Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Near-Infrared Absorbing Heterocyclic Quinoid Donors for Organic Photovoltaic Devices

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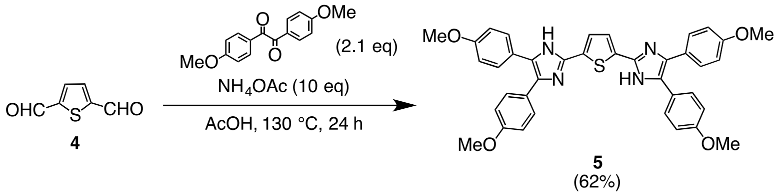
1. General consideration for synthesis and characterization

NMR spectra were recorded by JEOL ECA-500 spectrometer (^{1}H NMR, 500 MHz; ^{13}C NMR, 125 MHz) and JEOL ECX-400 spectrometer (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz). Chemical data for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$: δ 7.26, DMSO-d_6: δ 2.50). Chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.0, DMSO-d_6: δ 39.51). High resolution mass spectra were obtained with JEOL JMS-700P (FAB) mass spectrometer. UV-vis-NIR spectra were measured with a JASCO V-670 spectrometer in spectral grade dichloromethane. Transmittance and reflectance measurements of thin-films were also conducted by using the same spectrometer with an integrating sphere. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed on a HOKUTO DENKO HZ-5000 voltammetry analyzer. All CV measurements were carried out at room temperature in a one-compartment cell under N_2 gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag^+ reference electrode (10 mM $AgClO_4$ in 0.1 M Bu_4NPF_6). Melting points of solid materials were determined on a Mel-Temp II capillary melting-point apparatus and are uncorrected. Thermogravimetry-differential thermal analysis (TG-DTA) was performed with Rigaku TG8120. Temperature was raised at 10 K/min under N_2, and Al_2O_3 was used as a reference sample. Photoelectron Yield Spectroscopy (PYS) measurement was performed with PYS-201 (Sumitomo Heavy Industries, Ltd.). A Xe lamp was used as a light source for sample illumination. Column chromatography was performed using Kanto Silica Gel 60N. All reactions were carried out under argon atmosphere unless otherwise noted. Reagents and chemicals were purchased from Tokyo Chemical Industry Co., Sigma-Aldrich Co., Inc., Wako Pure Chemical Industries, or other commercial suppliers, and were used as received.

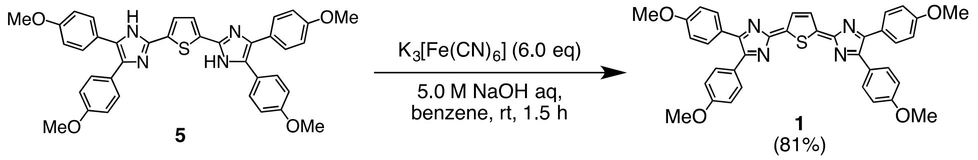
2. Experimental procedures and spectra data for all compounds

Synthesis of 2,5-bis(4,5-bis(4-methoxyphenyl)-1*H*-imidazol-2-yl)thiophene (5).



A mixture of thiophene-2,5-dicarbaldehyde (**4**)[1] (50 mg, 0.36 mmol), 1,2-bis(4-methoxyphenyl)ethane-1,2-dione (203 mg, 0.75 mmol), and ammonium acetate (275 mg, 3.57 mmol) was dissolved in acetic acid (5.0 mL), and heated at 130 °C for 24 h. After cooling to room temperature, the mixture was added water to precipitate the product. The solid was collected by filtration, and recrystallized from a mixture of acetone and toluene to give **5** (141 mg, 0.22 mmol, 62%) as a yellow solid. mp 172–180 ºC (dec.); ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.75 (s, 6H), 3.80 (s, 6H), 6.89 (d, J = 8.6 Hz, 4H), 7.03 (d, J = 8.6 Hz, 4H), 7.41 (d, J = 8.6 Hz, 4H), 7.44 (d, J = 8.6 Hz, 4H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 55.08, 55.25, 113.74, 114.24, 123.27, 124.32, 127.10, 127.43, 128.19, 129.69, 133.41, 136.37, 140.70, 158.07, 158.91 ; HRMS (FAB$^+$) m/z calcd for $C_{38}H_{33}N_4O_4S$ $[M]^+$ 640.2144, found: 641.2142.

Synthesis of 2,5-bis(4,5-bis(4-methoxyphenyl)-2*H*-imidazol-2-ylidene)-2,5-dihydrothiophene (1).



A solution of **5** (100 mg, 0.156 mmol) in benzene (20 mL) was added aqueous NaOH (5.0 M, 7.5 mL) at room temperature. The mixture was added potassium ferricyanide (514 mg, 1.56 mmol), and the color of the solution immediately changed to deep blue. After stirring for 1.5 h at room temperature, the organic layer was extracted chloroform, and then washed with water. The extract was dried over $MgSO_4$, and concentrated to give a crude product. The crude product was purified by silica gel column chromatography (chloroform:Et_2O = 3:1) and recrystallization from a mixture of toluene and chloroform to give **1** (81 mg, 0.126 mmol, 81%) as a green solid.

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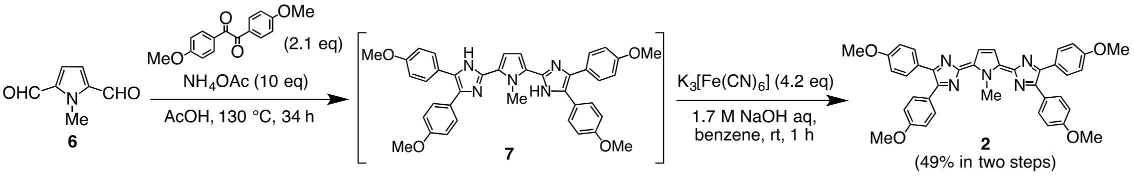
[1] P. K. De, D. C. Neckers, *Org. Lett.*, 2012, **14**, 78.

mp 252-256 ºC; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.88 (s, 12H), 6.92–6.96 (m, 8H), 7.71 (d, *J* = 8.0 Hz, 4H), 7.77 (d, *J* = 8.0 Hz, 4H), 8.29 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 55.42, 114.00 (2C), 125.90, 126.09, 131.31, 131.66, 138.46, 151.07, 159.64, 161.56, 161.83, 165.21, 165.93; HRMS (FAB$^+$) *m*/*z* calcd for $C_{38}H_{30}N_4O_4S$ (M$^+$) 638.1988, found: 638.1999.

Synthesis of 2,2'-(1-methyl-1*H*-pyrrole-2,5-diylidene)bis(4,5-bis(4-methoxyphenyl)-2*H*-imidazole) (2).



A mixture of 1-methyl-1*H*-pyrrole-2,5-dicarbaldehyde (**6**)[2] (300 mg, 2.19 mmol), 1,2-bis(4-methoxyphenyl)ethane-1,2-dione (1.24 g, 4.60 mmol), and ammonium acetate (1.69 g, 21.9 mmol) was dissolved in acetic acid (15.0 mL), and heated at 130 °C for 34 h. After cooling to room temperature, the mixture was poured into aqueous K_2CO_3 to precipitate the product. The solid was collected by filtration. ^{1}H NMR of the crude product suggested that a cyclized product **7** was successfully formed; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 3.75 (brs, 6H), 3.80 (brs, 6H), 6.74 (s, 2H), 6.88 (brd, *J* = 8.5 Hz, 4H), 7.00 (brd, *J* = 8.5 Hz, 4H), 7.40–7.49 (m, 8H), 12.29 (brs, 2H). However, the product was slightly air sensitive, and the color of the solid gradually changed to blue. So the crude product was used in the next step without further purification. A solution of the crude product (700 mg) in benzene (30 mL) was added aqueous NaOH (1.7 M, 20 mL) at room temperature. The mixture was added potassium ferricyanide (2.97 g, 9.02 mmol), and the color of the solution immediately changed to deep blue. After stirring for 1 h at room temperature, the organic layer was extracted chloroform, and then washed with water. The extract was dried over $MgSO_4$, and concentrated to give a green solid. The solid was purified by silica gel column chromatography (chloroform:Et_2O = 3:1) and recrystallization from toluene to give **2** (691 mg, 1.09 mmol, 49%) as green crystals. mp 236–238 ºC; ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.87 (s, 12H), 4.90 (s, 3H), 6.92–6.95 (m, 8H), 7.69 (d, *J* = 8.0 Hz, 4H), 7.78 (d, *J* = 8.0 Hz, 4H), 7.94 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 37.09, 55.36, 55.38, 113.87, 113.90,

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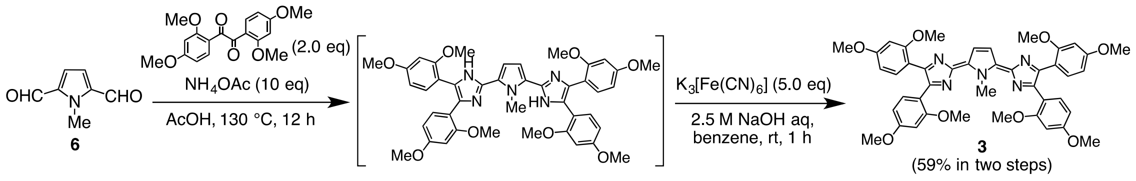
[2] J. F. A. Van Der Looy, G. J. H. Thys, P. E. M. Dieltiens, D. D. Schrijver, C. Van Alsenoy, H. J. Geise, *Tetrahedron*, 1997, **53**, 15069.

126.70, 126.80, 130.80, 130.87, 131.14, 146.03, 152.01, 160.86, 161.04, 161.20, 162.90; HRMS (FAB$^+$) *m*/*z* calcd for $C_{39}H_{33}N_5O_4$ (M$^+$) 635.2533, found: 635.2523; Anal. Calcd for $C_{39}H_{33}N_5O_4$: C, 73.68; H, 5.23; N, 11.02. Found: C, 73.32; H, 5.33; 10.83.

Synthesis of 2,2'-(1-methyl-1*H*-pyrrole-2,5-diylidene)bis(4,5-bis(2,4-dimethoxyphenyl)-2*H*-imidazole) (Z2).



A mixture of 1-methyl-1*H*-pyrrole-2,5-dicarbaldehyde (**6**) (200 mg, 1.46 mmol), 1,2-bis(2,4-dimethoxyphenyl)ethane-1,2-dione[3] (963 mg, 2.92 mmol), and ammonium acetate (1.13 g, 14.6 mmol) was dissolved in acetic acid (6.0 mL), and heated at 130 °C for 12 h. After cooling to room temperature, the mixture was poured into aqueous K_2CO_3 to precipitate the product. The solid was collected by filtration. The product was slightly air sensitive, and the color of the solid gradually changed to blue. So the crude product was used in the next step without further purification. A solution of the crude product in benzene (20 mL) was added aqueous NaOH (2.5 M, 20 mL) at room temperature. The mixture was added potassium ferricyanide (2.40 g, 7.30 mmol), and the color of the solution immediately changed to deep blue. After stirring for 1 h at room temperature, the organic layer was extracted chloroform, and then washed with water. The extract was dried over $MgSO_4$, and concentrated to give a greenish blue solid. The solid was purified by silica gel column chromatography (chloroform:AcOEt = 3:1) to give **3** (650 mg, 0.86 mmol, 59%) as a greenish blue solid. mp 143–145 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.31 (s, 6H), 3.32 (s, 6H), 3.84 (s, 6H), 3.85 (s, 6H), 4.88 (s, 3H), 6.36–6.37 (m, 4H), 6.54–6.58 (m, 4H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.96 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 37.08, 54.87, 54.90, 55.45, 98.26, 104.57, 104.76, 118.56, 130.94, 131.06, 131.49, 145.99, 151.91, 158.66, 158.89, 161.46, 161.66, 162.02, 163.78; HRMS (FAB$^+$) *m*/*z* calcd for $C_{43}H_{42}N_5O_8$ ([M+H]$^+$) 756.3028, found: 756.3036; Anal. Calcd for $C_{43}H_{41}N_5O_8$: C, 68.33; H, 5.47; N, 9.27. Found: C, 68.33; H, 5.47; 9.27.

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[3] J. A. VanAllan, *J. Org. Chem.*, 1958, **23**, 1679.

3. Thermogravimetry-differential thermal analysis

TG-DTA of quinoid compounds **1–3** was performed with a temperature increasing rate of 10 K/min under N_2, and Al_2O_3 was used as a reference sample.

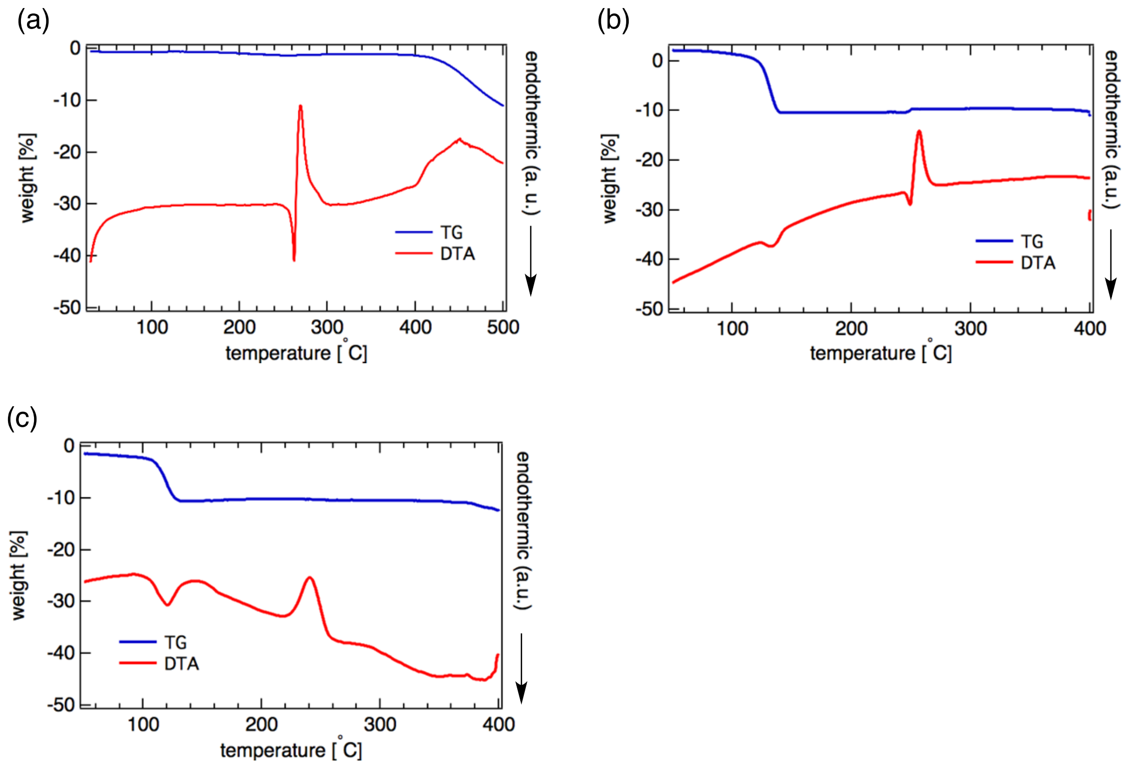

Fig. S1 TG-DTA traces for (a) **1**, (b) **2**, and (c) **3**.

4. CV Measurement

All CV measurements were carried out at room temperature in a one-compartment cell under N_2 gas, equipped with a glassy-carbon working electrode, a platinum wire counter electrode, and an Ag/Ag$^+$ reference electrode (10 mM $AgClO_4$ in 0.1 M Bu_4NPF_6).

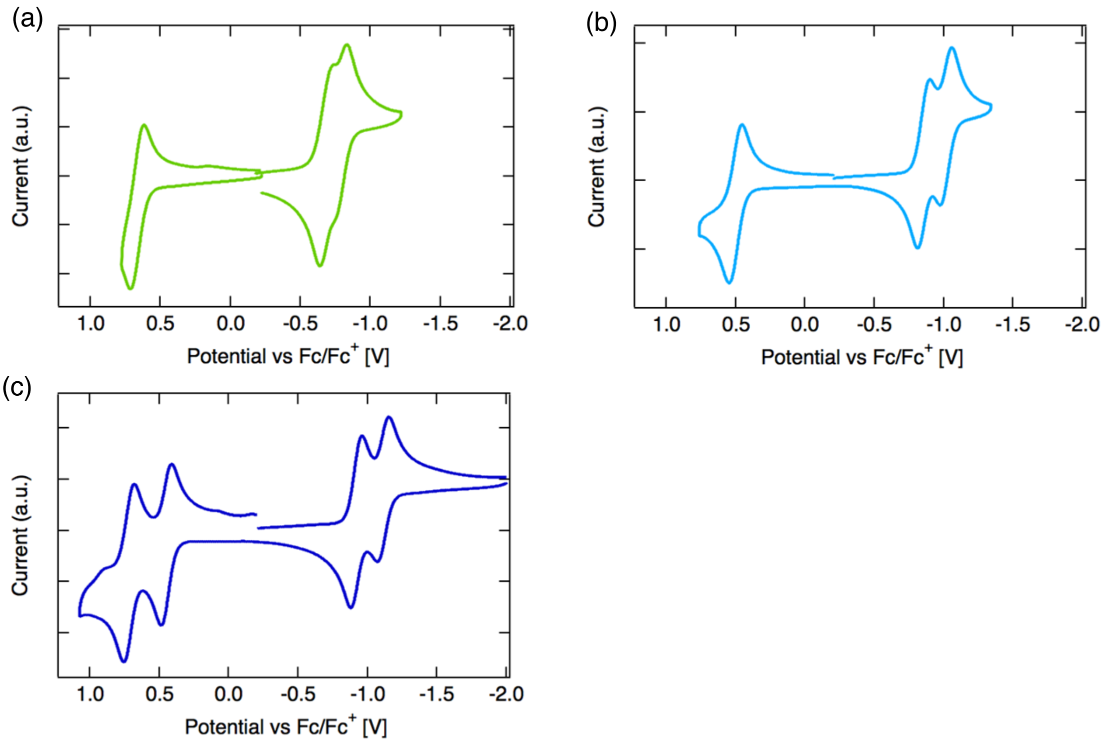

Fig. S2 CV traces for (a) **1**, (b) **2**, and (c) **3**.

5. Determination of the ionization potential by PYS

For the PYS measurement, we prepared a thin-film of **1**–**3** from a 0.5 wt% solution in chloroform. The solution was spun on ITO substrate at 1500 rpm for 30 sec to make the thin-film samples.

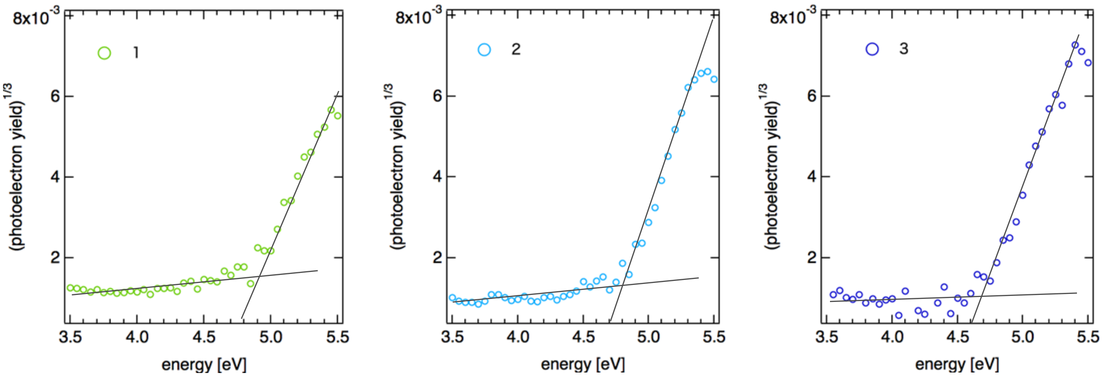

Fig. S3 PYS measurement of thin-films of **1**–**3** deposited on an ITO substrate

6. Device fabrication and characterization of the OPV devices

The OPV devices were fabricated in a nitrogen purged glove box unless otherwise noted. An ITO-coated glass substrate was exposed to UV/ozone prior to usage and was then spin-coated with PEDOT:PSS dispersed in water (CLEVIOS P VP AI4083) (3000 rpm) to form 30-nm-thick anode buffer layer. The resulting film was heated at 120 °C for 10 min under air and then heated at 180 °C for 10 min in a nitrogen glove box to remove residual water. For device **B** and **C**, 20-nm-thick molybdenum oxide layer was deposited on the PEDOT:PSS layer by vacuum deposition. For device **A**, a donor layer was formed on the PEDOT:PSS layer by spin-coating (1,500 rpm) a 0.3 wt% solution of **1** in chloroform. For device **B** and **C**, a donor layer was formed on the molybdenum oxide layer by spin-coating (1,500 rpm) a 0.15 wt% solution of **2** or **3** in chloroform, respectively. On the active layers, 5-nm-thick 2,9-bis(naphthalen-2-yl)-4,7-diphenyl-1,10-phenanthroline (NBphen) was deposited by vacuum deposition, and the devices were completed by depositing an Al layer (80 nm). Finally, the devices were encapsulated with backing glasses using a UV-curable resin under nitrogen atmosphere. The current density-voltage characteristics under AM 1.5 G solar illumination (100 mW cm^{-2}) was recorded using a Keithley 2400 source-measure unit.