Electronic Supplementary Information

Arenedithiocarboxyimide-containing extended π-conjugated systems with high electron affinity

Yutaka Ie, Seihou Jinnai, Masashi Nitani, and Yoshio Aso**

The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan, JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 333-0012, Japan.

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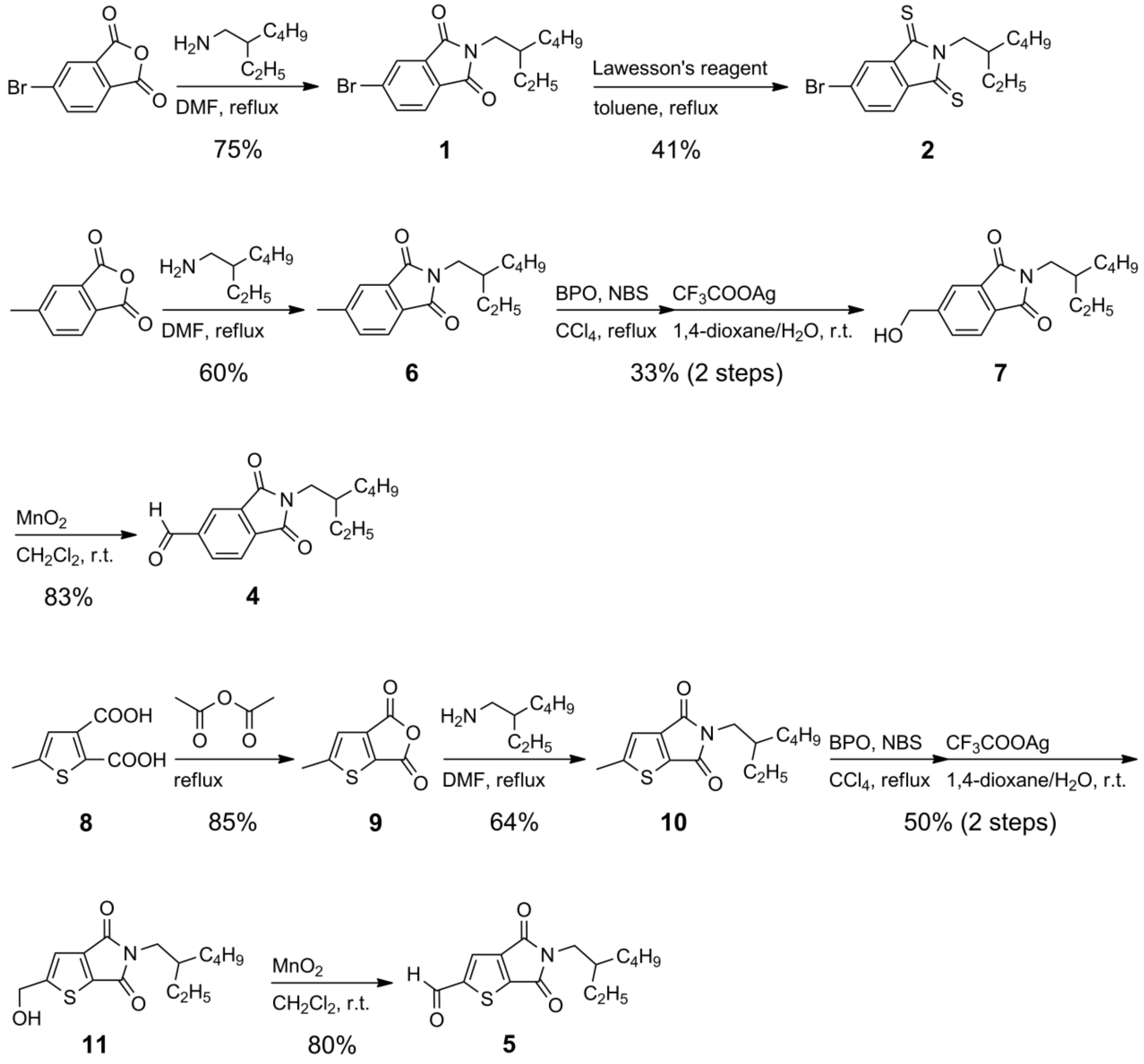
Scheme and Figures



Scheme S1. Synthesis of **1**, **2**, **4**, and **5**.

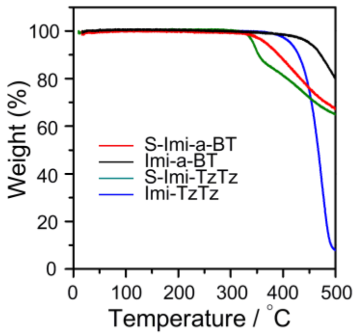


Fig. S1 TGA curves of compounds with a heating rate of 10 °C min^{-1} in N_2.

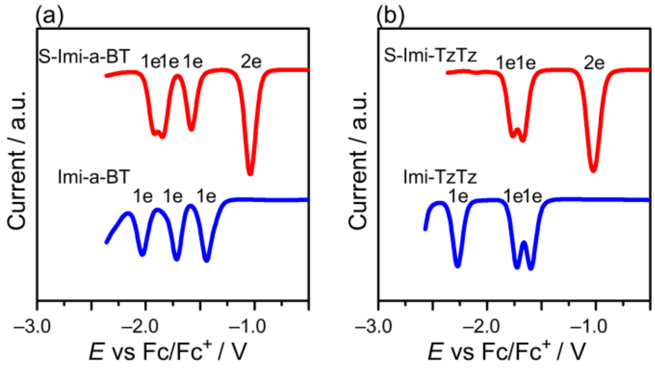


Fig. S2 Differential pulse voltammograms of (a) **S-Imi-a-BT** (red) and **Imi-a-BT** (blue) and (b) **S-Imi-TzTz** (red) and **Imi-TzTz** (blue) in $CHCl_3$ containing 0.1 M $TBAPF_6$.

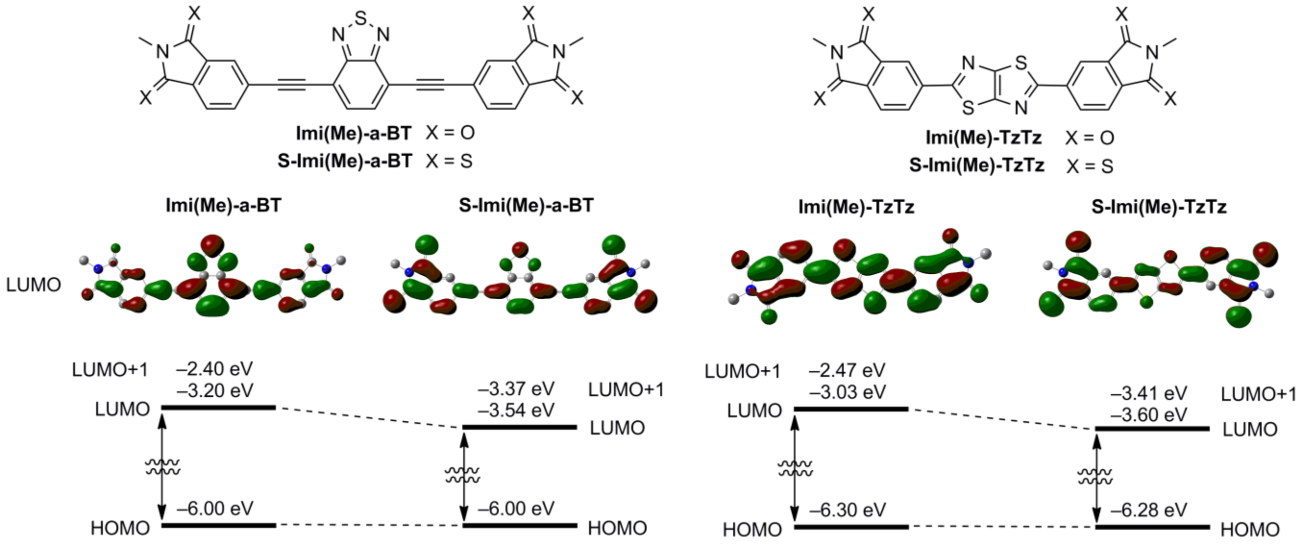


Fig. S3 HOMO, LUMO, and LUMO+1 energies calculated with DFT at the B3LYP/6-31G(d,p) level and LUMO orbitals. 2-Ethylhexyl groups were replaced with methyl groups to ease the calculation.

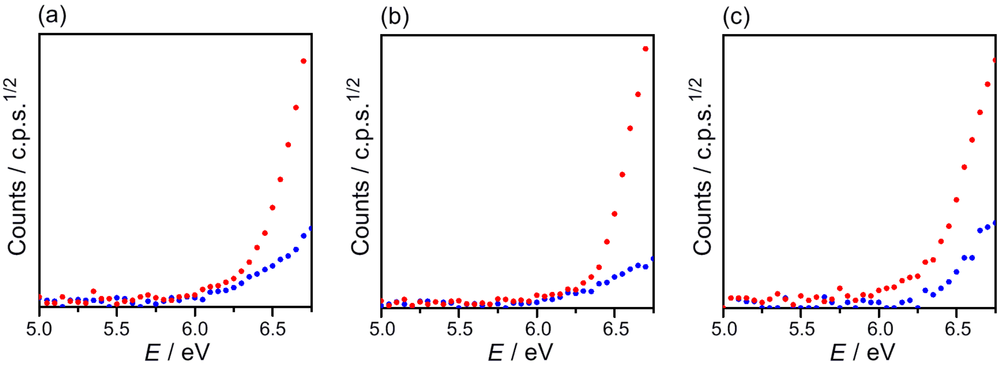


Fig. S4 Photoemission spectra of (a) **S-Imi-a-BT** (red) and **Imi-a-BT** (blue), (b) **S-Imi-TzTz** (red) and **Imi-TzTz** (blue), and (c) **S-TImi-TzTz** (red) and **TImi-TzTz** (blue) thin films.

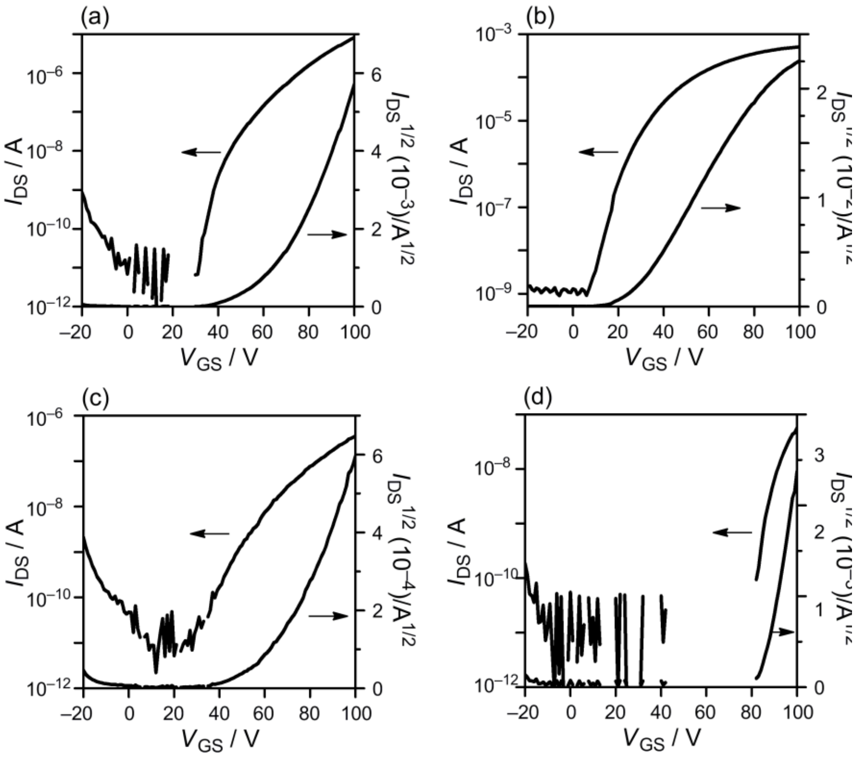


Fig. S5 Transfer characteristics of OFETs based on (a) **S-Imi-a-BT**, (b) **S-TImi-TzTz**, (c) **Imi-a-BT**, and (d) **Imi-TzTz**.

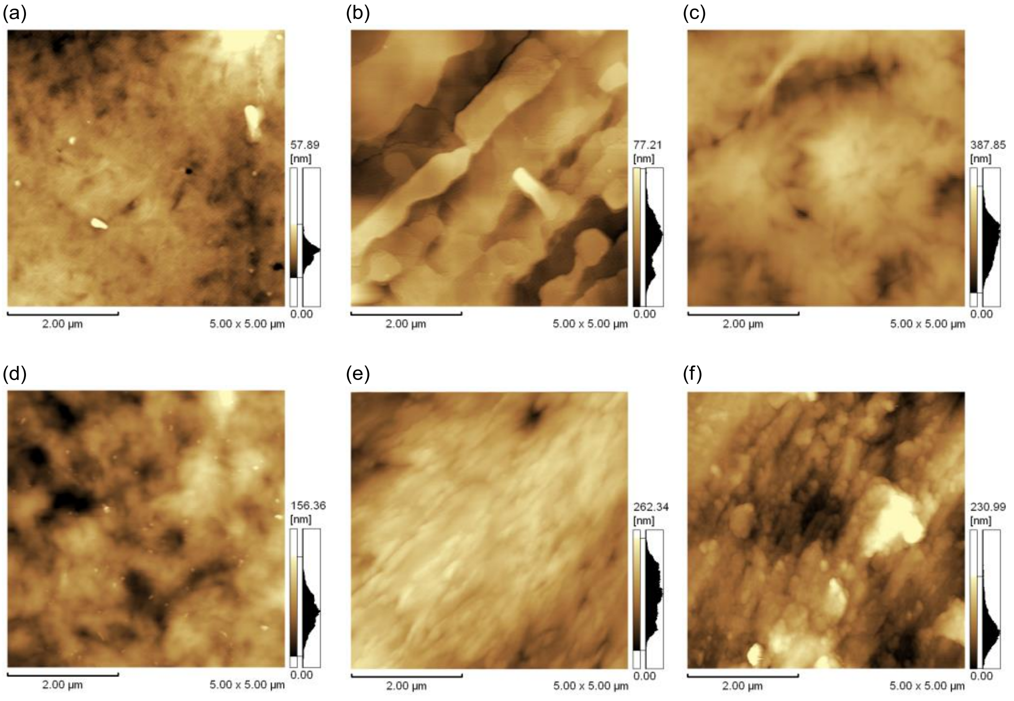


Fig. S6 AFM images of (a) **S-Imi-a-BT**, (b) **Imi-a-BT**, (c) **S-Imi-TzTz**, (d) **Imi-TzTz**, (e) **S-TImi-TzTz**, and (f) **TImi-TzTz**.

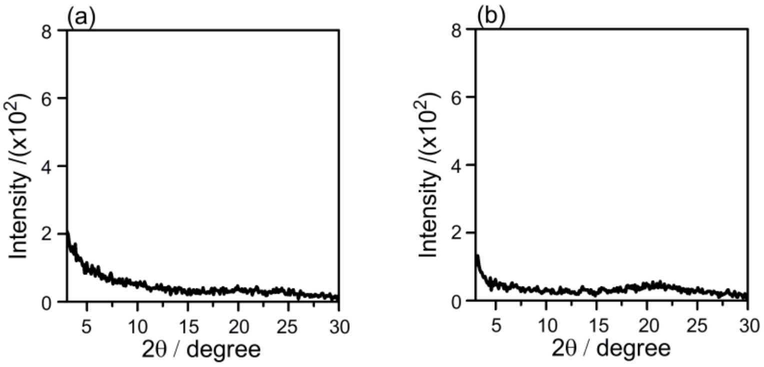


Fig. S7 In-plane XRDs of (a) **S-Imi-a-BT** and (b) **S-Imi-TzTz**.

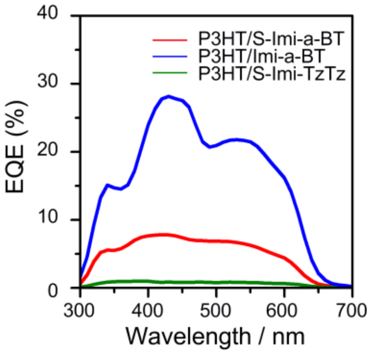


Fig. S8 EQE spectra of OPV devices.

Table S1. OPV characteristics of compounds.

Compounds	V_{oc}/V	J_{sc}/ mA cm^{-2}	FF	PCE/%
S-Imi-a-BT	0.41	0.64	0.26	0.07
S-Imi-TzTz	0.23	0.10	0.35	0.01
Imi-a-BT	0.89	3.99	0.45	1.58

Experimental Procedures

General Information. Column chromatography was performed on silica gel, KANTO Chemical silica gel 60N (40–50 μm). Thin-layer Chromatography (TLC) plates were visualized with UV light. Preparative gel-permeation chromatography (GPC) was performed on a Japan Analytical Industry LC-918 equipped with JAI-GEL 1H/2H. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECS-400 spectrometer in $CDCl_3$ or $CDCl_3/CS_2$ with tetramethylsilane (TMS) as an internal standard. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant (Hz), and integration. Mass spectra were obtained on a Shimadzu GCMS-QP-5050 or Shimadzu AXIMA-TOF. DSC and TGA were performed under nitrogen at a heating rate of 10 °C min^{-1} with a Shimadzu DSC-60 and a Shimadzu TGA-50, respectively. UV-vis-NIR spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were recorded using a Fluoromax-2 spectrometer in the photo-counting mode equipped with a Hamamatsu R928 photomultiplier. The bandpass for the emission spectra was 1.0 nm. All spectra were obtained in spectrograde solvents. Cyclic voltammetry was carried out on a BAS CV-620C voltammetric analyzer using a platinum disk as the working electrode, platinum wire as the counter electrode, and $Ag/AgNO_3$ as the reference electrode at a scan rate of 100 mV s^{-1}. Photoemission yield spectroscopy was carried out using a Riken Keiki Co. Ltd. AC-3 with a light intensity of 10 mW. Elemental analyses were performed on Perkin Elmer LS-50B by the Elemental Analysis Section of CAC, ISIR, Osaka University. The surface structures of the deposited organic film were observed by atomic force microscopy (Shimadzu, SPM9600), and the film crystallinity was evaluated by an X-ray diffractometer (Rigaku, SmartLab). X-ray diffraction patterns were obtained using Bragg-Brentano geometry with CuKα radiation as an X-ray source with an acceleration voltage of 45 kV and a beam current of 200 mA. The scanning mode was set to 2θ scans between 3º–30º with scanning steps of 0.01º.

Materials. All reactions were carried out under a nitrogen atmosphere. Solvents of the highest purity grade were used as received. Unless stated otherwise, all reagents were purchased from commercial sources and used without purification. 4,7-diethynyl-2,1,3-benzothiadiazole (**3**) and 5-methyl-2,3-thiophenedicarboxylic acid (**8**) were prepared by reported procedure, and ^{1}H NMR data of this compound was in agreement with those previously reported.[1,2]

Synthesis

*Synthesis of **1***: 4-Bromophthalic anhydride (2.0 g, 8.8 mmol) and 2-ethyl-1-hexylamine (1.2 g, 8.8 mmol) were placed in a round-bottomed flask and dissolved with DMF (50 mL), and the resulting mixture was stirred at 140 ºC for 12 h. After being cooled to room temperature, the reaction was quenched by the addition of H_2O. The aqueous layer was extracted with ethyl acetate (EtOAc), and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give **1** (2.3 g, 75%). Colorless solid; m.p.: 72-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.96 (d, J = 1.6 Hz, 1H), 7.83 (dd, J = 7.8, 1.6 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 3.56 (d, J = 7.3 Hz, 2H), 1.81 (m, 1H), 1.35-1.25 (m, 8H), 0.91-0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.91, 167.36, 136.85, 133.75, 130.62, 128.77, 126.58, 124.56, 42.12, 38.24, 30.46, 28.46, 23.80, 22.99, 14.07, 10.39; MS (GC) m/z 337 (M^+, Calcd 337). Anal. Calcd for $C_{16}H_{20}BrNO_2$: C, 56.82; H, 5.96; N, 4.14. Found: C, 56.88; H, 6.01; N, 4.06.

*Synthesis of **2***: **1** (100 mg, 0.30 mmol) and Lawesson's reagent (238 mg, 0.59 mmol) were placed in a test tube with screw cap and dissolved with toluene (5 mL), and the resulting mixture was stirred at 120 ºC for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give **2** (45 mg, 41%). Dark brown oil; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (d, J = 1.1 Hz, 1H), 7.79 (dd, J = 7.8, 1.1 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 4.36 (dd, J = 7.3, 2.1 Hz, 2H), 2.18 (m, 1H), 1.36-1.21 (m, 8H), 0.90-0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.07, 196.52, 135.75, 135.74, 133.23, 127.80, 126.25, 124.63, 48.06, 38.18, 30.55, 28.50, 23.94, 22.99, 14.05, 10.79; MS (GC) m/z 369 (M^+, Calcd 369). Anal. Calcd for $C_{16}H_{20}BrNS_2$: C, 51.89; H, 5.44; N, 3.78. Found: C, 51.62; H, 5.44; N, 3.80.

*Synthesis of **6***: 4-Methylphthalic anhydride (3.0 g, 18.5 mmol) and 2-ethyl-1-hexylamine (2.4 g, 18.5 mmol) were placed in a round-bottomed flask and dissolved with DMF (75 mL), and the resulting mixture was stirred at 140 ºC for 12 h. After being cooled to room temperature, the reaction was quenched by the addition of H_2O. The aqueous layer was extracted with EtOAc, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc =10/1) to give **6** (3.0 g, 60%). Colorless solid; m.p.: 47-49 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.71 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 1.1 Hz, 1H), 7.48 (dd, J = 7.6, 1.1 Hz, 1H), 3.55 (d, J = 7.3 Hz, 2H), 2.50 (s, 3H), 1.83-1.80 (m, 1H), 1.37-1.26 (m, 8H), 0.92-0.85 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.92, 168.82, 145.03, 134.32, 132.45, 129.47, 123.69, 123.03, 41.79, 38.23, 30.45, 28.47, 23.78, 22.96, 21.96, 14.03, 10.38; MS (GC) m/z 273 (M^+, Calcd 273). Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.66; H, 8.35; N, 5.12.

Synthesis of 7: To a stirred solution of **6** (1.00 g, 3.65 mmol) in CCl_4 (15 mL) was added NBS (0.97 g, 5.47 mmol), benzoyl peroxide (BPO) (88 mg, 0.37 mmol), and the resulting mixture was stirred at 90 ºC for 12 h. After being cooled to room temperature, the reaction was quenched by the addition of $NaHCO_3$ aq., and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give bromo compound **A** (1.00 g). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.84 (br, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.70 (dd, *J* = 7.3, 1.6 Hz, 1H), 5.56 (d, *J* = 6.9 Hz, 2H), 4.54 (s, 2H), 2.03 (m, 1H), 1.42-1.23 (m, 8H), 0.95-0.86 (m, 6H). This compound was used for next step without further purification.

A mixture of **A** (1.00 g), silver trifluoroacetate (748 mg, 3.39 mmol) in 1,4-dioxane (8 mL) and water (2mL) was stirred at room temperature. After stirring for 12 h, the reaction mixture was filtered over celite with $CHCl_3$ as an eluent, and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 3/1) to give alcohol **6** (350 mg, 33% (2 steps)). Colorless solid; m.p.: 80-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.85 (d, *J* = 1.6 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.71 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.87 (s, 2H), 3.57 (d, *J* = 7.4 Hz, 2H), 1.93 (br, 1H), 1.83 (m, 1H), 1.36-1.25 (m, 8H), 0.93-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.69, 168.62, 147.76, 132.57, 131.76, 131.19, 123.33, 121.21, 64.38, 41.94, 38.27, 30.49, 28.49, 23.81, 23.00, 14.07, 10.41; MS (GC) *m/z* 351 (M^+, Calcd 351). Anal. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.73; H, 7.32; N, 4.81.

Synthesis of ***4***: To a stirred solution of **6** (300 mg, 1.03 mmol) in CH_2Cl_2 (10 mL) was added MnO_2 (895 mg, 10.3 mmol), and the resulting mixture was stirred at room temperature. After stirring for 12 h, the reaction mixture was filtered over celite with $CHCl_3$ as an eluent. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 3/1) to give aldehyde **4** (245 mg, 83%). Colorless solid; m.p.: 47-50 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.17 (s, 1H), 8.34 (s, 1H), 8.25 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.02 (d, *J* = 1.4 Hz, 1H), 3.62 (d, *J* = 7.5 Hz, 2H), 1.85 (m, 1H), 1.36-1.26 (m, 8H), 0.94-0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.23, 167.52, 167.40, 140.56, 136.38, 135.24, 132.89, 124.02, 123.88, 42.29, 38.24, 30.46, 28.43, 23.80, 22.97, 14.04, 10.36; MS (GC) *m/z* 287 (M^+, Calcd 287). Anal. Calcd for $C_{17}H_{21}BNO_3$: C, 71.06; H, 7.37, N, 4.87. Found: C, 70.73; H, 7.32; N, 4.81.

Synthesis of ***Imi-a-BT***: **1** (189 mg, 0.67 mmol), **3** (89 mg, 0.30 mmol), CuI (5 mg, 0.03 mmol), and $Pd(PPh_3)_4$ (39 mg, 0.03 mmol) were placed in a test tube with screw cap and dissolved with THF (6 mL) and diisopropylethylamine (0.6 mL). After being cooled to room temperature, the reaction mixture was filtered over celite with $CHCl_3$ as an eluent. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$), followed by purification with preparative GPC ($CHCl_3$) to give **Imi-a-BT** (189 mg, 89%). Yellow solid; m.p.: 225-226 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.10 (d, *J* = 0.9 Hz, 2H), 7.98 (dd, *J* = 7.8, 0.9 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 2H), 7.86 (s, 2H), 3.59 (d, *J* = 7.3 Hz, 4H), 1.84 (m, 2H), 1.37-1.27 (m, 16H), 0.93-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.98, 167.86, 154.18, 137.17, 132.91, 132.43, 131.60, 128.37, 126.42, 123.29, 117.04, 95.83, 88.93, 42.13, 38.27, 30.48, 28.47, 23.83, 23.00, 14.06, 10.40; MS MALDI-TOF(1,8,9-trihydroxyanthracene matrix) *m/z* 698.14 (M^+, Calcd 698.29); Anal. Calcd for $C_{42}H_{42}N_4O_4S$: C, 72.18; H, 6.06; N, 8.02. Found: C, 71.92; H, 6.14; N, 7.90.

Synthesis of ***S-Imi-a-BT***: **Imi-a-BT** (230 mg, 0.24 mmol) and Davy's reagent (375 mg, 1.32 mmol) were placed in a test tube with screw cap and dissolved with toluene (36 mL), and the resulting mixture was stirred at 120 ºC for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$), followed by precipitation using $CHCl_3$ and acetone to give **S-Imi-a-BT** (220 mg, 88%). Red Solid; m.p.: > 300

°C; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$, TMS): δ 8.07 (d, J = 1.5 Hz, 2H), 7.90 (dd, J = 7.8, 1.5 Hz, 2H), 7.84 (d, J = 7.8 Hz, 2H), 7.82 (s, 2H), 4.37 (d, J = 7.0 Hz, 4H), 2.18 (m, 2H), 1.39-1.25 (m, 16H), 0.92-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$): δ 196.44, 196.39, 154.02, 135.75, 134.63, 133.88, 132.55, 127.17, 126.55, 123.24, 117.08, 96.76, 89.28, 47.81, 38.18, 30.62, 28.62, 24.09, 23.20, 14.16, 10.86; MS MALDI-TOF(1,8,9-trihydroxyanthracene matrix) *m/z* 762.09 (M^+, Calcd 762.20); Anal. Calcd for $C_{42}H_{42}N_4S_5$: C, 66.10; H, 5.55; N, 7.34. Found: C, 65.84; H, 5.79; N, 7.42.

Synthesis of ***Imi-TzTz***: **4** (220 mg, 1.03 mmol), etahnedithioamide (368 mg, 3.06 mmol) were placed in a test tube with screw cap and dissolved with DMF (10 mL), and the resulting mixture was stirred at 140 ºC for 12 h. After being cooled to room temperature, the reaction mixture was quenched by addition of water, and the organic layer was separated with $CHCl_3$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$), followed by precipitation using $CHCl_3$ and acetone to give **Imi-TzTz** (174 mg, 69%). Yellow solid; m.p.: 218-220 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.44 (d, J = 1.6 Hz, 2H), 8.38 (dd, J = 7.8, 1.6 Hz, 2H), 7.95 (d, J = 7.8 Hz, 2H), 3.62 (d, J = 7.1 Hz, 4H), 1.85 (m, 2H), 1.38-1.28 (m, 16H), 0.93-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.84, 167.75, 167.70, 152.36, 138.95, 133.25, 133.23, 131.57, 124.04, 121.01, 42.21, 38.25, 30.47, 28.46, 23.81, 22.99, 14.06, 10.39; MS MALDI-TOF(1,8,9-trihydroxyanthracene matrix) *m/z* 656.00 (M^+, Calcd 656.25); Anal. Calcd for $C_{36}H_{40}N_4O_4S_2$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.82; H, 6.14; N, 8.56.

Synthesis of ***S-Imi-TzTz***: **Imi-TzTz** (100 mg, 0.15 mmol) and Davy's reagent (173 mg, 0.61 mmol) were placed in a test tube with screw cap and dissolved with toluene (10 mL), and the resulting mixture was stirred at 120 ºC for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$), followed by precipitation using $CHCl_3$ and acetone to give **S-Imi-TzTz** (97 mg, 88%). Red solid; m.p.: 261-262 °C; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$, TMS): δ 8.38 (d, J = 1.4 Hz, 2H), 8.31 (dd, J = 7.8, 1.4 Hz, 2H), 7.89 (d, J = 7.8 Hz, 2H), 4.36 (dd, J = 7.3, 2.3 Hz, 4H), 2.17 (m, 2H), 1.38-1.24 (m, 16H), 0.92-0.86 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3/CS_2$): δ 196.01, 195.98, 167.57, 152.28, 137.61, 135.23, 135.18, 130.10, 123.85, 121.04, 47.81, 38.16, 30.63, 28.63, 24.13, 23.24, 14.20, 10.87; MS MALDI-TOF(1,8,9-trihydroxyanthracene matrix) *m/z* 719.85 (M^+, Calcd 720.16); Anal. Calcd for $C_{36}H_{40}N_4S_6$: C, 59.96; H, 5.59; N, 7.77. Found: C, 60.06; H, 5.64; N, 7.78.

Synthesis of ***9***: **8** (6.52 g, 35.0 mmol) were placed in a round-bottomed flask and dissolved with acetic anhydride (140 mL), and the resulting mixture was stirred at 140 ºC for 12 h. After being cooled to room temperature, hexane was added and the resulting precipitate was collected by filtration, and dried to give **9** (5.02 g, 85%). Pale yellow solid; m.p.: 221-222 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.39 (d, J = 0.9 Hz, 1H), 2.66 (d, J = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.29, 162.69, 144.71, 137.49, 134.35, 128.82, 15.02; MS (GC) *m/z* 168 (M^+, Calcd 168). This compound was used for next step without further purification.

Synthesis of ***10***: **9** (2.0 g, 11.9 mmol) and 2-ethyl-1-hexylamine (1.61 g, 12.5 mmol) were placed in a round-bottomed flask and dissolved with toluene (180 mL), and the resulting mixture was stirred at 140 ºC for 12 h. After being cooled to room temperature, the solvent was removed under reduced pressure and $SOCl_2$ (40 mL) was added. The resulting mixture was refluxed for 2 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 19/1) to give **10** (2.14 g, 64%). White solid; m.p.: 34-35 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 6.97 (s, 1H), 3.46 (d, J = 7.3 Hz, 2H), 2.61 (s, 3H), 1.80-1.76 (m, 1H), 1.36-1.26 (m, 8H), 0.92-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ164.69, 163.37, 153.85, 144.73, 137.93, 119.18, 42.15, 38.38, 30.39, 28.46, 23.71, 23.01, 16.31, 14.06, 10.40; MS (GC) *m/z* 279 (M^+, Calcd 279); Anal. Calcd for $C_{15}H_{21}NO_2S_2$: C, 64.48; H, 7.58; N, 5.01. Found: C, 64.30; H, 7.29; N, 5.04.

*Synthesis of **11***: To a stirred solution of **10** (2.14 g, 7.66 mmol) in CCl_4 (31 mL) was added NBS (2.04 g, 11.5 mmol), BPO (186 mg, 0.77 mmol), and the resulting mixture was stirred at 90 ºC for 12 h. After being cooled to room temperature, the reaction was quenched by the addition of $NaHCO_3$ aq., and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to give bromo compound **B** (1.82 g). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.29 (s, 1H), 4.71 (s, 2H), 3.49 (d, J = 7.3 Hz, 2H), 1.80-1.73 (m, 1H), 1.36-1.27 (m, 8H), 0.92-0.87 (m, 6H). This compound was used for next step without further purification.

A mixture of **B** (2.67 g), silver trifluoroacetate (1.98 g, 6.11 mmol) in 1,4-dioxane (15 mL) and water (3 mL) was stirred at room temperature. After stirring for 12 h, the reaction mixture was filtered over celite with $CHCl_3$ as an eluent, and the organic layer was separated. The aqueous layer was extracted with $CHCl_3$, and the combined organic layer was washed with water and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 3/1) to give alcohol **11** (1.12 g, 50% (2 steps)). Colorless solid; m.p.: 39-40 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.17 (s, 1H), 4.93 (s, 2H), 3.48 (d, J = 7.1 Hz, 3H), 2.05 (s, 1H), 1.81-1.75 (m, 1H), 1.36-1.24 (m, 8H), 0.92-0.87 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.45, 163.18, 158.02, 144.21, 139.68, 118.01, 60.26, 42.28, 38.37, 30.39, 28.45, 23.72, 23.00, 14.05, 10.39; MS (GC) *m/z* 295 (M^+, Calcd 295). Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74. Found: C, 60.94; H, 7.05; N, 4.80.

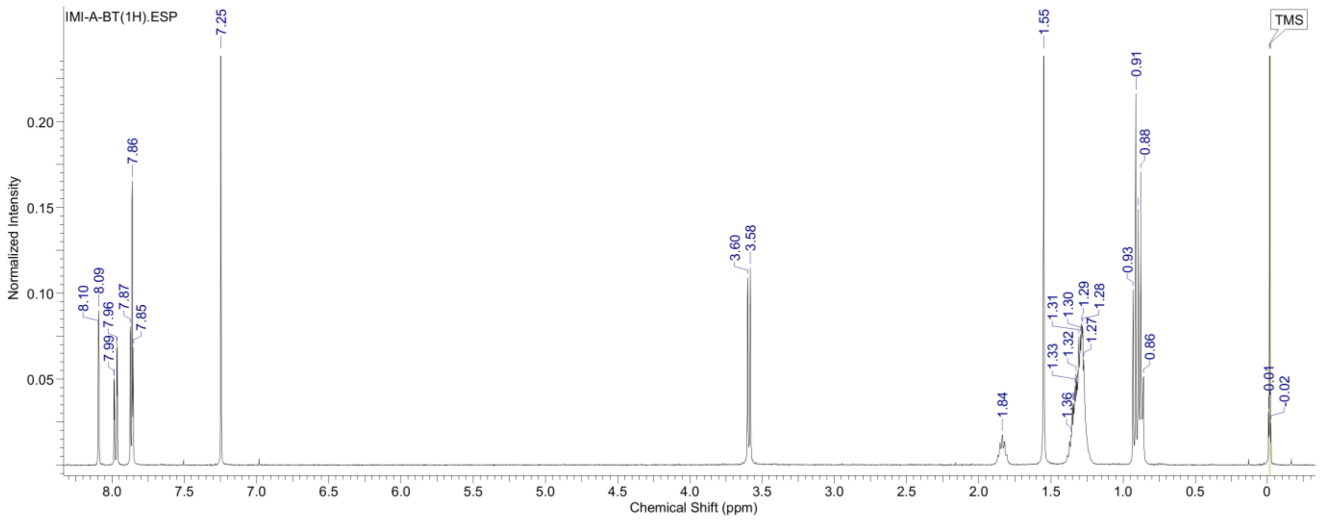
*Synthesis of **5***: To a stirred solution of **11** (1.12 g, 3.78 mmol) in CH_2Cl_2 (38 mL) was added MnO_2 (3.28 g, 37.8 mmol), and the resulting mixture was stirred at room temperature. After stirring for 12 h, the reaction mixture was filtered over celite with $CHCl_3$ as an eluent. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane/EtOAc = 3/1) to give aldehyde **5** (884 mg, 80%). Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 10.03 (s, 1H), 7.90 (s, 1H), 3.54 (d, J = 7.3 Hz, 2H), 1.82-1.76 (m, 1H), 1.38-1.24 (m, 8H), 0.93-0.867 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.87, 163.12, 162.12, 153.61, 146.75, 143.51, 127.59, 42.75, 38.32, 30.36, 28.38, 23.69, 22.96, 14.03, 10.33; MS (GC) *m/z* 293 (M^+, Calcd 293). Anal. Calcd for $C_{15}H_{19}NO_3S$: C, 61.41; H, 6.53; N, 4.77. Found: C, 61.25; H, 6.45; N, 4.77.

*Synthesis of **TImi-TzTz***: **5** (395 mg, 1.35 mmol), etahnedithioamide (81 mg, 0.67 mmol) were placed in a test tube with screw cap and dissolved with DMF (14 mL), and the resulting mixture was stirred at 140 ºC for 12 h. After being cooled to room temperature, the reaction mixture was quenched by addition of water, and the organic layer was separated with $CHCl_3$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$), followed by precipitation using $CHCl_3$ and acetone to give **TImi-TzTz** (360 mg, 80%). Yellow solid; m.p.: > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.71 (s, 2H), 3.54 (d, J = 7.7 Hz, 4H), 1.81 (m, 2H) , 1.38-1.28 (m, 16H), 0.94-0.88 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.65, 162.56, 153.76, 143.79, 141.08, 134.35, 132.84, 125.93, 42.57, 38.38, 30.40, 28.45, 23.74, 23.00, 14.06, 10.38; MS MALDI-TOF(1,8,9-trihydroxyanthracene matrix) *m/z* 667.82 (M^+, Calcd 668.16); Anal. Calcd for $C_{32}H_{36}N_4O_4S_4$: C, 57.46; H, 5.42; N, 8.38. Found: C, 57.37; H, 5.53; N, 8.37.

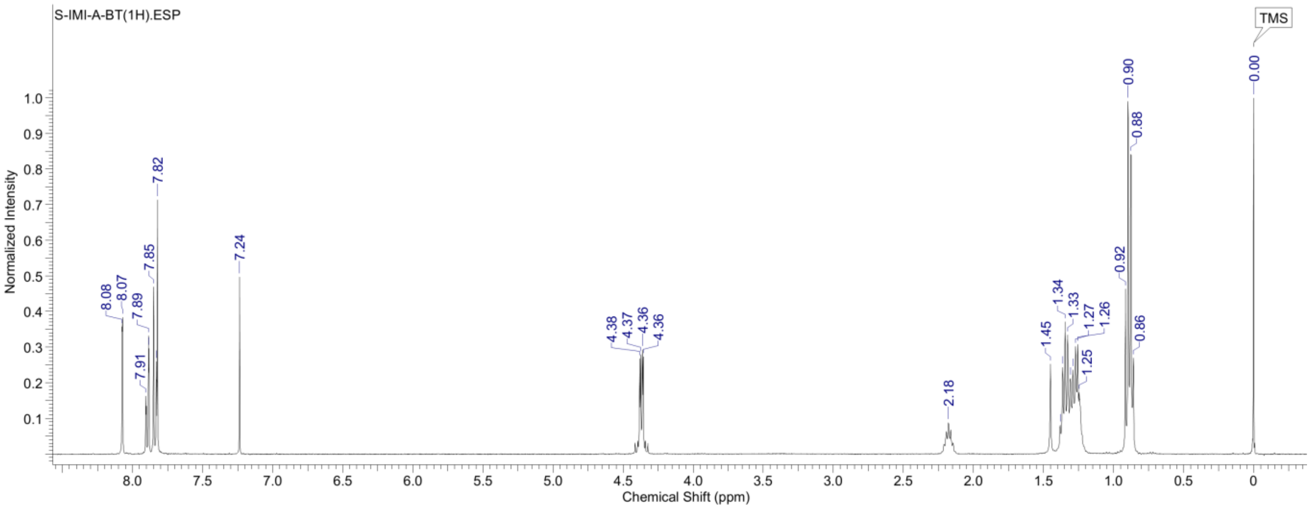
Synthesis of ***S-TImi-TzTz***: **TImi-TzTz** (227 mg, 0.34 mmol) and Davy's reagent (384 mg, 1.35 mmol) were placed in a test tube with screw cap and dissolved with toluene (36 mL), and the resulting mixture was stirred at 120 ºC for 12 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel ($CHCl_3$), followed by precipitation using $CHCl_3$ and acetone to give **S-TImi-TzTz** (219 mg, 88%). Black solid; m.p.: 245-253 °C decomp.; ^{1}H NMR (400 MHz, $CDCl_3/CS_2$, TMS): δ 7.71 (s, 2H), 4.23 (d, J = 7.3 Hz, 4H), 2.12 (m, 2H), 1.38-1.24 (m, 16H), 0.91-0.86 (m, 12H); MS MALDI-TOF(1,8,9-trihydroxyanthracene matrix) *m/z* 731.67 (M^+, Calcd 732.07); Anal. Calcd for $C_{32}H_{36}N_4S_8$: C, 52.42; H, 4.95; N, 7.64. Found: C, 52.29; H, 5.09; N, 7.78.

NMR Spectra

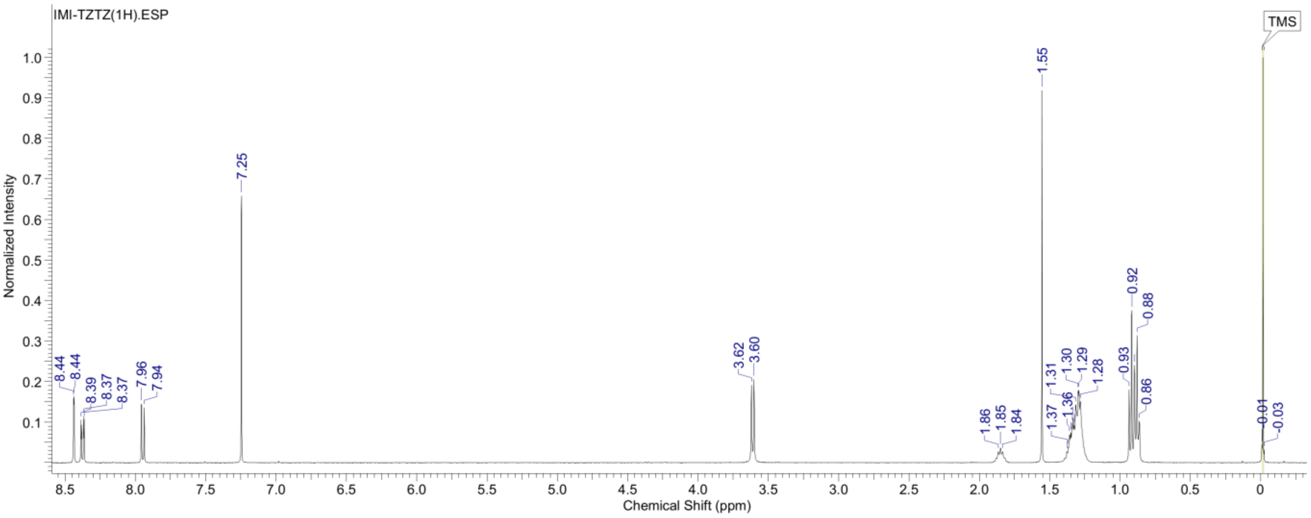
^{1}H NMR spectrum of **Imi-a-BT**.



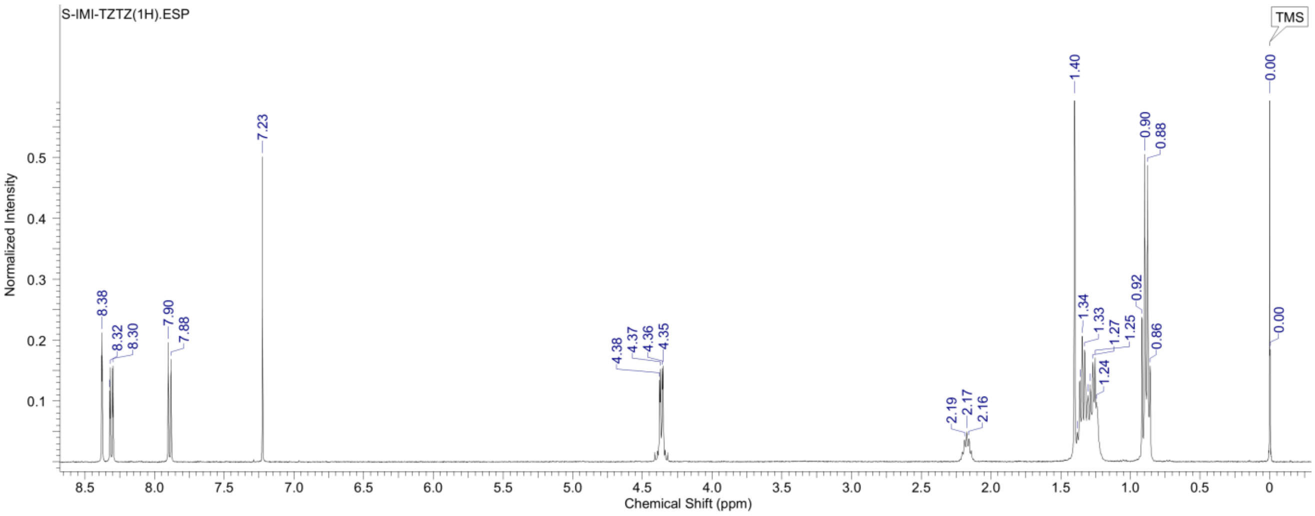
^{1}H NMR spectrum of **S-Imi-a-BT**.



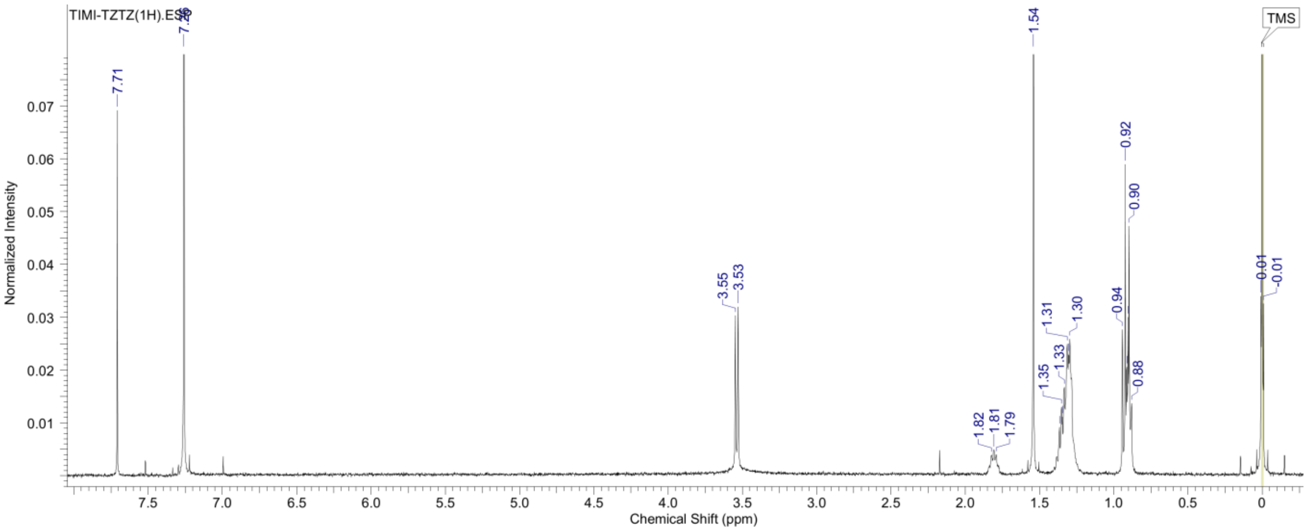
^{1}H NMR spectrum of **Imi-TzTz**.



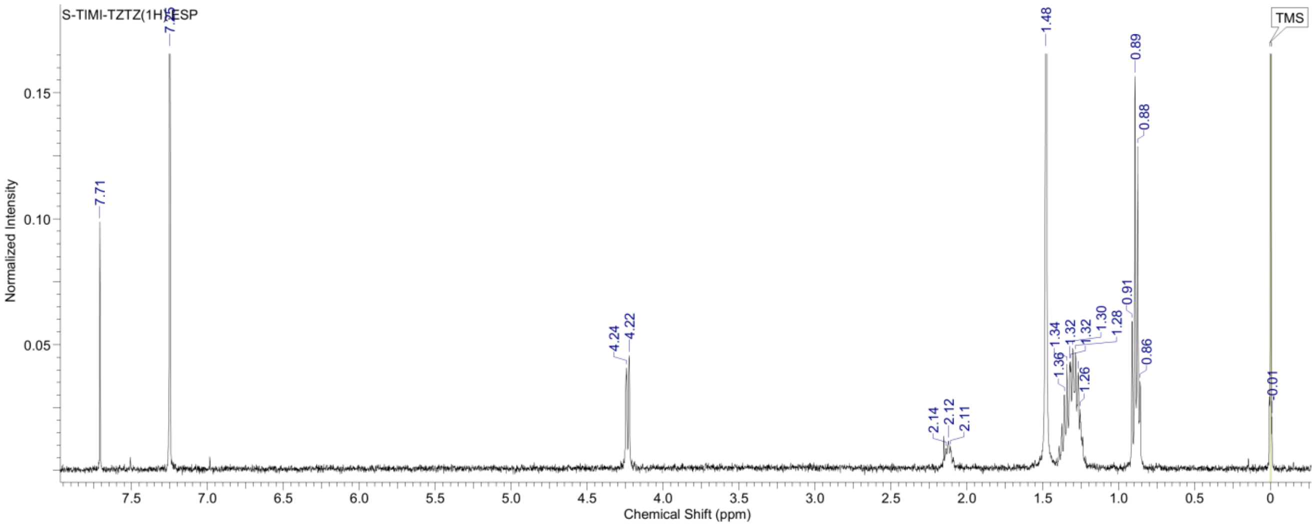
^{1}H NMR spectrum of **S-Imi-TzTz**.



^{1}H NMR spectrum of **TImi-TzTz**.



^{1}H NMR spectrum of **S-TImi-TzTz**



OFET Device Fabrication

The field-effect mobility was measured using bottom-contact thin-film field-effect transistor (FET) geometry. The p-doped silicon substrate functions as the gate electrode. A thermally grown silicon oxide dielectric layer on the gate substrate was 300 nm thick with a capacitance of 10.0 nF cm^{-2}. Interdigital source and drain electrodes were constructed with gold (30 nm) that were formed on the SiO_2 layer. The channel width (W) and channel length (L) were 294 mm and 25 μm, respectively. The silicon oxide surface was washed with toluene, acetone, water, and 2-propanol. The silicon oxide surface was then activated by ozone treatment and pretreated with ODTS. The semiconductor layer was drop-casted on the Si/SiO_2 substrate from 10 mg/mL chlorobenzene solution. The characteristics of the OFET devices were measured at room temperature under a pressure of 10^{-3} Pa. The current-voltage characteristics of devices were measured by using a KEITHLEY 4200SCS semiconductor parameter analyzer. The field-effect electron mobility (μ_e) was calculated in the saturated region at the V_{DS} of 100 V and the current on/off ratio was determined from the I_{DS} at V_{GS} = –20 V (I_{off}) and V_{GS} = 100 V (I_{on}) by the following equation.

$$I_{DS} = \frac{W}{2L} C_i \mu (V_{GS} - V_{th})^2$$

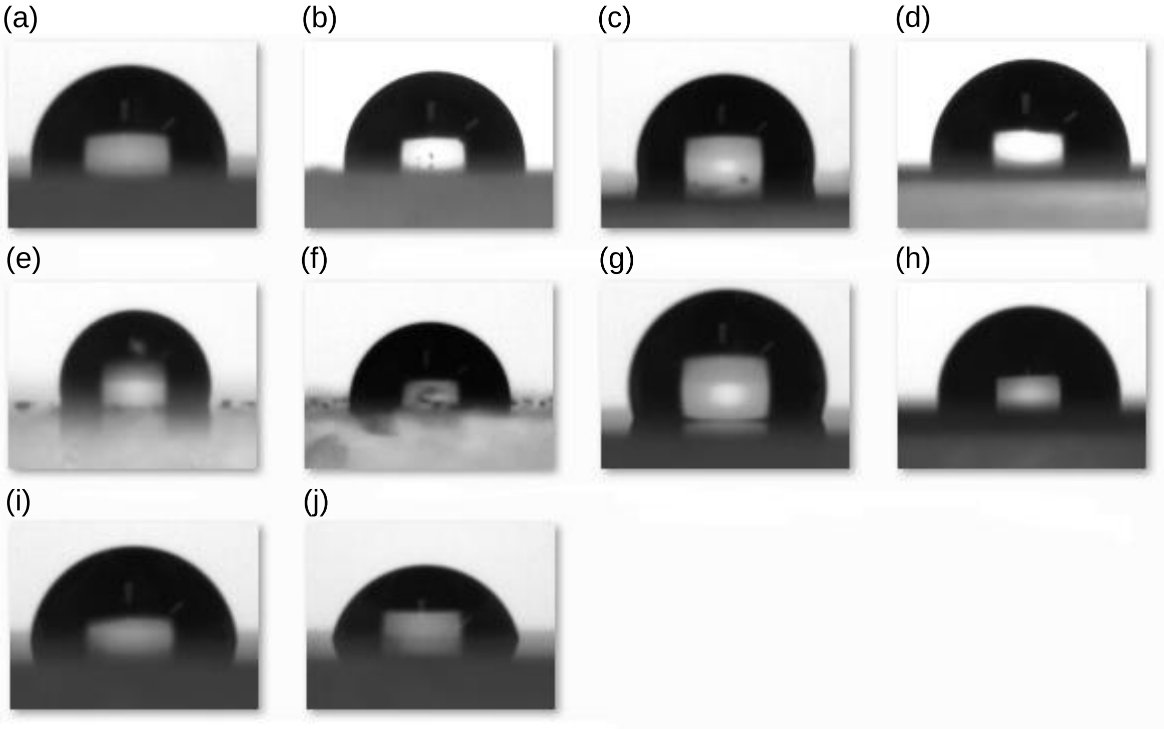
Photovoltaic Device Fabrication

Organic photovoltaic devices were prepared with a structure of ITO/PEDOT:PSS/active layer/Ca/Al. ITO-coated glass substrates were first cleaned by ultrasonication in toluene, acetone, H_2O, and 2-propanol for 10 min, respectively, followed by O_2 plasma treatment for 10 min. ITO-coated glass substrates were then activated by ozone treatment for 1 h. PEDOT:PSS was spin-coated on the ITO surface at 3000 rpm for 1 min and dried at 135 °C for 10 min. The active layers were then prepared by spin-coating on the ITO/PEDOT:PSS electrode at 1000 rpm for 2 min in a glove box. The typical thickness of the active layer was 90–110 nm. Ca and Al electrode were evaporated on the top of active layer through a shadow mask to define the active area of the devices (0.09 cm^2) under a vacuum of 10^{-5} Pa to a thickness of 30, 100 nm determined by a quartz crystal monitor. After sealing the device from the air, the photovoltaic characteristics were measured in air under simulated AM 1.5G solar irradiation (100 mW cm^{-2}) (SAN-EI ELECTRIC, XES-301S). The current-voltage characteristics of photovoltaic devices were measured by using a KEITHLEY 2400 source meter. The EQE spectra were measured by using a Soma Optics Ltd. S-9240. The thickness of active layer was determined by KLA Tencor Alpha-step IQ.

Surface Free Energy Estimation

The contact angles of compounds were measured by a NiCK LSE-ME1 with distilled water and glycerol. The surface free energy was estimated based on the established theory.[3,4]

Compounds	Contact angle (˚) (H_2O)	Contact angle (˚) (glycerol)	Surface free energy (m*J*/m^2)
Imi-a-BT	88.5	97.8	26.1
S-Imi-a-BT	101.4	95.2	13.12
S-Imi-TzTz	88.2	86.4	19.3
P3HT	107.2	102.6	9.7
$PC_{61}BM$	80.9	65.9	33.7



Contact angle measurements of (a) **Imi-a-BT** (H_2O), (b) **Imi-a-BT** (glycerol), (c) **S-Imi-a-BT** (H_2O), (d) **S-Imi-a-BT** (glycerol), (e) **S-Imi-TzTz** (H_2O), (f) **S-Imi-TzTz** (glycerol), (g) **P3HT** (H_2O), (h) **P3HT** (glycerol), (i) **$PC_{61}BM$** (H_2O), (j) **$PC_{61}BM$** (glycerol).

Computational Details

All calculations were conducted using Gaussian 09 program. The geometry was optimized with the restricted Becke Hybrid (B3LYP) at 6-31 G(d, p) level. TD-DFT calculation was performed at the Coulomb attenuated method (CAM) corrected B3LYP/6-31G(d,p) level.

The calculated excited state of **S-Imi(Me)-a-BT**

Excited State 1: 2.6651 eV (465.2 nm) *f* = 1.75

HOMO(145)-LUMO(146) 0.61020

HOMO(145)-LUMO+2(148) 0.24527

Excited State 2: 3.5648 eV (347.8 nm) *f* = 0.53

141 -147 0.41255

Excited State 3: 3.5738 eV (346.9 nm) *f* = 0.37

141 -146 0.40393

145 -148 0.23361

Excited State 4: 3.8235 eV (324.3 nm) *f* = 0.41

136 -146 0.41832

137 -147 0.40120

142 -146 0.22446

The calculated excited state of **S-Imi(Me)-TzTz**

Excited State 1: 2.8636 eV (433.0 nm) *f* = 1.15
HOMO(134) -LUMO(135) 0.63279
HOMO(134)-LUMO+2(137) 0.14336

Excited State 2: 3.5155 eV (352.7 nm) *f* = 1.12
125 -136 0.26660
130 -135 0.41381
131 -136 0.37283

Optimized structure of **Imi(Me)-a-BT**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.509313	-0.915028	-0.000137
2	6	0	-1.458367	-0.947305	-0.000182
3	6	0	-0.724566	0.292496	-0.000330
4	6	0	0.724247	0.292670	-0.000725
5	6	0	1.458340	-0.946956	-0.000829
6	6	0	0.707215	-2.116284	-0.000647
7	6	0	-0.706967	-2.116454	-0.000393
8	7	0	-1.260876	1.515276	-0.000168
9	16	0	-0.000433	2.570503	-0.000640
10	7	0	1.260264	1.515579	-0.000850
11	6	0	-2.871988	-0.953409	0.000059
12	6	0	2.871963	-0.952733	-0.000922
13	6	0	-4.089012	-0.950683	0.000147
14	6	0	4.088986	-0.949911	-0.000796
15	6	0	-5.509334	-0.915575	-0.000179
16	6	0	-6.252133	-2.119842	-0.004819
17	6	0	-7.647780	-2.113755	-0.005877
18	6	0	-8.288104	-0.882399	-0.000581
19	6	0	-7.564197	0.312982	0.004266
20	6	0	-6.182855	0.330202	0.003794
21	6	0	6.183064	0.330623	-0.004068
22	6	0	7.564407	0.313136	-0.004100
23	6	0	8.288095	-0.882374	0.001134
24	6	0	7.647540	-2.113604	0.006365
25	6	0	6.251893	-2.119431	0.004868
26	6	0	8.538312	1.448727	-0.005912
27	7	0	9.808328	0.852542	-0.001300
28	6	0	9.742775	-0.550342	0.003338
29	6	0	-9.742737	-0.550198	-0.002319
30	7	0	-9.808018	0.852789	0.002238
31	6	0	-8.537973	1.448693	0.006338
32	8	0	8.321631	2.643313	-0.005196
33	8	0	10.700047	-1.298290	0.013387
34	8	0	-10.699967	-1.298204	-0.012017
35	8	0	-8.321388	2.643299	0.005525
36	6	0	11.051586	1.601985	-0.006353
37	6	0	-11.050909	1.602838	0.007759
38	1	0	1.228039	-3.067693	-0.000706
39	1	0	-1.227565	-3.067987	-0.000299
40	1	0	-5.712533	-3.060834	-0.007931
41	1	0	-8.216621	-3.037609	-0.010586
42	1	0	-5.625940	1.260505	0.006363
43	1	0	5.626327	1.261032	-0.006921
44	1	0	8.216206	-3.037565	0.011372
45	1	0	5.712115	-3.060321	0.007932
46	1	0	10.888194	2.550812	0.506357
47	1	0	11.813561	1.014191	0.507139
48	1	0	11.387602	1.804016	-1.028500
49	1	0	-11.819076	1.002414	-0.481166
50	1	0	-11.372283	1.828413	1.029683
51	1	0	-10.896469	2.539916	-0.528929

Optimized structure of **S-Imi(Me)-a-BT**

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.508314	-0.979132	-0.000243
2	6	0	1.458251	-0.985749	-0.000198
3	6	0	0.724437	0.254089	-0.000223
4	6	0	-0.724447	0.254083	-0.000241
5	6	0	-1.458253	-0.985760	-0.000254
6	6	0	-0.706842	-2.155374	-0.000246
7	6	0	0.706848	-2.155368	-0.000215
8	7	0	1.260512	1.476804	-0.000198
9	16	0	-0.000013	2.531866	-0.000242
10	7	0	-1.260531	1.476795	-0.000273
11	6	0	2.871357	-0.993959	-0.000156
12	6	0	-2.871359	-0.993982	-0.000279
13	6	0	4.088657	-0.997022	-0.000024
14	6	0	-4.088659	-0.997043	-0.000307
15	6	0	5.508312	-0.979120	0.000077
16	6	0	6.235887	-2.195226	0.000363
17	6	0	7.627712	-2.207543	0.000465
18	6	0	8.292476	-0.984337	0.000270
19	6	0	7.581304	0.225490	-0.000024
20	6	0	6.196975	0.255146	-0.000121
21	6	0	-6.196974	0.255136	0.000020
22	6	0	-7.581302	0.225486	0.000091
23	6	0	-8.292476	-0.984339	-0.000102
24	6	0	-7.627717	-2.207549	-0.000369
25	6	0	-6.235892	-2.195237	-0.000434
26	6	0	-8.559404	1.326776	0.000328
27	7	0	-9.810844	0.719612	0.000241
28	6	0	-9.727001	-0.675055	0.000016
29	6	0	9.727003	-0.675047	0.000320
30	7	0	9.810851	0.719603	0.000043
31	6	0	8.559406	1.326781	-0.000188
32	6	0	-11.056661	1.473755	0.000532
33	6	0	11.056665	1.473753	-0.000010
34	1	0	-1.227694	-3.106760	-0.000262
35	1	0	1.227706	-3.106752	-0.000204
36	1	0	5.684306	-3.129089	0.000509
37	1	0	8.185661	-3.137945	0.000692
38	1	0	5.654602	1.193992	-0.000348
39	1	0	-5.654598	1.193980	0.000162
40	1	0	-8.185670	-3.137948	-0.000516
41	1	0	-5.684312	-3.129101	-0.000636
42	1	0	-11.103816	2.110593	-0.885830
43	1	0	-11.879420	0.760568	-0.000189
44	1	0	-11.104274	2.109262	0.887834
45	1	0	11.879426	0.760564	0.000289
46	1	0	11.104173	2.109667	-0.887023
47	1	0	11.103930	2.110171	0.886649
48	16	0	8.277252	2.950041	-0.000536
49	16	0	10.989016	-1.737636	0.000638
50	16	0	-8.277224	2.950044	0.000696
51	16	0	-10.989022	-1.737616	-0.000113

Optimized structure of **Imi(Me)-TzTz**

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	6.391261	0.923878	-0.000052
2	6	0	5.825844	-0.354199	-0.000166
3	6	0	4.458680	-0.548996	-0.000264
4	6	0	3.630360	0.596247	-0.000181
5	6	0	4.210362	1.880986	-0.000092
6	6	0	5.595636	2.059632	-0.000052
7	6	0	7.876490	0.783083	0.000013
8	7	0	8.120934	-0.600680	0.000109
9	6	0	6.938225	-1.354502	-0.000171
10	8	0	8.726204	1.651132	-0.000047
11	8	0	6.881380	-2.567053	-0.000398
12	6	0	9.447648	-1.189981	0.000687
13	6	0	2.177158	0.407405	-0.000143
14	7	0	1.608661	-0.778538	-0.000091
15	6	0	0.265130	-0.642384	-0.000027
16	6	0	-0.265130	0.642382	-0.000022
17	16	0	1.045021	1.791219	-0.000119
18	16	0	-1.045021	-1.791221	0.000073
19	6	0	-2.177158	-0.407406	0.000098
20	7	0	-1.608661	0.778536	0.000045
21	6	0	-3.630360	-0.596247	0.000145
22	6	0	-4.210362	-1.880986	0.000019
23	6	0	-5.595637	-2.059632	-0.000008
24	6	0	-6.391261	-0.923877	0.000050
25	6	0	-5.825844	0.354199	0.000198
26	6	0	-4.458680	0.548996	0.000278
27	6	0	-7.876490	-0.783082	0.000021
28	7	0	-8.120933	0.600681	-0.000049
29	6	0	-6.938224	1.354503	0.000255
30	8	0	-8.726205	-1.651131	0.000032
31	8	0	-6.881379	2.567053	0.000496
32	6	0	-9.447647	1.189984	-0.000606
33	1	0	4.021699	-1.540524	-0.000370
34	1	0	3.570750	2.758561	-0.000031
35	1	0	6.035957	3.050978	0.000001
36	1	0	10.169297	-0.372848	-0.011835
37	1	0	9.593804	-1.801523	0.894927
38	1	0	9.584259	-1.821581	-0.880866
39	1	0	-3.570751	-2.758562	-0.000084
40	1	0	-6.035959	-3.050978	-0.000090
41	1	0	-4.021698	1.540524	0.000410
42	1	0	-10.169299	0.372845	0.011342
43	1	0	-9.584473	1.821128	0.881243
44	1	0	-9.593585	1.801988	-0.894561

Optimized structure of **S-Imi(Me)-TzTz**

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	6.392217	0.944908	0.000012
2	6	0	5.827764	-0.339785	0.000019
3	6	0	4.457269	-0.533149	0.000002
4	6	0	3.627181	0.607306	0.000004
5	6	0	4.203978	1.895803	0.000056
6	6	0	5.585190	2.077705	0.000053
7	6	0	7.853908	0.807487	-0.000010
8	7	0	8.100178	-0.567282	0.000040
9	6	0	6.928930	-1.318277	0.000028
10	6	0	9.425863	-1.170485	-0.000001
11	6	0	2.175749	0.413333	-0.000051
12	7	0	1.610169	-0.774341	-0.000159
13	6	0	0.266862	-0.642082	-0.000098
14	6	0	-0.266862	0.642082	0.000066
15	16	0	1.038995	1.794382	0.000152
16	16	0	-1.038995	-1.794382	-0.000179
17	6	0	-2.175749	-0.413333	0.000013
18	7	0	-1.610169	0.774341	0.000131
19	6	0	-3.627181	-0.607306	-0.000028
20	6	0	-4.203978	-1.895803	-0.000077
21	6	0	-5.585190	-2.077705	-0.000062
22	6	0	-6.392217	-0.944908	-0.000013
23	6	0	-5.827764	0.339785	-0.000021
24	6	0	-4.457268	0.533149	-0.000014
25	6	0	-7.853908	-0.807487	0.000022
26	7	0	-8.100178	0.567282	-0.000005
27	6	0	-6.928930	1.318277	-0.000018
28	6	0	-9.425863	1.170485	0.000056
29	1	0	4.024845	-1.526777	-0.000028
30	1	0	3.562396	2.771767	0.000100
31	1	0	6.024570	3.069379	0.000089
32	1	0	10.160038	-0.366468	0.000167
33	1	0	9.546952	-1.796963	0.886710
34	1	0	9.547060	-1.796645	-0.886928
35	1	0	-3.562396	-2.771767	-0.000128
36	1	0	-6.024570	-3.069379	-0.000095
37	1	0	-4.024845	1.526777	0.000015
38	1	0	-10.160038	0.366469	0.000000
39	1	0	-9.547006	1.796726	0.886933
40	1	0	-9.547007	1.796883	-0.886705
41	16	0	-6.841013	2.963065	-0.000086
42	16	0	6.841013	-2.963064	0.000102
43	16	0	8.981356	2.011249	-0.000096
44	16	0	-8.981357	-2.011249	0.000120

Optimized structure of **Imi(Me)**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.907806	-0.704457	0.000005
2	6	0	-2.909765	0.695867	0.000003
3	6	0	-1.710653	1.420791	-0.000001
4	6	0	-0.527821	0.697066	-0.000004
5	6	0	-0.525836	-0.699429	-0.000003
6	6	0	-1.706723	-1.426169	0.000003
7	6	0	0.889784	1.168414	-0.000004
8	7	0	1.673199	0.002171	-0.000001
9	6	0	0.894206	-1.164387	-0.000013
10	6	0	3.124601	-0.000755	0.000011
11	1	0	-3.856960	1.226601	0.000006
12	1	0	-1.699558	2.505788	-0.000002
13	1	0	-1.692775	-2.511146	0.000003
14	1	0	3.453767	1.038667	-0.000073
15	1	0	3.505775	-0.511935	0.887959
16	1	0	3.505780	-0.512088	-0.887845
17	1	0	-3.853690	-1.237814	0.000009
18	8	0	1.332916	-2.297223	-0.000002
19	8	0	1.317753	2.305359	-0.000002

Optimized structure of **S-Imi(Me)**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.132143	-0.788287	-0.000006
2	6	0	-3.170705	0.613363	-0.000003
3	6	0	-1.993801	1.368014	0.000002
4	6	0	-0.785626	0.679583	0.000005
5	6	0	-0.747569	-0.722149	0.000004
6	6	0	-1.915097	-1.476694	-0.000004
7	6	0	0.599072	1.176840	0.000004
8	7	0	1.406652	0.038695	-0.000002
9	6	0	0.662980	-1.138139	0.000014
10	6	0	2.862842	0.055818	-0.000012
11	1	0	-4.131006	1.119738	-0.000005
12	1	0	-2.010136	2.452840	0.000002
13	1	0	-1.871006	-2.560768	-0.000003
14	1	0	3.185298	1.095852	-0.000097
15	1	0	3.239087	-0.459357	0.886791
16	1	0	3.239072	-0.459505	-0.886733
17	16	0	1.283951	-2.665321	0.000002
18	16	0	1.108902	2.745145	0.000001
19	1	0	-4.063243	-1.346931	-0.000009

Optimized structure of **S-TImi(Me)**:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.567916	-1.592037	-0.000016
2	16	0	2.630585	0.154221	-0.000070
3	6	0	0.911944	0.216188	0.000032
4	6	0	0.343252	-1.037619	0.000079
5	6	0	1.289891	-2.093797	0.000025
6	6	0	-0.123813	1.233938	-0.000074
7	7	0	-1.325382	0.512586	-0.000717
8	6	0	-1.112623	-0.869773	0.000004
9	16	0	-2.265291	-2.048604	0.000181
10	16	0	0.018571	2.876526	0.000245
11	6	0	-2.632672	1.153606	-0.000173
12	1	0	3.495952	-2.147459	0.000030
13	1	0	1.047409	-3.148728	0.000087
14	1	0	-3.387326	0.368337	-0.010547
15	1	0	-2.745985	1.772947	0.892702
16	1	0	-2.737586	1.789474	-0.882219

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