0011.

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REFERENCES AND NOTES

[1] de Silva, A. P.; McCaughan, B.; McKinney, B. O. F.; Querol, M. *Dalton Trans*. **2003**, 1902.

[2] Balzani, V. *Photochem. Photobiol. Sci*. **2003**, *2*, 459.

[3] Raymo, F. M.; Giordani, S. *J. Am. Chem. Soc*. **2002**, *124*, 2004.

[4] Brown, G. J.; de Silva, A. P.; Pagliari, S. *Chem. Commun*. **2002**, 2461.

[5] Ballardini, R.; Balzani, V.; Credi, A.; Gandolf, A. M. T.; Venturi, M. *Acc. Chem. Res*. **2001**, *31*, 445.

[6] Lavigne, J. J.; Anslyn, E. V. *Angew. Chem. Int. Ed*. **2001**, *40*, 3119.

[7] Beer, P. D.; Gale, P. A. *Angew. Chem. Int. Ed*. **2001**, *40*, 486.

[8] Czarnik, A. W. *Acc. Chem. Res*. **1994**, *27*, 302.

[9] Spichiger-Keller, U. S. *Chemical Sensors and Biosensors for Medical and Biological Applications*, Wiley VCH: Weinheim, Germany, **1998**.

[10] He, H.; Mortellaro, M. A.; Leiner, M. J. P.; Fraatz, R. J.; Tusa, J. K. *J. Am. Chem. Soc*. **2003**, *125*, 1468.

[11] Wiskur, S. L.; Ait-Haddou, H.; Lavigne, J. J.; Anslyn, E. V. *Acc. Chem. Res*. **2001**, *34*, 963.

[12] Hortala, M. A.; Fabbrizzi, L.; Marcotte, N.; Stomeo, F.; Taglietti, A. *J. Am. Chem. Soc*. **2003**, *125*, 20.

[13] Fabbrizzi, L.; Marcotte, N.; Stomeo, F.; Taglietti, A. *Angew. Chem. Int. Ed*. **2002**, *41* (20), 3811.

[14] Wang, W.; Escobedo, J. O.; Lawrence, C. M.; Strongin, R. M. *J. Am. Chem. Soc*. **2004**, *126* (11),3400.

[15] Valeur, B. *Molecular Fluorescence, Principle and Applications*, Wiley-VCH, Weinheim, **2002**; p11.

[16] Tsien, R. Y. In *Fluorescent and Photochemical Probes of Dynamic Biochemical Signals Inside Living Cells*; A. W. Czarmik, Ed.; American Chemical Society: Washington DC, **1993**; pp 130 -146.

[17] Rousseau, D. L. *Optical Techniques in Biological Research*, Academic Press: New York, **1984**, chapter 4.

[18] Thriernge, R.; Shio, H.; Han, Y. S.; Cohen, G.; Lazarow, P. B. *Mol. Cell. Biol*. **1991**, *11*, 510.

[19] Lakowicz, J. R. *Principle of Fluorescence and Spectroscopy*, Plenum Press: New York **1983**.

[20] de Silva, A. P.; Gurarantane, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem Rev*. **1997**, *97*, 1515.

[21] Fu, Y.; Li, H.; Hu, W.; Zhu, D. *Chem. Commun*. **2005**, 3189.

[22] Gunnlaugsson, T.; Leonard, J. P.; Murray, N. S. *Org. Lett*. **2004**, *6* (10), 1557.

[23] Gunnlaugsson, T.; Lee, T. C.; Parkesh, R. *Org. Lett*. **2003**, *5* (22), 4065.

[24] Granzhan, A.; Ihmels, H. *Org. Lett*. **2005**, *7* (23), 5119.

[25] Maeda, H.; Katayama, K.; Matsuno, H.; Uno, T. *Angew. Chem. Int. Ed*. **2006**, *45*, 1810.

[26] Cho, S. D.; Hwang, J.; Kim, H. K.; Yim, H. S.; Kim, J. J.; Lee, S. G.; Yoon, Y. J. *J. Heterocylic Chem*. **2007**, in press.

[27] Chung, H. A; Kang, Y. J.; Yoon, Y. J. *J. Heterocyclic Chem*. **1998**, *35*, 1257.

[28] Hsu, Y.; Penner, T. L.; Whitten, D. G. *Langmuir* **1994**, *10*, 2757.

[29] Yang, J. –S.; Liau, K. –L.; Wang, C. –M.; Hwang, C. –Y. *J. Am. Chem. Soc*. **2004**, *126*, 12325.

[30] Yang, J. –S.; Chiou, S. –Y.; Liau, K. –L. *J. Am. Chem. Soc*. **2002**, *124*, 2518.

[31] Marcus, Y. *Chem. Soc. Rev*. **1993**, 409.