Development of Thermally Stable and Highly Fluorescent IR Dyes

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PI: ***Xiu R. (James) Bu***
Clark Atlanta University
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Introduction

Fluorophores are the core component in various optical applications such sensors and probes. Fluorphores with low-energy or long wavelength emission, in particular, in NIR region, possess advantages of low interference and high sensitivity. In this study, we has explored several classes of imidazole-based compounds for NIR fluorescent properties and concluded: (1) thiazole-based imidazole compounds are fluorescent; (2) emission energy is tunable by additional donor groups; (3) they also possess impressive two-photon absorption properties; and (4) fluorescence emission can be induced by two-photon input. This report summarizes (1) synthesis of new series of fluorophore; (2) impact of electron-withdrawing groups on fluorescent property; (3) unique property of two-photon absorption; and (4) on-going development.

Chromophore/Fluorophore development

The first approach included two classes of compounds (**I** and **II**, Figure 1) that possessed tricyanovinyl as an electron-accepting group. The choice of this group is based on its high thermal stability and strong electron accepting property. These compounds have absorption bands around 550 nm. The emission would be in much lower energy region considering potential Stokes shift. The synthesis of these two series of compounds used the reported procedure developed in this group (Scheme 1). Simply, treatment of imidazole derivatives with butyl lithium in TFH, followed by the addition of tetracyanoethylene led to the formation of **I** or **II**. R groups in these two series could be H, Me or OMe. These groups did not affect the designated reaction but did slightly red-shift the absorption band of long wavelength. The examination of fluorescent properties in various solvents indicated that neither **I** nor **II** are fluorescent.

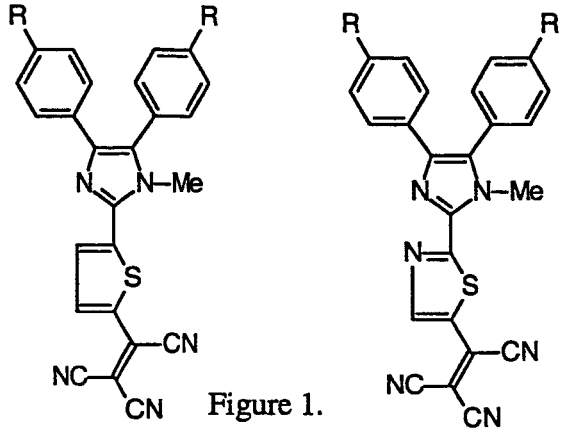
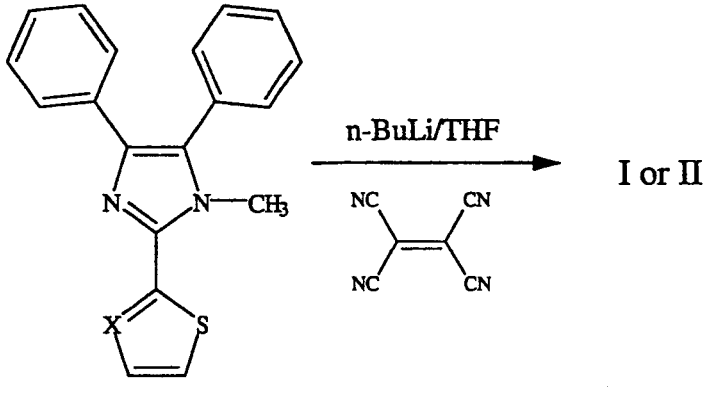


Figure 1.

I

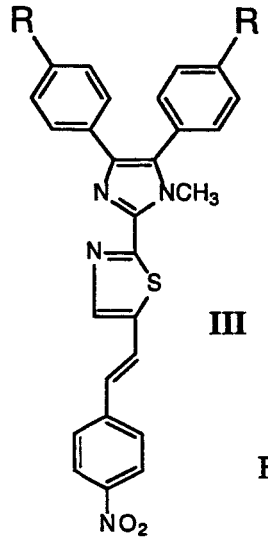
II



X = CH, N

Scheme 1. Synthetic route for **I** and **II**

The next approach included class **III** (Figure 2) compounds that possessed nitro group as electron accepting group. The nitro group is one of the strongest electron accepting groups, and has often been used as A (electron-accepting) component to pull electron in the charge transfer process. Again, this class of compounds is barely fluorescent.



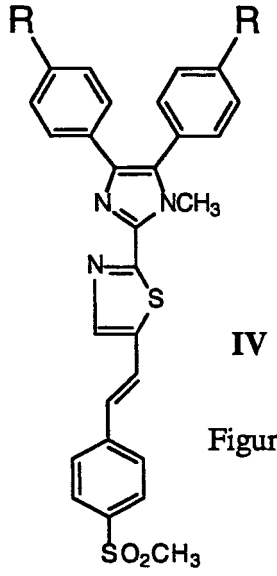
III

Figure 2.

All three classes (**I**, **II**, and **III**) undergo radiationless energy transfer from donor to acceptor or static quenching. Both tricyanovinyl and nitro groups are responsible for these mechanisms because of their extreme electron accepting properties. Moreover, these groups assembled in a conjugated pathway further facilitate charge transfer and static interaction.

Based on these results, we are prompted to investigate the role of electron-accepting groups on fluorescence. It is well known that the D-π-A structure possesses large molecular dipole, and will likely absorb at a longer wavelength originating from the charge transfer. The strength of D and A as well as length of the conjugation will dictate the location of the charge transfer band. It is obvious now that the strongest electron accepting groups will not generate radiative process. Thus, our new approach will be to retain the molecular design but use different electron accepting groups. This involves identification of new electron-accepting groups that will be conducive to the formation of radiative state. In order to maximize the electron accepting ability and have the charge transfer band in the lowest energy possible, we have chosen sulfonyl group. Measured by

Hammett constant, the σ_p is 0.73 for SO_2Me group, right behind that (0.81) of NO_2 group. This means that the strength of sulfonyl group as an electron acceptor is only next to that of nitro group. It should be an ideal candidate to be explored in the D-π-A architecture for fluorescence purpose.



IV

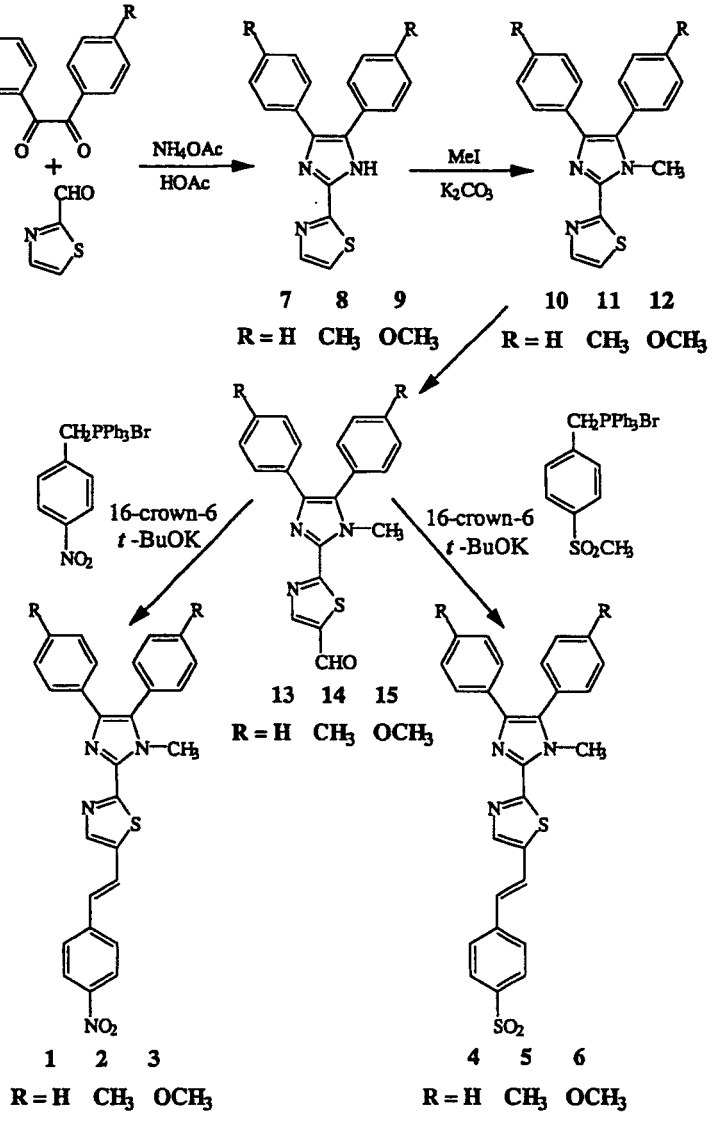
Figure 3.

Chromophores (class IV, Figure 3) will be designed to possess imidazole and thiazolevinyl as conjugated chain, sulfonyl as acceptor, and R with electron donating property.

The development of both classes (**III** and **IV**) of chromophores was illustrated in Schemes I, II, and III. Three chromophores in class **III** are designated as **1** (R=H), **2** (R=Me), and **3** (R =OMe). Three chromophores in class **IV** are designated as **4** (R=H), **5** (R=Me), and **6** (R=OMe).

Two new series of chromophores **1-3** and **4-5** were synthesized via intermediates **13-15**, which were obtained by starting the condensation of benzil derivatives with 2-formylthiazole to afford **7-9**. The methylation of **7-9** with iodomethane in the presence of a base gave **10-12**, which were treated with *n*-butyl lithium, followed by the addition of DMF to produce **13-15** (Scheme 2). The Wittig reactions of 4-nitrobenzyl triphenylphosphine bromide with **13-15** led to the formation of **1-3** while the reactions

with 4-methylsulfonylbenzyl triphenylphosphine bromide yielded **4-6**. Chromophores **1-3** absorb with λ_{max} in the range of 422-433 nm while **4-6** in the range of 398-410 nm.



Scheme 2.

Fluorescence study

All the chromophores in chloroform absorb around 400 nm (Table 1). Both series show substituent effect, and the bathochromic shift occurs in the increasing order when R goes

from H→Me→OMe. Fluorescence property strongly depends on solvents, in particular for the first series of compounds. The first series (class **III**, chromophores **1, 2, 3**) has quantum yield of ca. 0.01 (in chloroform) and in other polar solvents as well [DMSO (ϕ= 0.01) and MeCN (ϕ=0.01)]. However, in 1,4-dioxane, the emission has adequate efficiency. The quantum yields range from 0.27 to 0.43 (Table 2).

Table 1. Photophysical and electronic properties of chromophores **1-6** in chloroform

chromophore	**1**	**2**	**3**	**4**	**5**	**6**
λ_{max} (ε) (nm) ($M^{-1}cm^{-1}$)	422 (33,700)	427 (29,200)	433 (34,400)	403 (27,200)	407 (23,600)	415 (27,200)
Φ_f Stokes shift (cm^{-1})	0.02	0.01	0.01	0.48 4,612	0.47 4,368	0.52 4,489
λ_{em} (nm)	611	452	418	495	495	510

Table 2. Comparison of quantum yields in different solvents

	1	**2**	**3**	**4**	**5**	**6**
in $CHCl_3$						
ϕ	**0.02**	**0.01**	**0.01**	**0.48**	**0.47**	**0.52**
in 1,4-dioxane						
ϕ	**0.43**	**0.31**	**0.27**	**0.47**	**0.52**	**0.64**
λem	**524**	**534**	**554**	**474**	**496**	**502**

Unlike the first series, the second series (class **IV**, chromophores **4-6**) exhibits moderate quantum yields (ca. 0.5) in both chloroform and 1,4-dioxane . The value determined in MeCN (ϕ=0.43 for **4**) also suggests that the moderate efficiency is relatively consistent in different solvents.

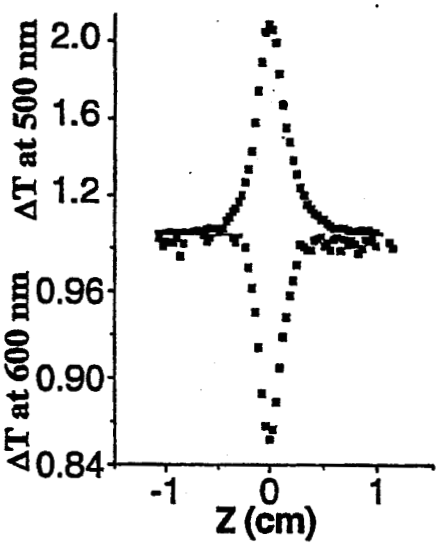
These results are quite interesting and significant in the following aspect: nitro group and tricyanovinyl groups are strong electron accepting groups with poor fluorescence properties; On the contrary, sulfonyl group possesses both strong electron accepting and fluorescent property, suggesting that chromophores can be furnished with sulfonyl group for fluorescent purpose.

The use of sulfonyl does not compromise the fluorescent property of fluorophores. Compound **7** (scheme 1) has intrinsic fluorescent property with (ϕ=0.48, in chloroform). Upon conversion of **7** to **4** to extend the conjugation and attach sulfonyl group, the fluorescent property is eventually retained except the fact that **7** emits at 405 nm while **4** does at a longer wavelength by 90 nm. The conjugation extension and acceptor attachment primarily shift the emission band to lower energy region and does not reduce the fluorescence efficiency. Thus, this establishes sulfonyl as an excellent group for both electron acceptor and fluorescence.

Two-photon absorption (2PA) study

Nonlinear optical measurements for two-photon absorption properties of **1-6** were carried out with the Z-scan technique. Nonlinear absorption coefficients are determined by monitoring the transmittance change as the sample is scanned through the laser beam focal plane. In non-resonant conditions, a 2PA process is characterized by the absorption Z-scan signature: a decrease in the transmittance. The magnitude of the nonlinear process can be extracted through a fitting procedure.

Figure 4 shows the open aperture Z-scan measurements obtained with three distinct wavelengths for **3**. For nonresonant excitation (λ= 600 nm), the decrease in the normalized transmittance indicates a 2PA process (Fig. 4, squares). When resonant excitation at 500 nm is used (circles), the transmittance increases, characteristic of saturated absorption due to the occurrence of excited state process. At 550 nm, no changes in the normalized transmittance are observed, where the 2PA and the SA effects cancel each other. Similar results were obtained for the other compounds.



The transmittance change (ΔT) measured through the Z-scan experiment as a function of the wavelength (solid circles) and the linear absorption spectrum (solid line) are displayed in Fig. 5 for **4**.

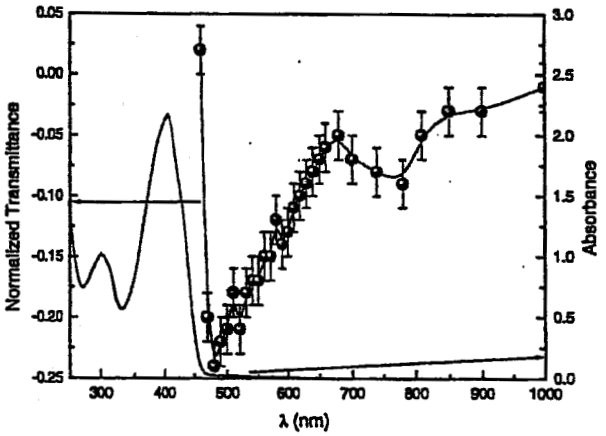


Figure 5 – Linear and nonlinear spectra for **4**

All 2PA spectra present a peak around 750 – 800 nm, which is almost twice the position of the lowest energy peak for the linear absorption, a feature generally observed in the 2PA spectrum of unsymmetric molecules. The increase in the 2PA intensity below 700 nm is due to resonance enhancement of the optical nonlinearity near the one photon transition, in agreement with the resonant denominator in the sum-over states model. By fitting each of the Z-scan signatures obtained at the nonresonant condition, the 2PA cross-section coefficients (δ) are determined and listed in Table 2.

Table 2. **TPA cross-section coefficients obtained in chloroform solutions**

Compound	Concentration	δ (GM)	δ (GM)
1	2.3	-	400
2	4.8	-	500
3	6.6	-	550
4	5.3	460	550
5	5.9	1200	1100
6	5.4	1300	1600

Two-photon excited fluorescence study

Figure 6 shows the two-photon excited fluorescence spectrum obtained for **5** with excitation at 650 nm. In order to verify the two-photon origin of this signal, measurements were carried out with two distinct laser irradiance. As seen in this figure, the fluorescence intensity decreases with the square of the excitation intensity, as expected for this kind of process. Furthermore the results were obtained at nonresonat conditions.

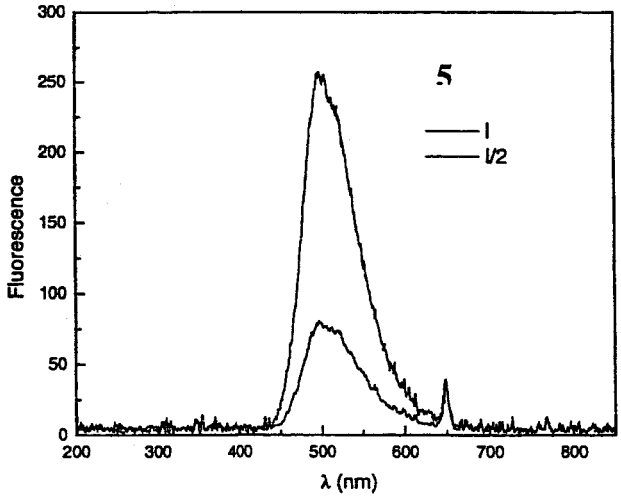


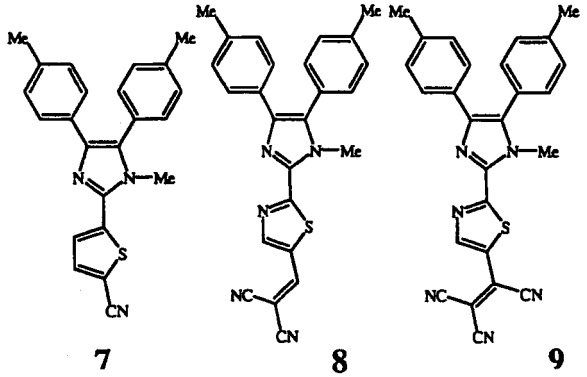
Figure 6 – Two photon excited fluorescence for **5**. The excitation wavelength employed was 650nm

Due to the higher 2PA cross section of the second series, the two-photon excited fluorescence signals observed is high. For the first series, a very low fluorescence (not shown) could be detected, due to their smaller 2PA cross-section and fluorescence quantum yield.

Two-photon absorption and excited fluorescence study again demonstrates that the sulfonyl group is advantageous in non-linear absorption and excitation process.

On-going fluorophore development

Since the fluorescence property is directly related to electron-accepting group as discussed above, we are interested in possible fine-tuning of fluorescence with electron-accepting groups. We have chosen the following compounds (**7**-**9**) to study this possibility. These three compounds have cyano-based electron-accepting groups. The number of cyano groups is from 1 to 3. In 1,4-dioxane, compound **7**, which possesses one cyano group, has quantum yield of 0.90. As the number of cyano groups increases, such as in **8** and **9**, the fluorescence decreases with $\varphi_f = 0.36$ for **8**, 0.01 for **9**, respectively. The same trend exists in acetonitrile as well: 0.74 for **7**, 0.25 for **8**, 0.02 for **9**.



	7	**8**	**9**	
λ_{em}	**440**	**441**	**503**	**(in dioxane)**
ϕ	**0.90**	**0.36**	**0.01**	
λ_{em}	**450**	**463**	**533**	**(in MeCN)**
ϕ	**0.74**	**0.25**	**0.02**	

These results indicate that mono-cyano or dicyano may be used as electron-accepting groups. In mono-cyano case, the quantum yield is higher. In di-cyano case, the quantum yield is moderate. But, the emission takes place in lower energy region compared to that from mono-cyano fluorophore, and this is particularly true in acetonitrile, a polar solvent.

Outlook-Future Development

As we have established the importance of electron-accepting group on fluorescence, it is expected that this finding will apply to the design of next generation of fluorophores. So far, we have concluded that three types of electron-accepting groups can be utilized in the building of molecules: mono-cyano, dicyanovinyl, and sulfonyl groups. The potential may also exist in a combination of these groups.

The D-π-A system is an important architecture in the design of NIR fluorescent molecules. It will offer an ability through push-pull motif to shift charge transfer band to visible region. To the end, emission will likely take place at even lower energy region: NIR region. The identification of sulfonyl group, mono-cyano, and di-cyanovinyl as an efficient fluorescent component will help design molecular systems with intriguing fluorescent properties. With an optimal combination with D components as well as π chain, the new NIR fluorophores with D-π-A motifs will be developed.

EXPERIMENTAL

All moisture-sensitive reactions were carried out under nitrogen atmosphere using flame-dried glassware. Solvents were dried over standard drying agents and freshly distilled prior to use. Other chemicals were used as received. Reactions were monitored by TLC on silica gel 60 F_{254}. Column chromatography purifications were performed on silica gel (63 – 200μm). ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker ARX-400 spectrometer using TMS as reference, and reported as ppm for chemical shifts. Elemental analysis was performed in Atlantic Microlab, Norcross of Georgia. MS spectra were obtained in an EI mode. UV-vis absorption spectra were

recorded on a Backman DU 650 spectrophotometer. Fluorescence spectra were recorded on a PTI steady state fluorometer.

The open aperture Z-scan experiments for nonlinear absorption employed laser pulses from an optical parametric amplifier (TOPAS, from Light Conversion) pumped by 150 fs pulses at 775 nm delivered by a Ti:sapphire chirped pulse amplified system (CPA-2001, from Clark-MXR Inc.) operating at a 1 kHz repetition rate. Pulse energies used here were limited to 0.01μJ to avoid photo-degradation of the chromophores. The FWHM pulse duration delivered by the OPA was about 120 fs, and the spatial profile of the laser beam presented an approximately Gaussian distribution. The beam waist size employed in our experiments was typically around 15 μm.

2-(2'-thiazol)-4,5-bis(phenyl)imidazole (7).
A mixture of benzil (4.185 g, 19.91 mmol) and ammonium acetate (15.35 g, 199 mmol) in glacial acetic acid (140 mL) was heated to 80 °C under nitrogen atmosphere. During stirring, 2-formylthiazole(2.930 g, 25.90 mmol) in 5 mL glacial acetic acid was added dropwise over 24 h. The resulting solution was cooled to room temperature and poured into 1200 ml of ice water. The viscous precipitate was obtained via filtration, then washed several times with water. Purification by chromatography on a silica gel (eluent: hexane/ethyl acetate/CH_2Cl_2 2:1:1 in volume) to give **7** (3.32 g, 55% yield) as a white solid. MP 218-220 °C. ^{1}H NMR ($CDCl_3$): δ 12.05 (s, 1H), 7.65 (d, 2H, J=7.2 Hz), 7.47 (d, 1H, J=3.2 Hz), 7.39-7.24 (m, 8H), 7.19 (d, 1H, J=3.2 Hz). ^{13}C NMR ($CDCl_3$): δ 160.1, 143.7, 143.1, 141.3, 134.6, 130.6, 130.0, 129.2, 128.9, 128.8, 128.6, 128.3, 127.7, 127.5, 119.9, 119.7. MS: *m/z* 303 (M^+). Anal. Calcd for $C_{18}H_{13}N_3S$: C, 71.26; H, 4.32; N, 13.85; S, 10.57. Found: C, 71.02; H, 4.30; N, 13.86.

2-(2'-thiazol)-4,5-bis(4'-methylphenyl)imidazole (8).
Similar procedure as for **7** led to **8** as a white solid (66% yield). MP 213-215 °C.
^{1}H NMR ($CDCl_3$): δ 11.06 (s, 1H), 7.61 (d, 1H, J=3.6 Hz), 7.55 (d, 2H, J=8.0 Hz), 7.31 (d, 2H, J=8.0 Hz), 7.27 (d, 1H, J=3.6 Hz), 7.13 (dd, 4H, J=8.0 Hz), 2.35 (s, 3H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 160.1, 143.2, 142.9, 141.0, 139.4, 138.3, 137.1, 131.9, 129.7, 129.6, 129.5, 129.3, 129.2, 128.5, 128.3, 128.2, 128.0, 127.8, 21.8, 21.1. MS: *m/z* 331

(M^+). Anal. Calcd for $C_{20}H_{17}N_3S$: C, 72.48; H, 5.17; N, 12.68; S, 9.67. Found: C, 72.55; H, 5.15; N, 12.76.

2-(2'-thiazol)-4,5-bis(4'-methoxyphenyl)imidazole (9).

Similar procedure as for **7** produced **9** as a white solid (71% yield). MP 199-200 °C. ^{1}H NMR ($CDCl_3$): δ 10.74 (s, 1H), 7.66 (d, 1H, J=3.2 Hz), 7.58 (d, 2H, J=8.8 Hz), 7.36 (d, 2H, J=8.8 Hz), 7.30 (d, 1H, J=3.2 Hz), 6.88 (dd, 4H, J=8.8, J=8.4 Hz), 3.88 (s, 3H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 160.3, 159.7, 159.2, 143.1, 142.8, 140.8, 138.9, 130.1, 129.9, 129.4, 129.2, 127.4, 123.1, 119.6, 119.3, 114.6, 114.3, 114.0, 56.3, 55.3. MS: *m/z* 363 (M^+). Anal. Calcd for $C_{20}H_{17}N_3O_2S$: C, 66.10; H, 4.71; N, 11.56; O, 8.80; S, 8.82. Found: C, 71.37; H, 4.81; N, 13.67.

1-methyl-2-(2'-thiazol)-4,5-bis(phenyl)imidazole (10).

To a mixture of **7** (2.500 g, 7.54 mmol) in anhydrous *N,N*-dimethylacetamide (80 mL) and potassium carbonate (2.08 g, 15.05 mmol) was added iodomethane (1.285 g, 9.05 mmol). The reaction mixture was stirred for 12 h at 45-50 °C under nitrogen atmosphere, and then poured into a water-ice bath. The precipitate was filtered and dried. The recrystallization in 300 mL methanol gave **10** as a greenish crystal (2.50 g, 96% yield). MP 190-191 °C. ^{1}H NMR ($CDCl_3$): δ 7.82 (d, 1H, J=3.2 Hz), 7.53 (d, 2H, J=7.6 Hz), 7.46-7.35 (m, 5H), 7.30 (d, 1H, J=3.2 Hz), 7.20-7.11 (m, 3H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 160.9, 143.5, 140.9, 139.1, 134.6, 132.5, 131.3, 130.9, 129.4, 129.3, 128.4, 127.4, 127.0, 119.7, 33.7. MS: *m/z* 317 (M^+). Anal. Calcd for $C_{19}H_{15}N_3S$: C, 71.90; H, 4.76; N, 13.24; S, 10.10. Found: C, 72.00; H, 4.75; N, 13.23.

1-methyl-2-(2'-thiazol)-4,5-bis(4'-methylphenyl)imidazole (11).

Similar procedure as for **10** led to **11** as a greenish crystal (90% yield). MP 159-160 °C ^{1}H NMR ($CDCl_3$): δ 7.86 (d, 1H, J=3.6 Hz), 7.43 (d, 2H, J=7.6 Hz), 7.35 (d, 1H, J=3.2 Hz), 7.28-7.22 (m, 4H), 7.04 (d, 2H, J=7.2 Hz), 3.92 (s, 3H), 2.44 (s, 3H), 2.29 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 161.0, 143.5, 140.6, 139.2, 139.0, 136.6, 132.3, 131.7, 131.1, 130.2,

129.2, 127.8, 127.2, 119.7, 33.7, 21.8, 21.6. MS: *m/z* 345 (M^+). Anal. Calcd for $C_{21}H_{19}N_3S$: C, 73.01; H, 5.54; N, 12.16; S, 9.28. Found: C, 72.84; H, 5.57; N, 12.21.

1-methyl-2-(2'-thiazol)-4,5-bis(4'-methoxyphenyl)imidazole (12).

Similar procedure as for **10** led to **12** as a greenish crystal (92% yield). MP 121-122 °C ^{1}H NMR ($CDCl_3$): δ 7.85 (d, 1H, J=3.6 Hz), 7.47 (d, 2H, J=8.8 Hz), 7.34 (d, 1H, J=3.2 Hz), 7.29 (d, 2H, J=8.8 Hz), 7.01 (d, 2H, J=8.8 Hz), 7.78 (d, 2H, J=8.8 Hz), 3.91 (s, 3H), 3.87 (s, 3H), 3.77 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 160.3, 158.8, 143.5, 140.6, 140.4, 138.8, 132.6, 131.5, 128.5, 127.4, 122.8, 119.6, 114.9, 114.0, 55.7, 55.5, 33.7. MS: *m/z* 377 (M^+). Anal. Calcd for $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13; O, 8.48; S, 8.50. Found: C, 67.02; H, 5.10; N, 11.19.

1-methyl-2-[2'-(5'-formyl)thiazol]-4,5-bis(phenyl)imidazole (13)

To a solution of **10** (0.368 g, 1.16 mmol) in anhydrous THF (22 mL) was added dropwise *n*-butyllithium (2.5 M in hexane, 1.39 mL, 3.48 mmol) at -63 °C under nitrogen atmosphere. The reaction mixture was warmed to 0 °C and stirred at this temperature for 30 m. After it was cooled to -63 °C, anhydrous *N,N*-dimethylformamide (0.325 mL, 4.18 mmol) was added. The mixture was stirred at 0 °C for 2 h, then poured into 100 mL H_2O and neutralized with 2N HCl to near pH 6. The product was extracted with acetyl acetate, dried with sodium sulfate, and concentrated. Recrystallization in mixture of acetyl acetate and hexane (1/5 in vol.) gave yellowish product (0.33 g, 83% yield). MP 193-195 °C. ^{1}H NMR ($CDCl_3$): δ 10.07 (s, 1H), 8.39 (s, 1H), 7.52-7.50 (m, 5H), 7.39-7.37 (m, 2H), 7.23-7.17 (m, 3H), 3.96 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 182.4, 167.4, 152.1, 140.4, 139.7, 138.9, 134.3, 133.8, 131.1, 130.1, 129.6, 128.6, 127.5, 127.3. MS: *m/z* 345 (M^+). Anal. Calcd for $C_{20}H_{15}N_3OS$: C, 69.54; H, 4.38; N, 12.17; O, 4.63; S, 9.28. Found: C, 69.37; H, 4.32; N, 12.15.

1-methyl-2-[2'-(5'-formyl)thiazol]-4,5-bis(4'-methylphenyl)imidazole (14)

Similar procedure as for **13** led to **14** as a yellowish product (77%yield). MP 201-203 °C. ^{1}H NMR ($CDCl_3$): δ 10.00 (s, 1H), 8.33 (s, 1H), 7.40 (d, 2H, J=8.0 Hz), 7.29 (d, 2H, J=8.0 Hz), 7.24 (d, 2H, J=8.0 Hz), 7.03 (d, 2H, J=8.0 Hz), 3.91 (s, 3H), 2.43 (s, 3H), 2.29

(s, 3H). ^{13}C NMR ($CDCl_3$): δ 182.4, 167.4, 152.3, 140.4, 139.6, 139.4, 138.7, 137.1, 134.1, 131.2, 130.9, 130.3, 129.3, 127.2, 127.1, 34.0, 21.8, 21.5. MS: *m/z* 373 (M^+). Anal. Calcd for $C_{22}H_{19}N_3OS$: C, 70.75; H, 5.13; N, 11.25; O, 4.28; S, 8.59. Found: C, 70.67; H, 5.11; N, 11.14.

1-methyl-2-[2'-(5'-formyl)thiazol]-4,5-bis(4'-methoxyphenyl)imidazole (15)

Similar procedure as for **13** led to **15** as a yellowish product (72%yield). MP 186-188 °C. ^1H NMR ($CDCl_3$): δ 10.04 (s, 1H), 8.37 (s, 1H), 7.47 (d, 2H, J=8.8 Hz), 7.29 (d, 2H, J=8.4 Hz), 7.03 (d, 2H, J=8.4 Hz), 6.79 (d, 2H, J=8.8 Hz), 3.93 (s, 3H), 3.90 (s, 3H), 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 182.5, 167.4, 160.6, 159.1, 152.3, 140.2, 139.3, 138.8, 138.6, 133.5, 132.4, 128.5, 126.7, 122.1, 115.1, 114.0, 55.7, 55.6, 34.0. MS: *m/z* 405 (M^+). Anal. Calcd for $C_{22}H_{19}N_3O_3S$: C, 65.17; H, 4.72; N, 10.36; O, 11.84; S, 7.91. Found: C, 65.32; H, 4.79; N, 11.25.

1-methyl-2-{2'-[5'-(4'-nitrophenylvinyl)]thiazol}-4,5-bis(phenyl)imidazole (1)

To a mixture of **13** (0.618 g, 1.80 mmol), triphenyl(4-nitrobenzyl)phosphonium bromide(0.948 g, 1.98 mmol) and 18-crown-6(0.120 g, 0.45 mmol) in anhydrous dichloromethane (50 mL) was added potassium *tert*-butoxide by three times (totally 0.846 g, 7.56 mmol) in 5 h under nitrogen atmosphere. The reaction mixture was continued to stir for more 10 h at room temperature. Then the mixture was poured into 500 mL H_2O, extracted with dichloromethane, dried with sodium sulfate, and concentrated. Purification was performed by column chromatography (eluent: n-hexane/EtOAc /CH_2Cl_2 6:1:12 in volume). Further purification by recrystallization in hexane/ CH_2Cl_2 gave yellowish solid (0.51 g, 61% yield). MP 247-249 °C. ^1H NMR ($CDCl_3$): δ 8.22 (d, 2H, J=8.4 Hz), 7.83 (s, 1H), 7.59 (d, 2H, J=8.4 Hz), 7.60-7.49 (m, 5H), 7.41-7.37 (m, 3H), 7.24-7.17 (m, 3H), 6.98 (d, 1H, J=16.0 Hz), 3.93 (s, 3H). MS: *m/z* 464 (M^+). Anal. Calcd for $C_{27}H_{20}N_4O_2S$: C, 69.81; H, 4.34; N, 12.06; O, 6.89; S, 6.90. Found: C, 69.72; H, 4.36; N, 11.98.

1-methyl-2-{2'-[5'-(4'-nitrophenylvinyl)]thiazol}-4,5-bis(4'-methylphenyl)-imidazole (2)

Similar procedure as for **1** led to **2** as a yellowish solid (43%yield). MP 231-233 °C. ^{1}H NMR ($CDCl_3$): δ 8.21 (d, 2H, J=8.8 Hz), 7.82 (s, 1H), 7.59 (d, 2H, J=8.8 Hz), 7.42 (d, 2H, J=8.0 Hz), 7.38 (d, 1H, J=16.0 Hz), 7.29 (d, 2H, J=7.6 Hz), 7.25 (d, 2H, J=7.6 Hz), 7.05 (d, 2H, J=8.8 Hz), 6.96 (d, 1H, J=16.0 Hz), 3.90 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H). MS: *m/z* 492 (M^+). Anal. Calcd for $C_{29}H_{24}N_4O_2S$: C, 70.71; H, 4.91; N, 11.37; O, 6.50; S, 6.51. Found: C, 70.82; H, 4.94; N, 11.32.

1-methyl-2-{2'-[5'-(4'-nitrophenylvinyl)]thiazol}-4,5-bis(4'-methoxyphenyl)-imidazole (3)

Similar procedure as for **1** led to **3** as a yellowish solid (59%yield). MP 206-208 °C. ^{1}H NMR ($CDCl_3$): δ 8.25 (d, 2H, J=8.8 Hz), 7.83 (s, 1H), 7.62 (d, 2H, J=8.8 Hz), 7.49 (d, 2H, J=9.2 Hz), 7.41 (d, 1H, J=16.0 Hz), 7.29 (d, 2H, J=8.8 Hz), 7.02 (d, 2H, J=8.8 Hz), 6.98 (d, 1H, J=16.0 Hz), 6.79 (d, 2H, J=8.8 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 3.78 (s, 3H). MS: *m/z* 524 (M^+). Anal. Calcd for $C_{29}H_{24}N_4O_4S$: C, 66.40; H, 4.61; N, 10.68; O, 12.20; S, 6.11. Found: C, 66.16; H, 4.64; N, 10.59.

1-methyl-2-{2'-[5'-(4'-methylsulfonylphenylvinyl)]thiazol}-4,5-bis(phenyl)-imidazole (4)

To a mixture of **13** (0.130 g, 0.376 mmol), triphenyl(4-methylsulfonylbenzyl)-phosphonium bromide(0.226 g, 0.442 mmol) and 18-crown-6(0.026 g, 0.10 mmol) in anhydrous dichloromethane (25 mL) was added potassium *tert*-butoxide by three times (totally 0.178 g, 1.585 mmol) in 3 h under nitrogen atmosphere. The reaction mixture was continued to stir for more 5 h at room temperature. Then the mixture was poured into 300 mL H_2O, extracted with dichloromethane, dried with sodium sulfate, and concentrated. Purification was performed by column chromatography (eluent: hexane/EtOAc 2:1 in volume). Further purification by recrystallization in hexane/ EtOAc gave yellowish solid(0.13 g, 71% yield).

^{1}H NMR ($CDCl_3$): δ 7.92 (d, 2H, J=8.4 Hz), 7.81 (s, 1H), 7.63 (d, 2H, J=8.0 Hz), 7.53-7.45 (m, 5H), 7.39-7.35 (m, 3H), 7.26-7.16 (m, 3H), 6.95 (d, 1H, J=16.0 Hz), 3.92 (s, 3H), 3.06 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 159.9, 144.0, 143.0, 142.3, 140.3, 139.5, 137.5,

134.2, 133.2, 131.3, 131.1, 130.4, 129.8, 129.7, 129.6, 129.4, 128.7, 128.5, 128.3, 127.4, 126.4, 122.7, 122.5, 44.9, 34.3, 33.5. MS: *m/z* 497 (M^+).

1-methyl-2-{2'-[5'-(4'-methylsulfonylphenylvinyl)]thiazol}-4,5-bis(4'-methyl-phenyl)imidazole (5)

Similar procedure as for **4** led to **5** as a yellowish solid (26%yield).

^{1}H NMR ($CDCl_3$): cis- δ 7.97 (d, 2H, J=8.4 Hz), 7.70 (s, 1H), 7.57 (d, 2H, J=8.4 Hz), 7.43-7.20 (m, 7H), 6.99 (d, 2H, J=7.6 Hz), 6.80 (dd, 1H, J=12.4 Hz, J=12.0 Hz), 3.85 (s, 3H), 3.14 (s, 3H), 2.42 (s, 3H), 2.27(s, 3H).trans- δ 7.92 (d, 2H, J=8.4 Hz), 7.81 (s, 1H), 7.64 (d, 2H, J=8.4 Hz), 7.43-7.20 (m, 7H), 7.05 (d, 2H, J=8.0 Hz), 6.96 (d, 1H, J=16.0 Hz), 3.91 (s, 3H), 3.07 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 160.4, 160.1, 145.7, 143.9, 142.9, 142.4, 140.1, 140.0, 139.5, 139.4,137.6, 136.8, 133.6, 133.0, 132.8, 131.5, 131.1, 130.9, 130.3, 130.1, 129.6, 129.3, 129.2, 128.3, 127.3, 127.1, 126.4, 122.7, 122.6, 45.0, 34.3, 33.4, 22.5, 22.2, 21.6, 21.0. MS: *m/z* 525 (M^+).

1-methyl-2-{2'-[5'-(4'-methylsulfonylphenylvinyl)]thiazol}-4,5-bis(4'-methoxy-phenyl)imidazole (6)

Similar procedure as for **4** led to **6** as a yellowish solid (52%yield). MP 217-219 °C.

^{1}H NMR ($CDCl_3$): δ 7.92 (d, 2H, J=8.4 Hz), 7.81 (s, 1H), 7.64 (d, 2H, J=8.4 Hz), 7.47 (d, 2H, J=8.4 Hz), 7.38 (d, 1H, J=16.0 Hz), 7.29 (d, 2H, J=8.8 Hz), 7.02 (d, 2H, J=8.8 Hz), 6.96 (d, 1H, J=16.0 Hz), 6.79 (d, 2H, J=8.4 Hz), 3.90 (s, 3H), 3.89 (s, 3H), 3.78 (s, 3H), 3.08 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 160.4, 160.1, 158.9, 143.9, 142.4, 140.0, 139.5, 139.3, 137.3, 132.6, 132.4, 132.3, 129.6, 128.6, 128.3, 127.3, 127.1, 122.7, 122.5, 115.0, 114.9, 114.1, 113.8, 56.2, 55.8, 55.3, 54.9, 44.9, 34.2. MS: *m/z* 557 (M^+). Anal. Calcd for $C_{30}H_{27}N_3O_4S_2$: C, 64.61; H, 4.88; N, 7.53; O, 11.48; S, 11.50. Found: C, 64.37; H, 4.94; N, 7.23;