Synthesis of Organic Dyes with Linkers Between 9,9-Dimethylfluorenyl Terminal and α-Cyanoacrylic Acid Anchor, Effect of the Linkers on UV-Vis Absorption Spectra, and Photovoltaic Properties in Dye-Sensitized Solar Cells

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Six metal-free organic dyes having thiophene (**1**), benzene-thiophene (**2**), thiophene-benzene (**3**), thiophene-pyridine (**4**), thiophene-thiophene (**5**), and pyridine (**6**) linkers between 9,9-dimethylfluorenyl terminal group and α-cyanoacrylic acid anchor were synthesized. Among them, organic dye **5** showed the longest λ_{max} value (424 nm) in UV-Vis absorption spectrum, better incident monochromatic photon-to-current conversion efficiency (IPCE), highest short circuit photocurrent density (J_{SC}, 9.33 mA^2/cm^2), and highest overall conversion efficiency (η, 3.91%).

Key Words: 9,9-Dimethylfluorenyl terminal, α-Cyanoacrylic acid anchor, Thiophene linker, Organic dye, Dye-sensitized solar cells

Introduction

Increasing energy demands, depletion of the carbon-based energy sources, and global warming have led to the interests on renewable energy sources.[1] And dye-sensitized solar cells (DSSC) have a significant potential as low-cost devices for generating electricity.[2] Among the many organic dyes developed so far, Ru(II) polypyridyl complexes have shown somewhat better power conversion efficiencies[3] and stabilities compared to those of the metal-free organic dyes although they are more expensive and hard to purify. Recently, improvements in photovoltaic performance (up to 9%) have been achieved in metal-free coumarin-,[4] indoline-,[5] oligoene-,[6] merocyanine-,[7] and hemicyanine-based dyes.[8] Most of these metal-free organic dyes have a structural unit in common such as the terminal donor group, α-cyanoacrylic acid anchor for the attachment to the TiO_2 nanoparticles, and linkers between them.

In this paper, we report the synthesis of metal-free organic dyes having different aromatic linkers between 9,9-dimethylfluorenyl terminal group and α-cyanoacrylic acid anchor, the effect of the linkers on the λ_{max} and molar absorptivity (ε_{max}) in the UV-Vis absorption spectra, and the photovoltaic properties of them in dye-sensitized solar cells.

Results and Discussion

Synthesis of organic dyes. Six metal-free organic dyes with thiophene (**1**), benzene-thiophene (**2**), thiophene-benzene (**3**), thiophene-pyridine (**4**), thiophene-thiophene (**5**), and pyridine (**6**) linkers were prepared (Figure 1).

Organic dye **1** was prepared as follows (Scheme 1). Iodination of fluorene (**7**) by iodine in AcOH and dimethylation of the corresponding iodide by CH_3I and KOH were accomplished to provide the iodide **8** in 61% and 78% yield, respectively.[9] Palladium-catalyzed Suzuki coupling of iodide **8** with 2-thiopheneboronic acid (**9**) afforded the intermediate **10** in 58% yield.[10] And formylation at C-2 position of thiophene by *n*-BuLi and DMF (68%)[11] and condensation of the resulting aldehyde with cyanoacetic acid in the presence of piperidine (78%) provided the organic dye **1**.[12]

Synthesis of organic dye **2** was summarized in Scheme 2. Sequential Suzuki coupling of the iodide **8** with 4-bromoben-

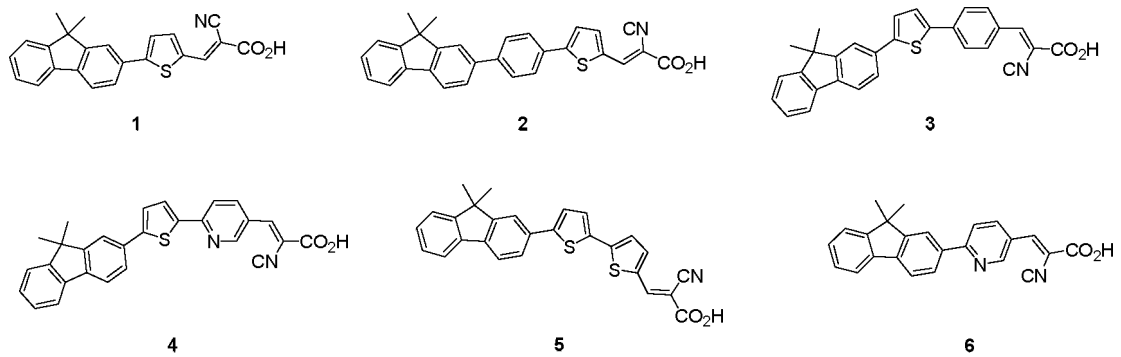
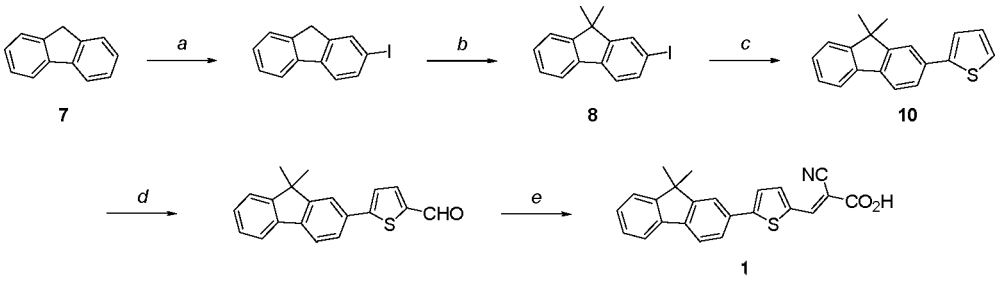


Figure 1. Structures of Organic Dyes **1** ~ **6**.

zeneboronic acid (**11**) and then 2-thiopheneboronic acid (**9**) in 52% and 71% yield provided the intermediate **12**.[10] Formylation at C-2 position of thiophene (68%)[11] and condensation of the aldehyde with cyanoacetic acid (65%) as in Scheme 1 provided the organic dye **2**.[12]

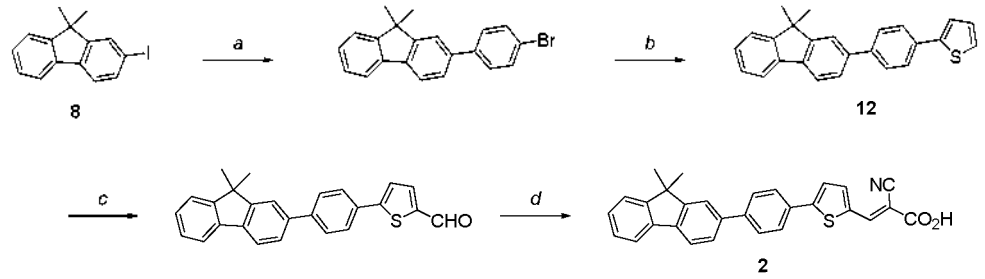
Preparation of organic dye **3** was initiated from the commercially available 4-bromobenzaldehyde (**13**) (Scheme 3). Protection of the aldehyde with neopentyl glycol (85%),[13] Suzuki coupling with 2-thiopheneboronic acid (**9**) (72%),[10] and metallation at the C2-position of thiophene moiety followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**) (51%) gave the boronate ester **15**.[14] Suzuki coupling of **15** with iodide **8** (59%), hydrolysis of the acetal protecting group under aqueous acidic condition (97%), and finally condensation of the resulting aldehyde with cyanoacetic acid (52%) completed the synthesis of organic dye **3**.[15]

Organic dye **4** was prepared from 6-chloronicotinic acid (**16**) (Scheme 4). Transformation of **16** into the boronate **17** was



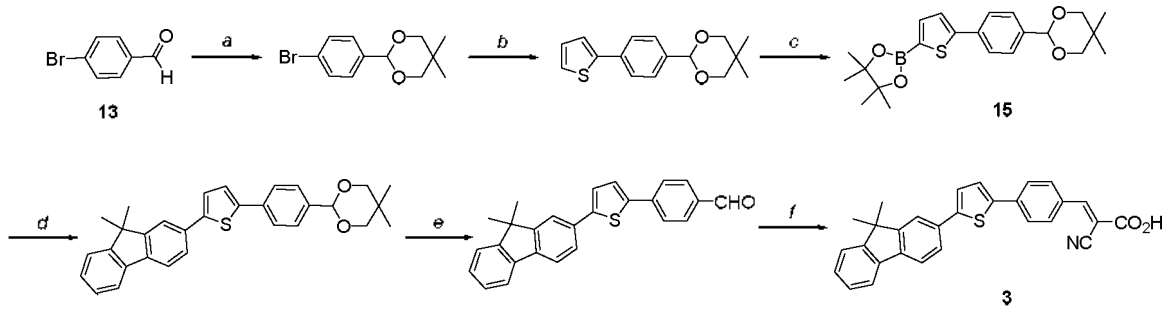
Reagents and Conditions: (a) I_2 (0.34 eq), HIO_4 (0.17 eq), AcOH-H_2O-H_2SO_4 (100 : 20 : 3), reflux, 12 hr, 61%. (b) KI (0.2 eq), CH_3I (10 eq), KOH (10 eq), DMSO, rt, 12 hr, 78%. (c) $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2-thiopheneboronic acid (**9**) (1.1 eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), reflux, 12 hr, 58%. (d) *n*-BuLi (2.15 M, 1.8 eq), THF, −25 °C to 0 °C, 2 hr; DMF (3 eq), −78 °C to rt. 12 hr, 68%. (e) $NCCH_2CO_2H$ (2 eq), piperidine (1 eq), CH_3CN, reflux, 12 hr, 78%.

Scheme 1. Preparation of Dye 1.



Reagents and Conditions: (a) 4-bromophenylboronic acid (**11**) (1.1 eq), $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), reflux, 12 hr, 52%. (b) $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2- thiopheneboronic acid (**9**) (1.4eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), reflux, 12 hr, 71%. (c) *n*-BuLi (2.15 M, 1. 8 eq), THF, −25 °C to 0 °C, 2 hr; DMF (3 eq), −78 °C to rt, 12 h, 68%. (d) $NCCH_2CO_2H$ (2 eq), piperidine (1 eq), CH_3CN, reflux, 12 hr, 65%.

Scheme 2. Preparation of Dye 2.



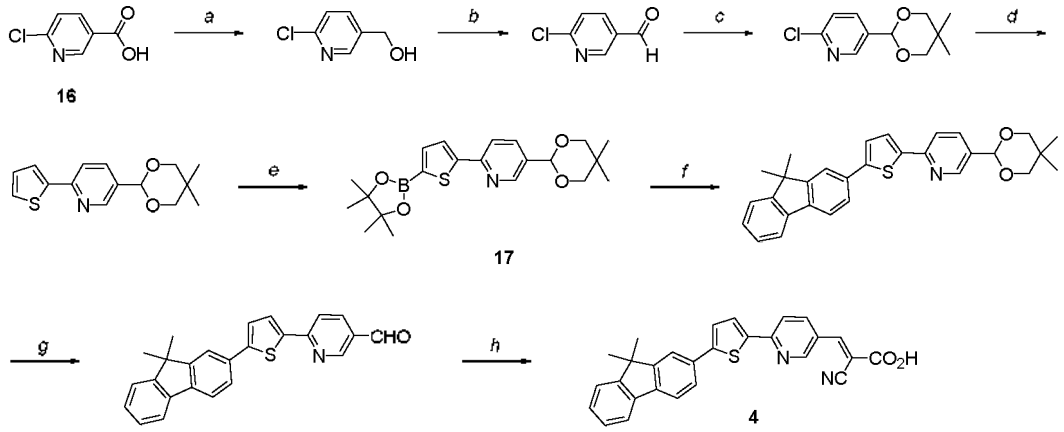
Reagents and Conditions: (a) Neopentyl glycol (1.2 eq), *p*-TsOH (0.11 eq), benzene, reflux, 5 hr, 85%. (b) $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2-thiopheneboronic acid (**9**) (1.1 eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), 100 °C, overnight, 72%. (c) *n*-BuLi (2.25 M, 1.7 eq), −25 °C to 0 °C, 2 hr; 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**) (2.2 eq), −78 °C to rt, overnight, 51%. (d) **8** (1.1 eq), $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), 100 °C, overnight, 59%. (e) THF : H_2O : TFA (10 : 1 : 1), reflux, overnight, 97%. (f) $NCCH_2CO_2H$ (2 eq), piperidine (1 eq), CH_3CN, reflux, overnight, 52%.

Scheme 3. Preparation of Dye 3.

accomplished *via* five-step sequences: reduction of carboxylic acid to the primary alcohol by LAH (70%), Swern oxidation to aldehyde (84%),[16] protection of the resulting aldehyde with neopentyl glycol (85%),[13] Suzuki coupling with 2-thiopheneboronic acid (**9**) (60%),[10] and finally metallation at the C2-position of thiophene moiety followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**) (50%).[14] Suzuki coupling of boronate **17** with iodide **8** (59%), hydrolysis of the acetal protecting group (94%) and condensation of the aldehyde group with cyanoacetic acid (50%) afforded the organic dye **4**.[15]

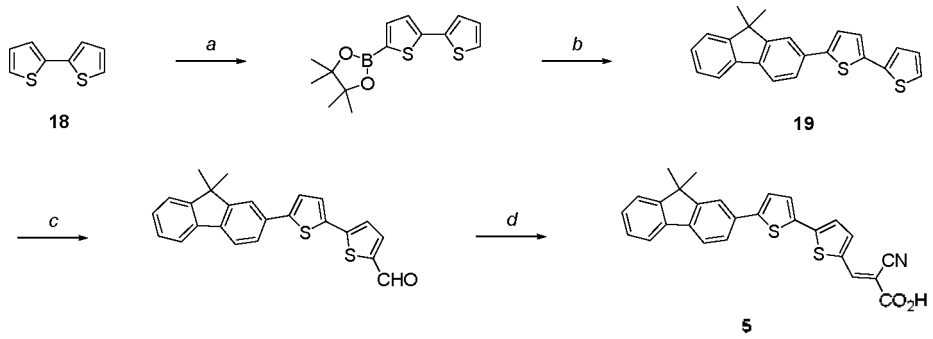
Synthesis of organic dye **5** was summarized in Scheme 5. Commercially available 2,2'-bithiophene (**18**) was transformed into the C-2 boronate ester (42%) by treatment of *n*-BuLi and quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**),[14] and the boronate ester was subsequently coupled with iodide **8** to produce the bis-thiophene intermediate **19** in 45% yield.[10] Formylation (63%)[11] and condensation (70%) as before gave the organic dye **5**.[12]

Synthesis of **6** was shown in Scheme 6. Iodide group in **8**



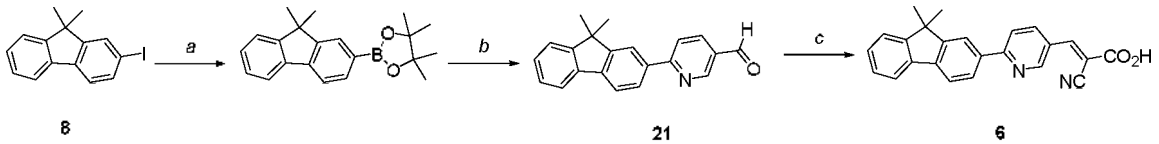
Reagents and Conditions: (a) LAH (1.23 eq), 0 °C, 3 hr, 70%. (b) oxalyl chloride (1.56 eq), DMSO (2.5 eq), TEA (2.45 eq), −78 °C to 0 °C, 84%. (c) Neopentyl glycol (1.2 eq), *p*-TsOH (0.11 eq), benzene, reflux, 5 hr, 85%. (d) $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2-thiopheneboronic acid (**9**) (1.1 eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), reflux, overnight, 60%. (e) *n*-BuLi (2.25 M, 1.7 eq), −25 °C to 0 °C, 2 hr; 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**) (2.2 eq), −78 °C to rt, overnight, 50%. (f) **8** (1.1 eq), $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), 100 °C, overnight, 59%. (g) THF : H_2O : TFA (10 : 1 : 1), reflux, overnight, 94%. (h) $NCCH_2CO_2H$ (2 eq), piperidine (0.3 eq), CH_3CN, reflux, overnight, 50%.

Scheme 4. Preparation of Dye **4**.



Reagents and Conditions: (a) *n*-BuLi (2.15 M, 1.7 eq), −25 °C to 0 °C, 2 hr; 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**) (2.5 eq), −78 °C to rt, overnight, 42%. (b) **8** (1.2 eq), $Pd(PPh_3)_2Cl_2$ (0.05 eq), 2 M Na_2CO_3-THF (1 : 4), reflux, 12 hr, 45%. (c) *n*-BuLi (2.15 M, 1.8 eq), THF, −25 °C, 2 hr; DMF (3 eq), rt, 12 hr, 63%. (d) $NCCH_2CO_2H$ (2 eq), piperidine (1 eq), CH_3CN, reflux, overnight, 70%.

Scheme 5. Preparation of Dye **5**.



Reagents and Conditions: (a) *n*-BuLi (2.25 M, 1.7 eq), −25 °C to 0 °C, 2 hr; 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**) (1.2 eq), −78 °C to rt, overnight, 50%. (b) 6-chloronicotinaldehyde (**20**) (1 eq), $Pd(PPh_3)_2Cl_2$ (0.09 eq), 2 M Na_2CO_3-DME-H_2O (5 : 9 : 1), 100 °C, overnight, 65%. (c) $NCCH_2CO_2H$ (2 eq), piperidine (0.3 eq), CH_3CN, reflux, overnight, 62%.

Scheme 6. Preparation of Dye **6**.

Table 1. UV-Vis Absorption Data of Organic Dyes **1** ~ **6**.

	1	**2**	**3**	**4**	**5**	**6**
λ_{max} (nm)	391	385	398	387	424	353
ε ($M^{-1}cm^{-1}$)	34,100	13,400	29,600	31,300	22,700	40,800

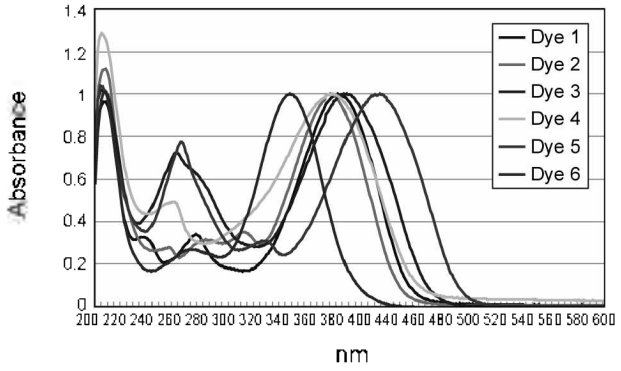


Figure 2. Normalized UV-Vis Absorption Spectra of Organic Dyes **1** ~ **6**.

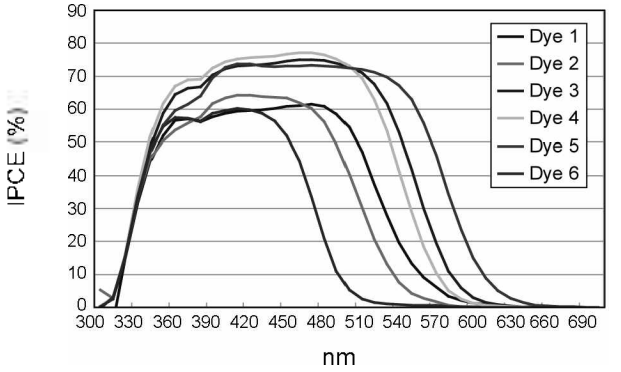


Figure 3. IPCE Spectra for Organic Dyes **1** ~ **6**.

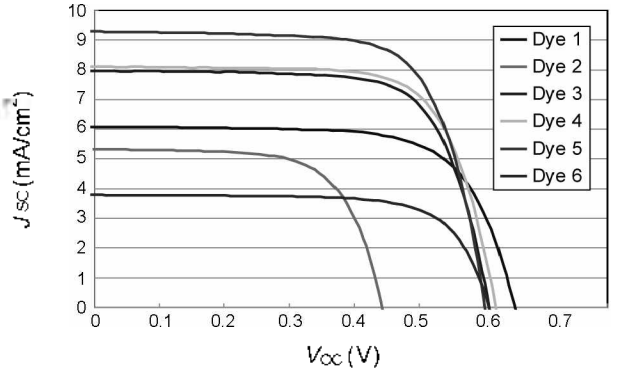


Figure 4. Short Circuit Photocurrent Density (J_{SC}).

was converted to the corresponding boronate ester (50%) by *n*-BuLi and quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**14**), which was then treated under Suzuki coupling conditions in the presence of 6-chloronicotinaldehyde (**20**) to afford the intermediate aldehyde **21** (65%).[10] Final condensation of the aldehyde group with cyanoacetic acid (62%) furnished the organic dye **6**.[15]

UV-Vis absorption spectra. UV-Vis absorption data and normalized UV-Vis spectrum of the six organic dyes (**1-6**) were shown in Table 1 and Figure 2. Having dye **1** as a reference material with λ_{max} of 391 nm and ε of 34,100 $M^{-1}cm^{-1}$, introduction of additional benzene ring between fluorenyl group and thiophene group (dye **2**) showed minor blue-shift (385 nm) and significant decrease in extinction coefficient (13,400 $M^{-1}cm^{-1}$). However, presence of additional benzene or pyridine ring between thiophene and α-cyanoacrylic acid anchor (dyes **3** or **4**) resulted in minor red- or blue-shifts (398 nm for **3** and 387 nm for **4**) with a somewhat reduced extinction coefficients (29,600 or 31,300 $M^{-1}cm^{-1}$). Relatively large red-shift (424 nm) was observed when thiophene ring was introduced between thiophene and α-cyanoacrylic acid anchor (dye **5**) although extinction coefficient was quite diminished (22,700 $M^{-1}cm^{-1}$) compared to the reference material **1**. Replacement of thiophene group in the reference material **1** by pyridine (dye **6**) showed large blue-shift (353 nm) and enhancement of the extinction coefficient (40,800 $M^{-1}cm^{-1}$).

Preparation of solar cell device. Screen-printable pastes of synthesized nanocrystalline TiO_2 particles (~ 20 nm) and large TiO_2 particles (CCIC, 400 nm, Japan) were prepared according to the procedures reported elsewhere.[17] Nanocrystalline TiO_2 films were deposited on fluorine-doped tin oxide (FTO) glass (Pilkington, TEC-8, 8 Ω/sq, 2.3 mm thick) precoated with Ti (IV) bis(ethyl acetoacetato)-diisopropoxide solution, which was heated at 500 °C for 30 min at heating rate of 5 °C/min. For the bi-layer structure, the CCIC TiO_2 particle layer was deposited on the annealed nanocrystalline TiO_2 films and heated at 500 °C for 30 min. The resulting TiO_2 double layered-films (8.5 + 4.5 μm) were immersed in anhydrous ethanol containing 0.5 mM of synthesized dyes and kept for 16 h at ambient temperature. Pt counter electrodes were prepared on the FTO glasses using 0.7 mM H_2PtCl_6 solution, followed by heating at 400 °C for 20 min in air. In the sealed cell, an electrolyte solution composed of 0.5 M 1-methyl-3-propyl imidazolium iodide (PMII), 0.2 M LiI, 0.03 M I_2, and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile (AN) and valeronitrile (VN) (85 : 15 v/v). Active areas of dye-coated TiO_2 films were in the range of 0.25 ~ 0.3 cm^2, which was measured by an image analysis program equipped with a CCD camera (Moticam 1000). TiO_2 film thickness was measured by α-step surface profiler (KLA tencor).

Photovoltaic properties. The incident monochromatic photon-to-current conversion efficiency (IPCE) was obtained with a sandwich cell using of 0.5 M PMII, 0.2 M LiI, 0.03 M I_2, and 0.5 M TBP in AN / VN (85:15 v/v) as redox electrolyte (Fig. 3). The IPCE data of dye **6** turned out to be worst both in the height of the IPCE value and in the width of the wavelengths. Those of dye **1** (reference) and **2** showed relatively comparable results. Highest plateau of 77% was obtained from dye **4** although the span of the wavelengths is not wide enough, and the result of dye **6** was not that much different from dye **4**. The dye **5**, which seemed to be the best dye among the six organic dyes from the UV-Vis absorption data, showed the plateau of 74%, IPCE value higher than 70% over a range of 150 nm (390 nm to 540 nm), and red-shift by 22 nm against dye **3** at 50% level of IPCE data.

As plotted in Figure 4, short-circuit photocurrent density (J_{SC})

showed the lowest value of 3.57 mA/cm^2 for dye **6** and the highest value of 9.33 mA/cm^2 for dye **5**. The tendency of photocurrent density is consistent with the observed IPCE data.

Under AM 1.5 global one sun light intensity of 100 mW/cm^2, J_{SC}, V_{OC}, fill factor (*FF*) and overall conversion efficiency (η) for dyes **1** ~ **6** were summarized in Table 2. The voltage changes within a relatively narrow band (596 ~ 614 mV) for dyes **3** ~ **6** except dye **1** (646 mV) and dye **2** (576 mV), and the fill factor is relatively constant (68.4 to 70.4%) for all dyes **1** ~ **6**. However, a dramatic difference was observed in photocurrent density which spans the lowest value of 3.57 mA/cm^2 for dye **6**, intermediate value of 5.31 and 5.84 mA/cm^2 for dye **1** and **2**, second intermediate value of 7.92 and 7.99 mA/cm^2 for dye **3** and **4**, and the highest value of 9.33 mA/cm^2 for dye **5**. Overall conversion efficiency ranges from the lowest value of 1.48% (dye **6**) to the highest value of 3.91% (dye **5**) as expected from the J_{SC}, V_{OC}, and *FF* values. Although the efficiencies are far below the ruthenium-based DSSCs with about $\eta \approx 11\%$,[18] we think that improvement would be achieved if we put electron-donating amine group on the terminal moiety.

In an effort to find some clues about the experimental results, HOMO-LUMO energy levels for dyes **1** ~ **6** were calculated at the HF-6-31G(d) level and those for dyes **22** ~ **25** (Figure 5), which were developed by J. Ko.[15,19] were also calculated at the same level for comparison purposes.

As summarized in Table 3, the HOMO levels of **1** ~ **6** turned out to be consistently and significantly lower than those of **22** ~ **25** and the LUMO levels are somewhat mixed up. These trends may be used to explain the higher λ_{max} value in UV-Vis absorption spectra for dyes **22** ~ **25** compared to dyes **1** ~ **6**. However, the calculated λ_{max} values of **1** ~ **6** from the HOMO-LUMO energy difference are much shorter than the experimental value. This is just because calculation does not fully consider the effects of solvents and many others, and therefore we should be very careful to use the calculated data quantitatively.

The HOMO and LUMO diagrams of dye **1** ~ **6** were also calculated at the HF-6-31G(d) level to check the smooth transfer of electron density when the dyes are excited by light. As shown in Figure 6, the HOMO and LUMO diagrams of **5** are likely to secure the efficient electron transfer from the aromatic region of the HOMO to the carboxylic region of the LUMO (Figure 6) if electronic transitions occur.

However, because IPCE, short circuit photocurrent density (J_{SC}), and the overall conversion efficiency was affected by many factors including the absolute and relative value of the HOMO and LUMO energy, surface environment on the TiO_2 particle, electrolyte and so on, we are not in a position to pinpoint the reason for the relatively low overall conversion efficiency from these calculation studies so far.

Table 2. J_{SC}, V_{OC}, *FF* and η values for dyes **1** ~ **6**.

Dye	J_{SC} (mA/cm^2)	V_{OC} (mV)	*FF* (%)	η (%)
1	5.84 ± 0.22	646 ± 4	69.9 ± 0.4	2.64 ± 0.09
2	5.31 ± 0.07	576 ± 12	70.4 ± 1.9	2.15 ± 0.10
3	7.92 ± 0.07	607 ± 2	68.4 ± 3.7	3.30 ± 0.22
4	7.99 ± 0.12	614 ± 4	70.4 ± 2.4	3.46 ± 0.18
5	9.33 ± 0.18	597 ± 5	70.3 ± 0.8	3.91 ± 0.05
6	3.57 ± 0.31	596 ± 16	69.3 ± 3.2	1.48 ± 0.24

Table 3. The Calculated HOMO-LUMO Energy Level.[a]

Dye	HOMO (eV)	LUMO(eV)	HOMO-LUMO (eV)	η (%)
1	-7.71474	0.80228	8.52	2.64
2	-7.57867	0.79520	8.37	2.15
3	-7.45212	0.84038	8.29	3.30
4	-7.44831	0.61940	8.07	3.46
5	-7.47117	0.65777	8.13	3.91
6	-7.72100	0.74295	8.46	1.48
22	-6.94566	0.89100	7.84	7.20
23	-6.83816	0.69179	7.53	8.01
24	-6.76822	0.58756	7.36	6.65
25	-6.71080	0.60035	7.31	4.70

[a]MM2 energy minimization and HF-6-31G geometry optimization were carried out before 6-31G(d) geometry optimization was done.

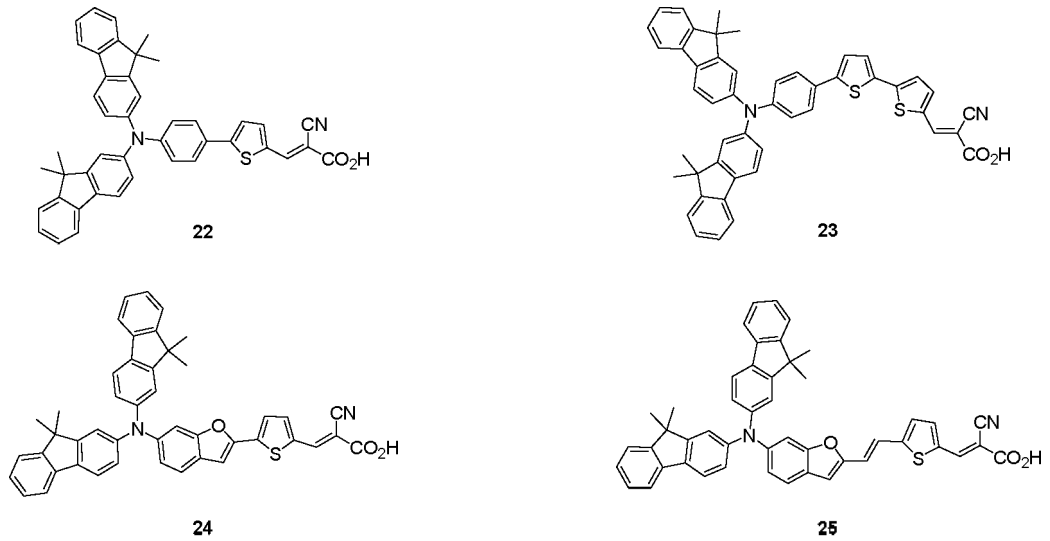


Figure 5. Structures of Organic Dyes **22** ~ **25**.

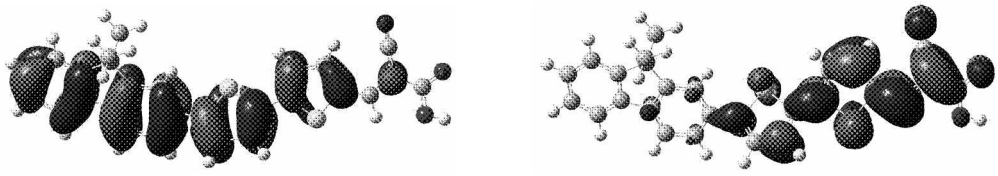


Figure 6. HOMO (left) and LUMO (right) of Dye **5**.

In summary, we investigated the effect of the aromatic linker groups in the absence of strong electron donor groups such as nitrogen on the photovoltaic properties in dye-sensitized solar cells, and we found that the identity (especially, thiophene ring) and/or the order of the aromatic rings are very critical. So far, the order of overall conversion efficiency (η) was as follows: thiophene-thiophene (dye **5**, 3.91%), thiophene-pyridine (dye **4**, 3.46%) and thiophene-benzene (dye **3**, 3.30%), thiophene (dye **1**, 2.64%), benzene-thiophene (dye **2**, 2.15%), and pyridine (dye **6**, 1.48%). We are now undergoing synthesis of newly designed compounds in an effort to improve the overall conversion efficiency, which is based on the previously well-known results and our experimental observations obtained in this project.

Experimental Section

Measurements. UV-Vis spectra of the dyes were recorded in a quartz cell with 1 cm path length on Agilent 8453, where ethanol was used as solvent. Photocurrent-voltage (I-V) measurements were performed using a Keithly model 2400 source measure unit. A solar simulator (Oriel) equipped with a 1000 W Xenon lamp was used as a light source, where light intensity was adjusted with an NREL-calibrated Si solar cell with KG-5 filter for approximating 1 sun light intensity. The photocurrent-voltage measurement of dye sensitized solar cells was performed with an aperture mask.[20] Incident photon-to-current conversion efficiency (IPCE) was measured as a function of wavelength from 300 to 800 nm using a specially designed IPCE system for dye-sensitized solar cell (PV measurements, Inc.). A 75 W Xenon lamp was used as a light source for generating monochromatic beam. Calibration was performed using a silicon photodiode, which was calibrated using the NIST-calibrated photodiode G425 as a standard, and IPCE values were collected under bias white light at a low chopping speed of 10 Hz.

Synthesis of organic dyes. All reactions were carried out under an atmosphere of nitrogen in flame-dried or oven-dried glassware with magnetic stirring. Air sensitive reagents and solutions were transferred via syringe or cannula and were introduced to the apparatus through rubber septa. Tetrahydrofuran (THF), diethyl ether, benzene and toluene were distilled from sodium/benzophenone ketyl. Dichloromethane was distilled from phosphorous pentoxide. Acetonitrile, 1,2-dimethoxyethane (DME) and dimethylformamide (DMF), dimethyl sulfoxide (DMSO), triethylamine (TEA), and other nitrogen containing bases were simple- or vacuum-distilled from calcium hydride. Reactions were monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates (60 F254). Visualization was accomplished with either UV light, or by immersion in solutions of p-anisaldehyde, or phosphomolybdic acid (PMA) followed by heating on a hot plate for ~15 sec. Purification of reaction products was carried out by flash chromatography using EM reagent silica gel 60 (230 ~ 400 mesh). Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Varian Gemini-300 (300 MHz for ^{1}H, and 75 MHz for ^{13}C), or a Varian Inova-500 (500 MHz for ^{1}H, and 125 MHz for ^{13}C) spectrometer. Chemical shifts are reported relative to chloroform (δ 7.26) for ^{1}H NMR and chloroform (δ 77.2) for ^{13}C NMR. Data are reported as (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constant(s) in Hz). The IR spectra were recorded on Mattson galaxy 2020 FT-IR spectrometer. Elemental analyses were performed by the Organic Chemistry Research Center (OCRC) at Sogang University using a Carlo Erba EA 1180 elemental analyzer. LC-Mass was recorded on a Waters Autopurification system LC/MS. High resolution mass spectra were recorded on a 4.7 Tesla IonSpec ESI-FTMS or a Micromass LCT ESI-TOF mass spectrometer. All commercially available compounds were used as received unless stated otherwise.

Synthesis of organic dye 1 [(E)-2-cyano-3-(5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophen-2-yl)acrylic acid] (Scheme 1).

(a) Fluorene (**7**) (0.3 g, 1.80 mmol) was dissolved in the boiling solvent (CH_3COOH : H_2O : H_2SO_4 = 100 : 20 : 3, 6.05 mL) with stirring and the solution was cooled to 60 ~ 65 °C. After addition of periodic acid (70 mg, 0.31 mmol) and iodine (155 mg, 0.62 mmol), the reaction mixture was refluxed for 12 h and cooled to room temperature. The pale yellow solid was collected by filtration, and washed with 2 M aqueous Na_2CO_3 and water. The crude product was purified by recrystallization from hexane to give a white solid (320 mg, 61%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (s, 1H), 7.80-7.68 (m, 2H), 7.53 (d, J = 6.90 Hz, 2H), 7.40-7.31 (m, 2H), 3.87 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.2, 145.6, 142.8, 141.9, 140.9, 135.9, 134.3, 127.5, 127.1, 125.2, 121.7, 120.2, 36.8; GC/mass (*m/z*) calcd. for $C_{13}H_9I$ (M+) 291.97, found : 292.

(b) To a solution of 2-iodo-9*H*-fluorene (1.3 g, 4.45 mmol) and potassium iodide (150 mg, 0.89 mmol) in DMSO (15 mL) were added iodomethane (6.39 g, 45.0 mmol) and potassium hydroxide (2.5 g, 45.0 mmol). The reaction mixture was stirred at room temperature for 12 h. The organic layer was separated and the aqueous layer extracted with EtOAc. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (Hexane, R_f = 0.5) to give adduct (1.1 g, 78%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.89 (s, 1H), 7.80-7.68 (m, 2H), 7.53 (d, J = 6.90 Hz, 2H),

7.40-7.31 (m, 2H), 3.87 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.0, 153.1, 139.0, 138.3, 136.3, 136.1, 132.2, 128.0, 127.3, 122.7, 121.9, 120.2, 47.1, 27.1; GC/mass (*m/z*) calcd. for $C_{15}H_{13}I$ (M+) 320.01, found : 320.

(c) A mixture of 2-iodo-9,9-dimethyl-9*H*-fluorene (**8**) (0.2 g, 0.62 mmol), 2-thiophene boronic acid (88 mg, 0.68 mmol) and $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol) in 2 M aqueous Na_2CO_3 solution (1.15 mL), H_2O (0.23 mL), and dimethoxyethane (2.06 mL) was refluxed for 12 h. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (Hexane, R_f = 0.5) to give adduct (100 mg, 58%) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, J = 8.10 Hz, 2H), 7.68 (s, 1H), 7.64-7.61 (m, 1H), 7.47-7.45 (m, 1H), 7.47-7.45 (m, 1H), 7.39-7.34 (m, 3H), 7.31 (d, J = 5.10 Hz, 1H), 7.13 (dd, 1H), 1.56 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.5, 154.0, 145.2, 138.9, 133.6, 128.2, 127.5, 127.2, 125.3, 124.7, 123.1, 122.8, 120.6, 120.4, 120.2, 47.1, 31.1, 27.4; GC/mass (*m/z*) calcd. for $C_{19}H_{16}S$ (M+) 276.10, found : 276.

(d) *n*-BuLi (2.9 mL, 2.15 M solution in hexane) was added to 2-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophene (**10**) (0.94 g, 3.40 mmol) in dry THF (11.3 mL) at −25 °C. After stirring at 0 °C for 2 h, DMF (0.84 mL, 10.2 mmol) was added at −78 °C. The reaction mixture was stirred at room temperature for 12 h. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EtOAc : Hexane = 1 : 3, R_f = 0.5) to give product (0.7 g, 68%) as a orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.90 (s, 1H), 7.78-7.66 (m, 8H), 7.45 (t, J = 3.50 Hz, 2H), 7.37 (t, J = 4.20 Hz, 2H), 1.54 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 182.9, 155.2, 154.8, 154.2, 142.2, 140.9, 138.4, 137.7, 132.1, 128.2, 127.4, 125.8, 124.0, 122.9, 120.8, 120.8, 120.6, 47.2, 27.3; GC/mass (*m/z*) calcd. for $C_{20}H_{16}OS$ (M+) 304.09, found : 304.

(e) To a mixture of 5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophene-2-carbaldehyde (0.5 g, 1.64 mmol) and cyanoacetic acid (0.28 g, 3.29 mmol) were added acetonitrile (5.5 mL) and piperidine (0.16 mL, 1.64 mmol) at room temperature. The solution was refluxed for 12 h. After cooling to room temperature, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was washed by ether (EtOAc : MeOH = 1 : 1, R_f = 0.6) to give adduct (480 mg, 78%) as a red solid. IR (neat) 1684, 1569, 1419, 1335, 1291, 1250, 1221, 1071 cm^{-1}; ^{1}H NMR (DMSO, 500 MHz) δ 8.47 (s, 1H), 8.02 (d, J = 4.50 Hz, 2H), 7.94 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 4.30 Hz, 1H), 7.85 (d, J = 4.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 4.0 Hz, 1H), 7.37 (t, J = 4.0 Hz, 2H), 1.50 (s, 6H); ^{13}C NMR (DMSO, 125 MHz) δ 163.6, 154.1, 153.9, 153.0, 145.9, 141.0, 140.3, 137.6, 134.5, 131.4, 128.0, 127.2, 125.6, 124.3, 122.9, 121.1, 120.8, 120.6, 116.9, 103.1, 46.7, 26.7; LC/mass (*m/z*) calcd. for $C_{19}H_{16}S$ $C_{23}H_{17}NO_2S$ (M+H) 372.45, found : 372.

Synthesis of organic dye 2 [(E)-3-(5-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl)thiophen-2-yl)-2-cyanoacrylic acid] (Scheme 2).

(a) A mixture of **8** (1.0 g, 3.12 mmol), 4-bromophenylboronic acid (815 mg, 3.43 mmol) and $Pd(PPh_3)_2Cl_2$ (200 mg, 0.28 mmol) in 2 M aqueous Na_2CO_3 solution (5.7 mL), H_2O (1.15 mL), and dimethoxyethane (10.4 mL) was refluxed for 12 h. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 70, R_f = 0.5) to give adduct (570 mg, 52%) as a white solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.79 (s, 1H), 7.76-7.74 (m, 2H), 7.59 (s, 1H), 7.57 (s, 1H), 7.53 (s, 1H), 7.51 (m, 1H), 7.46-7.44 (m, 1H), 7.35-7.33 (m, 2H), 1.53 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 154.6, 154.0, 140.9, 139.3, 139.0, 138.8, 132.0, 129.0, 127.6, 127.3, 126.2, 122.8, 121.5, 121.3, 120.6, 120.3, 47.1, 27.4; GC/mass (*m/z*) calcd. for $C_{21}H_{17}Br$ (M+) 348.05, found : 348.

(b) A mixture of 2-(4-bromophenyl)-9,9-dimethyl-9*H*-fluorene (1.30 g, 3.72 mmol), 2-thiopheneboronic acid (670 mg, 5.21 mmol) and $Pd(PPh_3)_2Cl_2$ (240 mg, 0.34 mmol) in 2 M aqueous Na_2CO_3 solution (7.0 mL), H_2O (1.38 mL), and dimethoxyethane (12.4 mL) was refluxed for 12 h. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 20, R_f = 0.3) to give adduct (920 mg, 71%) as a yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.80-7.78 (m, 2H), 7.74-7.67 (m, 5H), 7.62-7.59 (m, 2H), 7.46 (d, J = 6.3 Hz, 1H) 7.37-7.30 (m, 3H), 7.11 (s, 1H); GC/mass (*m/z*) calcd. for $C_{25}H_{20}S$ (M+) 352.13, found : 352.

(c) *n*-BuLi (0.60 mL, 2.15 M solution in hexane) was added to 2-(4-(9,9-dimethyl-9*H*-fluoren-2-yl)phenyl)thiophene (**12**) (0.20 g, 0.72 mmol) in dry THF (2.4 mL) at −25 °C. After stirring at 0 °C for 2 h, DMF (0.17 mL, 2.16 mmol) was added at −78 °C. The reaction mixture was stirred at room temperature for 12 h. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EtOAc : Hexane = 1 : 3, R_f = 0.4) to give product (0.7 g, 68%) as a orange solid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.91 (s, 1H), 7.82-7.60 (m, 11H), 7.47 (d, J = 4.5 Hz, 2H), 7.36 (t, J = 3.5 Hz, 2H), 1.55 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.2, 154.5, 154.1, 144.3, 140.8, 139.8, 139.0, 138.8, 133.4, 128.3, 127.8, 127.5, 127.2, 126.5, 126.1, 125.0, 123.3, 122.81, 121.3, 120.5, 120.3, 47.1, 27.4; LC/mass (*m/z*) calcd. for $C_{26}H_{20}OS$ (M+H) 381.12, found : 381.

(d) To a mixture of 5-(4-(9,9-dimethyl-9*H*-fluoren-2-yl) phenyl) thiophene-2-carbaldehyde (0.33 g, 1.08 mmol) and cyanoacetic acid (0.28 g, 2.16 mmol) were added acetonitrile (5.4 mL) and piperidine (92 mg, 1.08 mmol) at room temperature. The solution was refluxed for 12 h. After cooling to room temperature, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were

washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was washed by ether (EtOAc : MeOH = 1 : 1, R_f = 0.8) to give adduct (260 mg, 65%) as a red solid. IR (neat) : 1693, 1576, 1424, 1289, 1259, 1223 cm^{-1}; ^1H NMR (DMSO, 300 MHz) 8.48 (s, 1H), 8.03 (s, 1H), 7.95-7.85 (m, 7H), 7.73 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 6.5 Hz, 1H), 7.35 (m, 2H), 1.51 (s, 6H); ^{13}C NMR (DMSO, 125 MHz) δ 154.2, 153.7, 141.4, 138.5, 138.2, 138.1, 131.2, 127.7, 127.1, 126.7, 125.8, 125.2, 122.8, 121.1, 120.7, 120.4, 104.3; GC/mass (*m/z*) calcd. for $C_{29}H_{21}NO_2S$ (M+) 447.13 , found : 447.

Synthesis of organic dye 3 [(E)-3-(4-(5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid] (Scheme 3).

(a) To a solution 4-bromobenzaldehyde (5 g, 27 mmol) in benzene (44 mL) were added neopentyl glycol (3.38 g, 32.4 mmol) and *p*-TsOH (56.5 mg 2.97 mmol). The resulting mixture was stirred at 80 °C for 5 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL) and washed with saturated aqueous $NaHCO_3$ (30 mL × 3) and saturated aqueous NaCl. The solution was concentrated *in vacuo* to yield 2-(4-bromophenyl)-5,5-dimethyl-1,3-dioxane as a white solid 6.19 g (85%). (EA : Hexane = 1 : 6, R_f = 0.45); IR (neat) 2957, 2862, 1467, 1415, 1384, 1101 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.51-7.37 (dd, 4H), 5.35 (s, 1H), 3.78-3.62 (dd, 4H), 1.28 (s, 3H), 0.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.6, 131.4, 127.9, 122.9, 30.9, 30.2, 23.0, 21.9; GC/mass (*m/z*) calcd. for $C_{12}H_{15}BrO_2$ (M+) 270.02, found : 270.

(b) A mixture of 2-(4-bromophenyl)-5,5-dimethyl-1,3-dioxane (5 g, 18.52 mmol), 2-thiopheneboronic acid (2.61 g, 20.4 mmol) and $Pd(PPh_3)_2Cl_2$ (1.2 g, 1.7 mmol) in 2 M aqueous Na_2CO_3 solution (140 mL), H_2O (46.6 mL) and dimethoxyethane (125 mL) was stirred at 100 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with EtOAc. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 6, R_f = 0.40) to give adduct (3.65 g, 72%) as a light brown solid.; IR (neat) 2952, 2850, 1097, 811 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.64-7.50 (dd, 4H), 7.33-7.31 (dd, 1H), 7.29-7.27 (dd, 1H), 7.09-7.07 (m, 1H), 5.41 (s, 1H), 3.81-3.65 (dd, 4H), 1.31 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.1, 137.7, 134.9, 128.0, 126.7, 125.9, 124.9, 123.3, 30.6, 30.3, 23.1, 21.9; GC/mass (*m/z*) calcd. for $C_{16}H_{18}O_2S$ (M+) 274.10, found : 274.

(c) *n*-BuLi (2.25 M, 2.7 mL) was added dropwise to a solution of 5,5-dimethyl-2-(4-(thiophen-2-yl)phenyl)-1,3-dioxane (1 g, 3.65 mmol) in THF (18 mL) at −25 °C. After stirring at 0 °C for 2 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.5 g, 8.03 mmol) was added at −78 °C. The reaction mixture was stirred at room temperature overnight. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 6, R_f = 0.33) to give adduct (744.9 mg, 51%) as a dark blue solid.; IR (neat) 2952, 1534, 1512, 1458, 1141, 1104, 754 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.67-7.64 (d, 2H), 7.59-7.58 (d, 1H), 7.53-7.50 (d, 2H), 7.39-7.38 (d, 1H), 5.40 (s, 1H), 3.79-3.64 (dd, 4H), 1.36 (s, 12H), 1.29 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.0, 138.2, 138.1, 134.7, 126.8, 126.1, 124.7, 101.3, 30.9, 30.3, 24.9, 24.8, 23.1, 21.9; GC/mass (*m/z*) calcd. for $C_{22}H_{29}BO_4S$ (M+) 400.18, found : 400.

(d) A mixture of **8** (700 mg, 2.19 mmol), **15** (964.5 mg, 2.41 mmol) and $Pd(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol) in 2 M aqueous Na_2CO_3 solution (16.53 mL), H_2O (5.51 mL) and dimethoxyethane (14.77 mL) was stirred at 100 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with EtOAc. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 2, R_f = 0.40) to give adduct (602 mg, 59%) as a yellow solid.; IR (neat) 2945, 1601, 1439, 1377, 1103, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.74-7.61 (m, 5H), 7.55-7.53 (d, 2H), 7.46-7.44 (s, 1H), 7.34 (s, 4H), 5.42 (s, 1H), 3.82-3.66 (dd, 4H), 1.32 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.5, 153.9, 144.5, 143.1, 138.9, 137.8, 134.9, 133.4, 127.5, 127.2, 126.9, 125.6, 124.9, 124.4, 124.0, 122.8, 120.6, 120.2, 120.0, 101.5, 78.4, 77.8, 76.0, 47.1, 30.4, 27.3, 23.2, 22.0; LC/mass (*m/z*) calcd. for $C_{31}H_{30}O_2S$ (M+H) 467.20, found : 467.

(e) A solution of 2-(4-(5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophen-2-yl)phenyl)-5,5-dimethyl-1,3-dioxane (450 mg, 0.965 mmol) in TFA (6 mL), THF (60 mL) and H_2O (6 mL) was stirred refluxed overnight. The solution was poured into saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 2, R_f = 0.30) to give adduct (355.8 mg, 97%) as a yellow solid.; IR (neat) 2955, 2923, 1694, 1598, 1442, 831, 802 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 10.00 (s, 1H), 7.92-7.79 (dd, 4H), 7.76-7.74 (d, 2H), 7.69 (s, 1H), 7.66-7.63 (d, 1H), 7.48-7.45 (m, 2H), 7.40-7.34 (m, 3H), 1.55 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 191.6, 154.6, 153.9, 146.7, 141.4, 140.2, 139.5, 138.7, 135.1, 132.9, 130.7, 127.7, 127.3, 126.3, 125.7, 125.0, 124.4, 122.8, 120.7, 120.3, 120.1, 47.1, 27.3; LC/mass (*m/z*) calcd. for $C_{26}H_{20}OS$ (M+H) 381.12, found : 381.

(f) To a mixture of 4-(5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophen-2-yl)benzaldehyde (400 mg, 1.05 mmol) and cyanoacetic acid (178.6 mg, 2.10 mmol) were added acetonitrile (10 mL) and piperidine (26.8 mg, 0.315 mmol) at room temperature. The solution was refluxed overnight. After cooling to room temperature, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EtOAc : MeOH = 1 : 1, R_f = 0.73) to give adduct (244.1 mg, 52%) as a yellow solid.; IR (neat) 3446, 2955, 2924, 2320, 1628, 1583, 1470, 1440, 1374, 801 cm^{-1}; ^1H NMR (DMSO, 300 MHz) δ 7.95-7.93 (m, 4H), 7.85-7.83 (m, 3H), 7.72-7.68 (m, 4H), 7.58-7.56 (d, 1H), 7.26-7.33 (m, 2), 1.49 (s, 6H); ^{13}C NMR (DMSO, 125 MHz) δ 163.0, 154.3, 153.6, 152.8, 151.2, 147.1, 143.7, 142.6, 138.7, 137.9, 135.8, 132.6, 128.1, 127.7, 127.5, 127.2, 125.2, 124.7, 122.8, 120.9, 120.4, 119.9, 119.2, 118.4, 46.7, 26.8; LC/mass (*m/z*) calcd. for $C_{29}H_{21}NO_2S$ (M+H)

448.13, found : 448.

Synthesis of organic dye 4 [(E)-3-(6-(5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophen-2-yl)pyridin-3-yl)-2-cyanoacrylic acid] (Scheme 4).

(a) To a solution of 6-chloronicotinic acid (12.8 g, 81.2 mmol) in THF (150 mL) was added a LAH (3.795 g, 100 mmol) at 0 °C. The resulting orange mixture was stirred at 0 °C for 3 h and the reaction was quenched by the sequential addition of 3.0 mL H_2O, 3.0 mL of 15% aqueous NaOH, and 9.0 mL H_2O. The reaction mixture was diluted with THF, the precipitate were then filtered through celite with the aid of EtOAc. The solution was concentrated *in vacuo* to yield 6-chloro-3-pyridylcarbinol as a yellow oil (8.15g, 70%), which was used directly in the next step.; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.39-8.38 (d, 1H), 7.73-7.69 (dd, 1H), 7.35-7.32 (s, 1H), 4.74 (s, 2H).

(b) To a solution of oxalyl chloride (8.0 mL, 92.0 mmol) in CH_2Cl_2 (250 mL) was added DMSO (10.50 mL, 148.0 mmol) at -78 °C. After 10 min at -78 °C, a solution of 6-chloro-3-pyridylcarbinol (8.47g, 59 mmol) in CH_2Cl_2 (50 mL) was added via cannula. After 15 min's stirring at -78 °C, TEA (20.0 mL, 144.0 mmol) was added and the reaction mixture was warmed to 0 °C. The reaction mixture was diluted with Et_2O (500 mL), saturated aqueous $NaHCO_3$ (500 mL), and then saturated aqueous NaCl. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to yield 6.78 g of 6-chloropyridine-3-carboxyaldehyde (3) as light yellow solid (84%). (EA : Hexane = 1 : 1, R_f = 0.7); IR (neat) 1697, 1584, 1567, 1459 835 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.09 (s, 1H), 8.87-8.86 (d, 1H), 8.16-8.12 (dd, 1H), 7.53-7.50 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.2, 160.0, 152.4, 138.0, 130.4, 125.2; GC/mass (*m/z*) calcd. for C_6H_4ClNO (M+) 140.99, found : 141.

(c) To solution of 6-chloropyridine-3-carboxyaldehyde (1.54 g, 11 mmol) in benzene (18 mL) were added neopentyl glycol (1.36 g, 13 mmol) and *p*-TsOH (230 mg 1.21 mmol). The resulting mixture was stirred for 5 h at 80 °C. The reaction mixture was diluted with CH_2Cl_2 (30 mL), and washed with saturated aqueous $NaHCO_3$ (30 mL × 3) and saturated aqueous NaCl. The solution was concentrated *in vacuo* to yield 2.38 g of 2-chloro-5-(5,5-dimethyl-1,3-dioxan-2-yl)pyridine as a yellow solid (85%). (EA : Hexane = 1 : 3, R_f = 0.7); IR (neat) 2953, 2867, 1587, 1461, 1103, 753 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.49-8.48 (d, 1H), 7.81-7.78 (dd, 1H), 7.35-7.32 (s, 1H), 5.42 (s, 1H), 3.79-3.63 (dd, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.9, 151.7, 148.1, 136.8, 133.1, 123.9, 99.0, 30.9, 30.2, 23.0, 21.83; GC/mass (*m/z*) calcd. for $C_{11}H_{14}ClNO_2$ (M+) 227.02, found : 277.

(d) A mixture of 2-chloro-5-(5,5-dimethyl-1,3-dioxan-2-yl) pyridine (2.38 g, 10.48 mmol), 2-thiopheneboronic acid (1.48 g, 11.53 mmol) and $Pd(PPh_3)_2Cl_2$ (622 mg, 0.943 mmol) in 2 M aqueous Na_2CO_3 solution (79.2 mL), H_2O (26.4 mL) and dimethoxyethane (70.95 mL) was stirred at 100 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with EtOAc. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 4, R_f = 0.35) to give adduct (1.54 g, 60%) as a ivory solid.; IR (neat) 2955, 2858, 1596,1535, 1497, 1428, 1387, 827, 695 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.65-8.64 (d, 1H), 7.86-7.82 (dd, 1H), 7.67-7.60 (m, 2H), 7.40-7.38 (dd, 1H), 7.11-7.09 (m, 1H), 5.43 (s, 1H), 3.79-3.63 (dd, 4H), 1.28 (s, 3H), 0.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.1, 153.0, 148.0, 144.6, 134.6, 132.3, 128.0, 127.7, 124.8, 118.3, 99.8, 30.9, 30.3, 23.0, 21.9; GC/mass (*m/z*) calcd. for $C_{15}H_{17}NO_2S$ (M+) 275.09, found : 275.

(e) *n*-BuLi (2.25 M, 2.7 mL) was added dropwise to a solution of 5-(5,5-dimethyl-1,3-dioxan-2-yl)-2-(thiophen-2-yl)pyridine (1 g, 3.64 mmol) in THF (18 mL), at −25 °C. After stirring at 0 °C for 2 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.49 g, 8 mmol) was added at −78 °C. The reaction mixture was stirred at room temperature. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 4, R_f = 0.30) to give adduct (730.2 mg, 50%) as a light yellow solid.; IR (neat) 2956, 2861, 1567,1533, 1453, 1141, 1102 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.67 (s, 1H), 7.86-7.82 (dd, 1H), 7.68 (s, 1H), 7.65 (s, 1H), 7.61-7.60 (d, 1H), 5.44 (s, 1H), 3.79-3.64 (dd, 4H), 1.35 (s, 12H), 1.28 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.9, 152.8, 150.9, 148.1, 137.9, 134.6, 132.6, 126.2, 119.0, 30.9, 30.3, 24.9, 24.8, 22.9, 21.9; GC/mass (*m/z*) calcd. for $C_{21}H_{28}BNO_4S$ (M+) 401.13, found : 401.

(f) A mixture of **8** (700 mg, 2.19 mmol), 5-(5,5-dimethyl-1,3-dioxan-2-yl)-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)pyridine (**17**) (966.8 mg, 2.41 mmol) and $Pd(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol) in 2 M aqueous Na_2CO_3 solution (16.53 mL), H_2O (5.51 mL) and dimethoxyethane (14.77 mL) was stirred at 100 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with EtOAc. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 4, R_f = 0.75) to give adduct (603 mg, 59%) as a yellow solid.; IR (neat) 2957, 1470,1443, 1390, 1103 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.68 (s, 1H), 7.90-7.88 (d, 1H), 7.75-7.65 (m, 6H), 7.46-7.44 (m, 1H), 7.40-7.39 (d, 1H), 7.36-7.32 (m, 2H), 5.46 (s, 1H), 3.82-3.66 (dd, 4H), 1.53 (s, 6H), 1.30 (s, 3H), 0.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.9, 154.4, 153.9, 152.9, 148.0, 147.1, 143.3, 139.1, 138.7, 134.5, 133.2, 132.2, 127.4, 127.1, 125.7, 124.7, 123.8, 122.6, 120.4, 120.1, 120.1, 118.0, 99.8, 46.9, 30.9, 30.3, 27.2, 23.0, 21.9; LC/mass (*m/z*) calcd. for $C_{30}H_{29}NO_2S$ (M+H) 468.19, found : 468.

(g) A mixture of 5-(5,5-dimethyl-1,3-dioxan-2-yl)-2-(5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophen-2-yl)pyridine (450 mg, 0.963 mmol) in TFA (6 mL), THF (60 mL) and H_2O (6 mL) was refluxed overnight. The solution was poured into saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 4, R_f = 0.55) to give adduct (344.9 mg, 94%) as a light yellow solid.; IR (neat) 2958, 1699, 1474, 1441, 1415 cm^{-1}; ^{1}H NMR (DMSO, 300 MHz) δ 9.05 (s, 1H), 8.34-8.23 (dd, 2H), 8.18 (s, 1H), 7.99-7.67 (d, 2H),

7.91 (s, 2H), 7.76-7.74 (d, 1H), 7.60 (s, 1H), 7.40-7.38 (d, 2H), 1.49 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.9, 157.1, 154.5, 154.0, 152.9, 149.9, 141.9, 139.7, 138.5, 136.2, 132.7, 129.5, 128.2, 127.7, 127.2, 124.9, 124.3, 122.6, 120.5, 120.2, 120.2, 118.4, 47.0, 27.2 ; GC/mass (*m/z*) calcd. for $C_{25}H_{19}NOS$ (M+) 381.62, found : 382.

(h) To a mixture of 6-(5-(9,9-dimethyl-9*H*-fluoren-2-yl)thiophen-2-yl)nicotinaldehyde (578 mg, 1.52 mmol) and cyanoacetic acid (258.6 mg, 3.04 mmol) were added acetonitrile (20 mL) and piperidine (38.83 mg, 0.456 mmol) at room temperature. The solution was refluxed overnight. After cooling to room temperature, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EtOAc : MeOH = 1 : 1, R_f = 0.8) to give adduct (341 mg, 50%) as a yellow solid. ; IR (neat) 3446, 3006, 2988, 2359, 1626, 1461, 1385, 1375 cm^{-1}; ^{1}H NMR (DMSO, 300 MHz) δ 8.99 (s, 1H), 8.48 (s, 1H), 8.24-8.12 (m, 2H), 8.00-7.98 (m, 2H), 7.90-7.88 (d, 2H), 7.75 (s, 2H), 7.583 (s, 1H), 7.36 (s, 2H), 1.49 (s, 6H); ^{13}C NMR (DMSO, 125 MHz) δ 154.3, 153.6, 147.0, 144.4, 142.3, 141.2, 138.5, 137.9, 135.7, 132.5, 132.2, 130.3, 128.8, 127.6, 127.2, 126.4, 125.6, 125.3, 125.2, 124.6, 122.8, 120.8, 120.3, 119.7, 119.2, 40.6, 26.8; LC/mass (*m/z*) calcd. for $C_{28}H_{20}N_2O_2S$ (M+H) 449.12, found : 449.

Synthesis of organic dye 5 [(E)-2-cyano-3-(5'-(9,9-dimethyl-9*H*-fluoren-2-yl)-2,2'-bithiophen-5-yl)acrylic acid] (Scheme 5).

(a) *n*-BuLi (2.25 M, 2.7 mL) was added dropwise to a solution of 2,2-bithiophene (300 mg, 1.80 mmol) in THF (6 mL) at -25 °C. The solution was stirred at 0 °C for 2 h. After cooling to -78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8.37 mg, 4.5 mmol) was added and the reaction mixture was stirred at room temperature overnight. The solution, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 20, R_f = 0.4) to give adduct (220 mg, 42%) as a blue solid.; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (d, J = 3.6 Hz, 1H), 7.24-7.22 (m, 3H), 7.02-6.99 (m, 1H), 1.34 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.1, 138.0, 137.2, 128.0, 125.0, 124.9, 124.4, 84.2, 24.8, 24.7; GC/mass (*m/z*) calcd. for $C_{14}H_{17}BO_2S_2$ (M+) 292.22, found : 292.

(b) A mixture of 2-(2,2'-bithiophen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.30 g, 0.94 mmol), **8** (0.33 g, 1.12 mmol) and $Pd(PPh_3)_4$ (0.055 mg, 0.047 mmol) in 2 M aqueous K_2CO_3 solution (0.8 mL), and THF (3.0 mL) was refluxed for 12 h. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with EtOAc. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 20, R_f = 0.3) to give adduct (150 mg, 45%) as a yellow solid. ; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.72 (d, J = 7.2 Hz, 1H), 7.64-7.58 (m, 2H), 7.43 (m, 1H), 7.34-7.33 (m, 1H), 7.29-7.16 (m, 3H), 7.05-7.04 (m, 1H), 1.54 (s, 6H); GC/mass (*m/z*) calcd. for $C_{23}H_{18}S_2$ (M+) 358.08, found : 358.

(c) *n*-BuLi (0.60 mL, 2.15 M solution in hexane) was added to 5-(9,9-dimethyl-9*H*-fluoren-2-yl)-2,2'-bithiophene (**19**) (0.20 g, 0.72 mmol) in dry THF (2.4 mL) at −25 °C. After stirring at 0 °C for 2 h, DMF (0.17 mL, 2.16 mmol) was added at −78 °C. The reaction mixture was stirred at room temperature for 12 h. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EtOAc : Hexane = 1 : 3, R_f = 0.4) to give product (0.7 g, 63%) as a orange solid. ; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.80 (s, 1H), 7.68-7.61 (m, 3H), 7.58-7.52 (m, 2H), 7.37 (m, 1H), 7.29-7.18 (m, 6H), 1.47 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 131.9, 128.0, 127.0, 126.2, 124.2, 122.8, 121.4, 120.6, 120.4, 154.6, 154.2, 154.1, 137.7; LC/mass (*m/z*) calcd. for $C_{24}H_{18}OS_2$ (M+H) 387.08, found : 387.

(d) To a mixture of 5'-(9,9-dimethyl-9*H*-fluoren-2-yl)-2,2'-bithiophene-5-carbaldehyde (280 mg, 0.73 mmol) and cyanoacetic acid (123 mg, 1.45 mmol) were added acetonitrile (10 mL) and piperidine (62 mg, 0.73 mmol) at room temperature. The solution was refluxed overnight. After cooling to room temperature, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was washed by ether (EtOAc : MeOH = 1 : 1, R_f = 0.6) to give adduct (200 mg, 70%) as a red solid.; IR (neat) 1613, 1579, 1379, 1264, 1137, 1047 cm^{-1}; ^{1}H NMR (DMSO, 300 MHz) δ 8.02 (s, 1H), 7.92-7.83 (m, 4H), 7.71-7.64 (m, 4H), 7.57-7.53 (m, 2H), 7.47 (m, 1H), 7.36-7.33 (m, 3H) 1.50 (s, 6H); ^{13}C NMR (DMSO, 75 MHz) δ 163.8, 154.6, 153.9, 144.8, 141.5, 140.5, 138.9, 138.2, 136.7, 135.9, 134.8, 132.3, 127.9, 127.4, 127.1, 125.3, 124.8, 124.5, 123.0, 121.0, 120.5, 120.0, 119.4, 109.5, 46.9, 26.9; LC/mass (*m/z*) calcd. for $C_{27}H_{19}NO_2S_2$ (M+H) 454.09 , found : 454.

Synthesis of organic dye 6 [(E)-3-(6-(9,9-dimethyl-9*H*-fluoren-2-yl)pyridin-3-yl)-2-cyanoacrylic acid] (Scheme 6).

(a) *n*-BuLi (2.25 M, 2.7 mL) was added dropwise to a solution of **8** (2 g, 6.25 mmol) in THF (50 mL) at −78 °C. After stirring the reaction mixture for 1 h at −78 °C, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.4 g, 7.5 mmol) was added and the reaction mixture was stirred at room temperature overnight. The organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with Na_2SO_4. The solution was concentrated *in vacuo* to yield 2-(9,9-dimethyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a yellow oil (1 g, 50%), which was used directly in the next step.; GC/mass (*m/z*) calcd. for $C_{21}H_{25}BO_2$ (M+) 320.19, found : 320.

(b) A mixture of 6-chloropyridine-3-carboxyaldehyde (900 mg, 6.4 mmol), 2-(9,9-dimethyl-9*H*-fluoren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.24 g, 7.02 mmol) and $Pd(PPh_3)_2Cl_2$ (404.3 mg, 0.576 mmol) in 2 M aqueous Na_2CO_3 solution (11.8 mL), H_2O (2.37 mL) and dimethoxyethane (21 mL) was stirred at 100 °C overnight. After cooling to room temperature, the reaction mixture was filtered through celite, and the filtrate was poured into water and extracted with EtOAc. The combined organic phases were washed with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EA : Hexane = 1 : 2,

R_f = 0.45) to give adduct (1.244 g, 65%) as a light yellow solid.; IR (neat) 2961, 1697, 1556, 1479, 1448, 1363, 831 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 10.1 (s, 1H), 9.15-9.14 (d, 1H), 8.26-8.25 (d, 1H), 8.23-8.22 (m, 1H), 8.08-8.05 (dd, 1H), 7.99-7.96 (d, 1H), 7.86-7.83 (d, 1H), 7.80-7.77 (m, 1H), 7.49-7.46 (m, 1H), 7.39-7.36 (m, 2H), 1.57 (s, 6H); ^{13}C NMR (DMSO, 125 MHz) δ 190.5, 162.3, 154.4, 152.4, 141.6, 138.3, 137.9, 136.8, 136.4, 129.6, 128.0, 127.2, 126.8, 122.7, 121.8, 120.6, 120.5, 120.4, 47.1, 27.1 ; GC/mass (*m/z*) calcd. for $C_{21}H_{17}NO$ (M+) 299.13, found : 299.

(c) To a mixture of 6-(9,9-dimethyl-9*H*-fluoren-2-yl)nicotinaldehyde (**21**) (2.3 g, 7.7 mmol) and cyanoacetic acid (1.31 g, 15.4 mmol) were added acetonitrile (10 mL) and piperidine (196.7 mg, 2.31 mmol) at room temperature. The solution was refluxed overnight. After cooling to room temperature, the organic phase was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic phases were washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*. The crude residue was purified by column chromatography (EtOAc : MeOH = 1 : 1, R_f = 0.6) to give adduct (1.747 g, 62%) as a yellow solid. ; IR (neat) 3446, 2360, 1731, 1584, 1474, 1379 cm^{-1}; ^1H NMR (DMSO, 300 MHz) δ 9.19 (s, 1H), 8.62-8.59 (d, 1H), 8.45-8.42 (d, 2H), 8.35-8.32 (d, 1H), 8.25-8.22 (d, 1H), 8.00-7.97 (d, 1H), 7.92 (s, 1H), 7.60 (s, 1H), 7.39-7.38 (d, 2H), 1.52 (s, 6H); ^{13}C NMR (DMSO, 125 MHz) δ 163.0, 159.2, 154.1, 154.0, 152.6, 151.0, 140.8, 137.8, 137.0, 136.4, 128.1, 127.2, 126.5, 126.0, 122.9, 121.5, 120.7, 120.6, 120.3, 116.2, 104.8, 46.7, 26.8; LC/mass (*m/z*) calcd. for $C_{24}H_{18}N_2O_2$ (M+H) 367.14, found : 367.

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