Supporting information

Biazulene Diimides: A New Building Block for Organic Electronic Materials.

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Experimental Section

1. Materials and General Methods.

Bis(1,5-cyclooctadiene)nickel(0), Bis(triphenylphosphine)palladium(II) dichloride were purchased from Aldrich and used without further purification. Other reagents were obtained commercially and used as received. $^1$H NMR (300 MHz or 400 MHz) and $^{13}$C NMR (100 MHz) spectra were measured on Varian Mercury (300 MHz and 400 MHz) instruments. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Mass spectra (DART-FT, ESI-FT and MALDI-FT) were carried out on a Thermo Fisher Scientific LTQ FT Ultra Mass Spectrometer. Optical absorption spectra were measured on a U-3900 UV-vis spectrophotometer. Fluorescence spectra were measured on a HITACHI F-2700 fluorescence spectrophotometer (for room temperature measurements) or Perkin-Elmer spectrofluorometer LS 55 (for –198 °C measurements). TGA measurements were conducted on a TGA Q500 instruments under a dry nitrogen flow at a heating rate of 10 °C/min, heating from room temperature to 500 °C or 600 °C. DSC analyses were performed on a DSC Q2000 instruments under a dry nitrogen flow at a heating rate of 5 °C/min, heating from –30 °C to 300 °C for BAzDI-1 and from –25 °C to 330 °C for BAzDI-2. Electrochemical measurements was carried out on a CHI610D instruments in a conventional three-electrode cell with a platinum button working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode. Melting point were measured on an SGW X-4 microscopic melting point apparatus.

2. Synthesis

\[ \text{EtO} \quad \text{EtO} \quad \text{Cl} \quad \text{Ni(COD)}_2 \quad \text{DMF/50°C} \quad \text{71%} \quad \text{EtO} \quad \text{EtO} \quad \text{Et} \]

$^1$H NMR (300 MHz or 400 MHz) and $^{13}$C NMR (100 MHz) spectra were measured on Varian Mercury (300 MHz and 400 MHz) instruments. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Mass spectra (DART-FT, ESI-FT and MALDI-FT) were carried out on a Thermo Fisher Scientific LTQ FT Ultra Mass Spectrometer. Optical absorption spectra were measured on a U-3900 UV-vis spectrophotometer. Fluorescence spectra were measured on a HITACHI F-2700 fluorescence spectrophotometer (for room temperature measurements) or Perkin-Elmer spectrofluorometer LS 55 (for –198 °C measurements). TGA measurements were conducted on a TGA Q500 instruments under a dry nitrogen flow at a heating rate of 10 °C/min, heating from room temperature to 500 °C or 600 °C. DSC analyses were performed on a DSC Q2000 instruments under a dry nitrogen flow at a heating rate of 5 °C/min, heating from –30 °C to 300 °C for BAzDI-1 and from –25 °C to 330 °C for BAzDI-2. Electrochemical measurements was carried out on a CHI610D instruments in a conventional three-electrode cell with a platinum button working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) reference electrode. Melting point were measured on an SGW X-4 microscopic melting point apparatus.
Tetraethyl 2,2'-biazulene-1,1',3,3'-tetracarboxylate 2: A mixture of Diethyl 2-chloroazulene-1,3-dicarboxylate (920 mg, 3 mmol) I and Ni(COD)$_2$ (454 mg, 1.65 mmol) was dissolved in DMF (10 mL) under nitrogen atmosphere. The reaction mixture was heated at 50 °C for 6 h. It was then poured into water and extracted with dichloromethane. The combined organic phases was washed with water and dried over Na$_2$SO$_4$. After concentrated under reduced pressure, the residue was purified by column chromatography on silica gel with dichloromethane/ hexane (2:1) to give product as red crystals (572 mg, 71% yield). $^1$H NMR (400 MHz, CDCl$_3$), $\delta$ (ppm): 9.81 (d, $J = 10.1$ Hz, 4H), 7.92 (t, $J = 9.7$ Hz, 2H), 7.74 (dd, $J = 10.1$ Hz, 9.7 Hz, 4H), 3.89 (q, $J = 7.0$ Hz, 8H), 0.52 (t, $J = 7.0$ Hz, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$), $\delta$ (ppm): 165.2, 155.3, 143.3, 139.6, 138.2, 130.4, 116.1, 59.3, 13.3. MS (MALDI) m/z: 542.0 (M)$^+$. HRMS (DART-FT) (m/z): (M+H)$^+$ Calcd for C$_{32}$H$_{31}$O$_8$ 543.2013; Found, 543.2000.

$2,2'$-biazulene-1,1',3,3'-tetracarboxylic acid 3: A mixture of tetraethyl 2,2'-biazulene-1,1',3,3'-tetracarboxylate 2 (542 mg, 1.0 mmol), EtOH (16 mL) and 12 M KOH aq. (1 mL) was refluxed for 4 h. The mixture was diluted with water and filtered to remove insoluble materials. The filtrate was then acidified with 2 M HCl and red crystals separated out were collected by filtration to give product as a red solid (386 mg, 90% yield). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm): 11.86 (s, 4H), 9.71 (d, $J = 10.3$ Hz, 4H), 8.08 (t, $J = 9.9$ Hz, 2H), 7.86 (dd, $J = 10.3$ Hz, 9.9 Hz 4H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$ 166.0, 155.6, 142.5, 139.9, 137.6, 130.1, 116.5. MS (MALDI) m/z: 452.4 (M+Na)$^+$. HRMS (DART-FT) (m/z): (M+H)$^+$ Calcd for C$_{24}$H$_{14}$O$_8$Na 453.0581; Found, 453.0577.
2,2'-biazulene-1,1',3,3'-tetracarboxylic dianhydride 4: A mixture of 2,2'-biazulene-1,1',3,3'-tetracarboxylic acid 3 (430 mg, 1.0 mmol) and acetic anhydride (5 mL) was refluxed for 2 h. Then the mixture was filtrated to give product as a red solid (374 mg, 95% yield). FT-IR (KBr, cm⁻¹) ν 3079.8, 2396.4, 1705.1, 1686.1, 1579.7, 1453.1, 1431.0, 1381.8, 1368.0, 1327.3, 1299.1, 1240.9, 1159.9, 1132.9, 1091.3, 1067.7, 1016.8, 956.4, 884.7, 857.3, 760.7, 687.8, 592.7, 476.7, 417.7. Anal. Calcd for C₂₄H₁₀O₆: C, 73.10; H, 2.56. Found: C, 73.00; H, 2.60.

1',3'-bis(octylcarbamoyl)-2,2'-biazulene-1,3-dicarboxylic acid 5: A solution of n-octylamine solution (113 mg, 0.88 mmol) in 5 mL of dichloromethane was added dropwise to the solution of 2,2'-biazulene-1,1',3,3'-tetracarboxylic dianhydride 4 (160 mg, 0.4 mmol) in 10 mL of dichloromethane. The reaction was stirred under reflux for 4h. Upon removal of solvent, the residue was purified by column chromatography with dichloromethane/ethanol (20:1) to give product as a purple solid (204 mg, 77% yield). ¹H NMR (400 MHz, DMSO-d₆), δ (ppm): 9.55 (d, J = 10.0 Hz, 2H), 9.02 (d, J = 9.8 Hz, 2H), 8.20 (t, J = 9.8 Hz, 1H), 7.95 (t, J = 10.0 Hz, 1H), 7.95 (dd, J = 10.0 Hz, 9.8 Hz, 2H), 7.60 (dd, J = 10.0 Hz, 9.8 Hz, 2H), 6.89 (t, J = 5.6 Hz, 2H), 2.99 (m, J = 4H), 1.20-1.13 (m, 4H), 1.06-0.98 (m, 4H), 0.86-0.59 (m, 22H). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 166. 6, 166.4, 146.5, 143.7, 142.6, 141.2, 140.1, 137.6, 130.7, 126.6, 120.3, 117.8, 39.7, 31.7, 29.0, 28.8, 28.7, 26.3, 26.4, 22.5, 14.1. MS (MALDI) m/z: 675.3 (M+Na)⁺. HRMS (MALDI-FT) (m/z): (M+H)⁺ Caled for C₄₀H₄₀O₆N₂ 653.3585;
Found, 653.3586.

\[ \text{BAzDI-1} \]

\[ \text{SOCl}_2 \] reflux 78\%

\[ \text{N,N'}-\text{bis(n-octyl)}-2,2'-\text{biazulene-1,1',3,3'-tetracarboxdiimide} \]

\[ \text{BAzDI-1:} \] A solution of 1',3'-bis(octylcarbamoyl)-2,2'-biazulene-1,3-dicarboxylic acid 5 (90 mg, 0.14 mmol) in 5 mL of thionyl chloride was refluxed for 3 h. Then all thionyl chloride was removed under vacuum. The residual oil was purified by column chromatography using dichloromethane/hexane (2:1) as eluent to provide product as a green solid (66 mg, 78% yield). M.p. = 205 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 9.83 (d, \(J = 10.6\) Hz, 4H), 8.04 (t, \(J = 9.3\) Hz, 2H), 7.82 (dd, \(J = 10.6\) Hz, 9.3 Hz, 4H), 4.40 (t, \(J = 7.4\) Hz, 4H), 1.86 (m, 4H), 1.47 – 1.26 (m, 20H), 0.86 (t, \(J = 6.6\) Hz, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 165.9, 143.9, 142.2, 140.7, 136.7, 131.3, 118.6, 46.6, 31.8, 29.4, 29.3, 29.0, 27.4, 22.7, 14.1. FT-IR (KBr, cm\(^{-1}\)) \(\nu\) 2919.2, 2851.1, 2359.5, 1647.1, 1614.4, 1452.0, 1420.4, 1389.7, 1317.3, 1253.2, 1296.4, 1235.2, 1167.6, 1138.4, 1034.4, 959.3, 886.7, 855.3, 806.8, 772.9, 746.6, 734.5, 707.3, 684.1, 612.8, 569.9. Anal. Calcd for C\(_{40}\)H\(_{44}\)O\(_4\)N\(_2\): C, 77.89; H, 7.19; N, 4.54. Found: C, 77.74; H, 7.24; N, 4.55. MS (MALDI) m/z: 616.2 (M\(^+\)) HRMS (DART-FT) (m/z): (M+H\(^+\)) Calcd for C\(_{40}\)H\(_{45}\)O\(_4\)N\(_2\) 617.3374; Found, 617.3362.

\[ \text{Diethyl 2-chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)azulene-1,3-dicarboxylate 7:} \] Dry hydrogen chloride gas passed through a solution of Diethyl 2-amino-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)azulene-1,3-dicarboxylate 6 (1.24 g, 3.0 mmol) in toluene (75 mL) at 5 °C. After isoamyl nitrite (1.76 g, 15 mmol)
was added dropwise, the mixture was stirred and green precipitates began to separate out. It was then left to sit at room temperature to react for 72 h until the color changed to dark red. The mixture was poured into water (150 mL) and extracted with toluene. The organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography with hexane/ethyl acetate (5:1) to give product as Reddish violet crystals (1.12 g, 86% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 9.44 (d, $J = 10.2$ Hz, 2H), 8.21 (d, $J = 10.2$ Hz, 2H), 4.47 (d, $J = 7.1$ Hz, 4H), 1.46 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 164.2, 144.8, 142.7, 136.8, 115.0, 85.2, 60.6, 24.9, 14.4. MS (MALDI) m/z: 433.1 (M+H)$^+$. HRMS (DART-FT) (m/z): (M+H)$^+$ Calcd for C$_{22}$H$_{27}$O$_6$BCl 432.1620; Found, 432.1616.

**Diethyl 2'-chloro-2,6'-biazulene-1',3'-dicarboxylate 9:** A mixture of Pd(PPh$_3$)$_2$Cl$_2$ (140 mg, 0.2 mmol), 2-bromoaizulene 8 (414 mg, 2.0 mmol), Diethyl 2-chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)azulene-1,3-dicarboxylate 7 (1.56 g, 3.6 mmol), 2M NaHCO$_3$ aq. (4 mL) in toluene (8 mL) and EtOH (4 mL) was reacted at 60 °C for 2 h under nitrogen atmosphere. The mixture was poured into water (50 mL) and extracted with dichloromethane. The organic phase was dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The residual was purified by column chromatography using dichloromethane/hexane (2:1) as eluent to provide product as dark green solid (510 mg, 59% yield). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ (ppm): 9.44 (d, $J = 11.1$ Hz, 2H), 8.71 (d, $J = 11.1$ Hz, 2H), 8.50 (d, $J = 9.6$ Hz, 2H), 8.08 (s, 2H), 7.73 (t, $J = 9.8$ Hz, 1H), 7.32 (dd, $J = 9.8$ Hz, 9.6 Hz, 2H), 4.44 (q, $J = 7.1$ Hz, 4H), 1.42 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 164.3, 149.9, 148.4, 142.9, 141.3, 140.5, 138.7, 138.2, 136.9, 130.8, 124.5, 116.3, 115.3, 60.6, 14.5. MS (MALDI) m/z: 433.1 (M+H)$^+$. HRMS (DART-FT) (m/z): (M+H)$^+$ Calcd for C$_{26}$H$_{22}$O$_6$Cl 433.1201; Found, 433.1201.
Tetraethyl 2,6':2''':6'',2'''-quaterazulene-1',1'',3',3''-tetracarboxylate 10: A mixture of Diethyl 2'-chloro-2,6'-biazulene-1',3'-dicarboxylate 9 (1.68 g, 3.7 mmol) and Ni(COD)$_2$ (1.0 g, 3.7 mmol) was dissolved in DMF (12 mL) under nitrogen atmosphere. The reaction mixture was heated at 50 °C for 6 h. It was then poured into water and extracted with dichloromethane. The combined organic phases was washed with water and dried over Na$_2$SO$_4$. After concentrated under reduced pressure, the residue was purified by column chromatography on silica gel with dichloromethane/hexane (8:1) to give product as dark green crystals (1.49 g, 97% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ (ppm): 9.86 (d, $J = 10.8$ Hz, 4H), 8.43 (d, $J = 10.8$ Hz, 4H), 8.41 (d, $J = 9.6$ Hz, 4H), 7.86 (s, 4H), 7.62 (t, $J = 10.0$ Hz, 2H), 7.23 (dd, $J = 10.0$ Hz, 9.6 Hz, 4H), 3.97 (q, $J = 7.0$ Hz, 8H), 0.64 (t, $J = 7.0$ Hz, 12H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ (ppm): 165.3, 155.4, 151.1, 147.8, 142.3, 141.5, 138.4, 138.0, 137.2, 130.4, 124.5, 116.5, 116.4, 59.4, 13.4. MS (MALDI) m/z: 817.1 (M+Na)$^+$. HRMS (DART-FT) (m/z): (M+H)$^+$ Calcd for C$_{52}$H$_{43}$O$_8$ 795.2952; Found, 795.2945.

2,6':2'',6'',2'''-quaterazulene-1',1'',3',3''-tetracarboxylic acid 11: A mixture of tetraethyl 2,6':2'',6'',2'''-quaterazulene-1',1'',3',3''-tetracarboxylate (794 mg, 1.0 mmol), THF (12 mL), EtOH (16 mL) and 12 M KOH aq. (1 mL) was refluxed for 24 h. The mixture was diluted with water and filtered to remove insoluble materials. The filtrate was then acidified with 2 M HCl and crystals separated out were collected by filtration to give product as a brown solid (636 mg, 83% yield). MS (ESI) m/z: 681.2 (M–H)$^–$. HRMS (ESI Negative) (m/z): (M–H)$^–$ Calcd for C$_{44}$H$_{25}$O$_8$ 681.1555; Found, 681.1544.
2,6':2',2''':6'',2''''-quaterazulene-1',1'',3',3'''-tetracarboxylic dianhydride 12: A mixture of 2,6':2',2''':6'',2''''-quaterazulene-1',1'',3',3'''-tetracarboxylic acid (205 mg, 0.3 mmol) and acetic anhydride (5 mL) was refluxed for 2 h. Then the mixture was filtrated to give product as a brown solid (169 mg, 87% yield). FT-IR (KBr, cm\(^{-1}\)) \(\nu\) 2970.7, 1690.0, 1566.1, 1433.2, 1405.0, 1366.7, 1329.4, 1250.9, 1214.2, 1189.4, 1122.0, 993.6, 913.2, 895.2, 859.5, 810.2, 756.5, 691.2, 571.9, 532.4. MS (MALDI) m/z: 647.2 (M+H\(^+\)).

\(N,N'\)-bis(2-hexyldecan)-2,6':2',2''':6'',2''''-quaterazulene-1',1'',3',3'''-tetracarboxdiimide BAzDI-2: A solution of 2-hexyldecan-1-amine solution (73 mg, 0.3 mmol) in 5 mL of dichloromethane was added dropwise to the solution of 2,6':2',2''':6'',2''''-quaterazulene-1',1'',3',3'''-tetracarboxylic dianhydride 12 (65 mg, 0.1 mmol) in 10 mL of dichloromethane. The reaction was stirred under reflux for 4h. Upon removal of solvent, the residue was then added 10 mL of acetic anhydride and CH\(_3\)COONa (82 mg, 1.0 mmol). The resulting mixture was heated to reflux for another 4 h. The reaction mixture was diluted with water and thoroughly extracted with dichloromethane. The combined organic phases was washed with water and dried over Na\(_2\)SO\(_4\). After concentrated under reduced pressure, the residue was purified by column chromatography on silica gel with dichloromethane/ hexane (1:2) to give product as red crystals (46 mg, 42% yield). M.p. = 282 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 9.63 (d, \(J = 11.2\) Hz, 4H), 8.30 (d, \(J = 11.2\) Hz, 4H), 8.27 (d, \(J = 9.3\) Hz, 4H), 7.68 (s, 4H), 7.50 (t, \(J = 9.9\) Hz, 2H), 7.12 (dd, \(J = 9.9\) Hz, 9.3 Hz, 4H), 4.45 (d, \(J = 7.5\) Hz, 4H), 2.10 (s, 2H), 1.29 (m, 48H), 0.79 (t, \(J = 6.7\) Hz, 12H). \(^{13}\)C NMR
(100 MHz, CDCl₃) δ 165.7, 149.4, 149.3, 142.2, 140.9, 138.6, 138.3, 137.9, 135.8, 130.3, 124.0, 118.2, 116.0, 49.7, 36.9, 31.4, 29.8, 29.4, 29.2, 29.0, 26.0, 22.2, 22.2, 13.6. FT-IR (KBr, cm⁻¹) ν 2921.1, 2850.3, 2363.1, 1646.2, 1613.4, 1567.8, 1479.6, 1425.5, 1386.8, 1329.2, 1256.1, 1171.5, 1017.8, 943.4, 915.6, 895.9, 853.9, 803.4, 779.8, 759.8, 724.2, 681.5, 607.8, 573.9, 533.2, 408.5. Anal. Calcd for C₇₆H₈₈O₄N₂: C, 83.47; H, 8.11; N, 2.56. Found: C, 83.61; H, 8.03; N, 2.39. MS (MALDI) m/z: 1093.7 (M+H)⁺. HRMS (MALDI-FT) (m/z): (M+H)⁺ Calcd for C₇₆H₈₉O₄N₂ 1093.6817; Found, 1093.6812.

3. TGA and DSC curves for BAzDI-1 and BAzDI-2.
Figure S1. (a) TGA measurements for \textbf{BAzDI-1}. (b) TGA measurements for \textbf{BAzDI-2}. (c) DSC measurements for \textbf{BAzDI-1}. (d) DSC measurements for \textbf{BAzDI-2}.

4. X-ray Crystallographic Structure for \textbf{BAzDI-1}.

Figure S2. (a) ORTEP diagram of \textbf{BAzDI-1}. (b) Interplannar distance of \textbf{BAzDI-1}.

Table S1. Crystal data and structure refinement for \textbf{BAzDI-1}.
Empirical formula C40 H44 N2 O4
Formula weight 616.77
Temperature 293(2) K
Wavelength 0.71073 Å
Crystal system Triclinic
Space group P -1
Unit cell dimensions
\[ \begin{align*}
    a &= 10.124(2) \text{ Å} \\
    b &= 10.455(3) \text{ Å} \\
    c &= 17.030(4) \text{ Å} \\
    a &= 90.017(5)°. \\
    b &= 94.225(7)°. \\
    c &= 109.592(6)°.
\end{align*} \]

Volume 1693.0(7) Å³
Z 2
Density (calculated) 1.210 Mg/m³
Absorption coefficient 0.078 mm⁻¹
F(000) 660
Crystal size 0.180 x 0.110 x 0.040 mm³
Theta range for data collection 2.068 to 25.498°.
Index ranges \[-11 <= h <= 12, -12 <= k <= 12, -16 <= l <= 20\]
Reflections collected 9989
Independent reflections 6310 [R(int) = 0.0476]
Completeness to theta = 25.242° 99.9 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.7456 and 0.5895
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 6310 / 98 / 491
Goodness-of-fit on F² 0.990
Final R indices [I>2sigma(I)] R1 = 0.0785, wR2 = 0.1806
R indices (all data) R1 = 0.1956, wR2 = 0.2416
Largest diff. peak and hole 0.247 and -0.214 e.Å⁻³

5. The geometries of 2,2'-biazulene, BAzDI-1 and BAzDI-2 obtained by DFT calculations.
Figure S3. The geometries of 2,2′-biazulene (a, b), BAzDI-1 (c, d), and N,N’-bis(methyl)-substituted model molecule for BAzDI-2 (e, f), obtained by DFT calculations.

6. UV-Vis spectra of BAzDI-1 and BAzDI-2 in solution and thin film.

Figure S4. UV-vis spectra of BAzDI-1 (green, in CH₂Cl₂; pink, as-spun film) and BAzDI-2 (red, in CH₂Cl₂; blue, as-spun film).

7. Spectra and color of BAzDI-1 and PDI.
Figure S5. (a) Absorption spectra of BAzDI-1 and N,N'-bis(1-ethylpropyl)-3,4:9,10-perylenebis(dicarboximide) PDI. (b) Emission spectra of BAzDI-1 (no fluorescence was observed at room temperature, and only very weak fluorescence was measured at –198 °C) and PDI (very strong fluorescence, measured at room temperature). (c) Color of BAzDI-1 (violet, in CH₂Cl₂) and PDI (yellow, in CH₂Cl₂). (d) Color of BAzDI-1 (green, solid state) and PDI (red, solid state).


Table S2. Characteristics of OFETs Based on BAzDI-2 at Different Annealing
Temperatures.

<table>
<thead>
<tr>
<th>Annealing Temperature(°C)</th>
<th>$\mu_e (\mu_{ave})$ $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$</th>
<th>$I_{on}/I_{off}$ $10^4$–$10^5$</th>
<th>$V_T$ (V) $38$–$58$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>$3.0 \times 10^{-4} (2.3 \times 10^{-4})$</td>
<td>$10^4$–$10^5$</td>
<td>$38$–$58$</td>
</tr>
<tr>
<td>80 °C</td>
<td>$1.2 \times 10^{-2} (0.8 \times 10^{-2})$</td>
<td>$10^4$–$10^5$</td>
<td>$42$–$56$</td>
</tr>
<tr>
<td>120 °C</td>
<td>$1.5 \times 10^{-2} (1.3 \times 10^{-2})$</td>
<td>$10^4$–$10^5$</td>
<td>$50$–$65$</td>
</tr>
</tbody>
</table>

9. XRD and AFM measurements for BAzDI-2.

Figure S6. XRD patterns of spin-coated thin films of BAzDI-2 annealed at room temperature (a), 80 °C (b) and 120 °C (c).

Figure S7. AFM images of spin-coated thin films of BAzDI-2 annealed at room temperature (a), 80 °C (b) and 120 °C.

10. NMR, MS and IR spectra.
Figure S8. $^1$H NMR spectrum of 2 (400 MHz, CDCl$_3$).

Figure S9. $^{13}$C NMR spectrum of 2 (100 MHz, CDCl$_3$).
Figure S10. $^1$H NMR spectrum of 3 (400 MHz, DMSO-$d_6$).

Figure S11. $^{13}$C NMR spectrum of 3 (100 MHz, DMSO-$d_6$).
Figure S12. $^1$H NMR spectrum of 5 (400 MHz, DMSO-$d_6$).

Figure S13. $^{13}$C NMR spectrum of 5 (100 MHz, CDCl$_3$).
Figure S14. $^{1}$H NMR spectrum of BAzDI-1 (400 MHz, CDCl$_3$).

Figure S15. $^{13}$C NMR spectrum of BAzDI-1 (100 MHz, CDCl$_3$).
Figure S16. $^1$H NMR spectrum of 7 (400 MHz, CDCl$_3$).

Figure S17. $^{13}$C NMR spectrum of 7 (100 MHz, CDCl$_3$).
Figure S18. $^1$H NMR spectrum of 9 (300 MHz, DMSO-$d_6$).

Figure S19. $^{13}$C NMR spectrum of 9 (100 MHz, CDCl$_3$).
Figure S20. $^1$H NMR spectrum of 10 (300 MHz, CDCl$_3$).

Figure S21. $^{13}$C NMR spectrum of 10 (100 MHz, CDCl$_3$).
Figure S22. $^1$H NMR spectrum of BAzDI-2 (400 MHz, CDCl$_3$).

Figure S23. $^{13}$C NMR spectrum of BAzDI-2 (100 MHz, CDCl$_3$).
Figure S24. MS spectrum of 2.
Figure S25. HRMS spectrum of 2.
Figure S26. MS spectrum of 3.
Figure S27. HRMS spectrum of 3
Figure S28. MS spectrum of 5
Figure S29. HRMS spectrum of 5
Figure S30. MS spectrum of BAzD1-1
Figure S31. HRMS spectrum of BAzD1-1
Figure S32. MS spectrum of 7
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number: D160858

Sample Serial Number: 4-69-1

Operator: HUAQIN Date: 2016/03/31

Operation Mode: DART Positive

Elemental composition search on mass 432.16

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<th>Theo. Mass</th>
<th>Delta (ppm)</th>
<th>RDB equiv.</th>
<th>Composition</th>
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<td>432.1620</td>
<td>-1.03</td>
<td>9.0</td>
<td>C_{22} H_{27} O_{6} B Cl</td>
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Figure S33. HRMS spectrum of 7
Figure S34. MS spectrum of 9
Instrument: Thermo Fisher Scientific LTQ FT Ultra
Card Serial Number: D160170
Sample Serial Number: 4-78-1
Operator: HUAQIN Date: 2016/01/14
Operation Mode: DART-Positive

Elemental composition search on mass 433.12

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Figure S35. HRMS spectrum of 9
Figure S36. MS spectrum of 10
Figure S37. HRMS spectrum of 10
Figure S38. MS spectrum of 11
Instrument: Thermo Fisher Scientific LTQ FT Ultra

Card Serial Number: E161398

Sample Serial Number: 2013128-5-48-1

Operator: ZHUFJ Date: 2016/05/16

Operation Mode: ESI Negative

Elemental composition search on mass 681.15

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**Figure S39.** HRMS spectrum of 11
Figure S40. MS spectrum of 12
Figure S41. MS spectrum of BAZD1-2
Figure S42. HRMS spectrum of BAzDI-2
Figure S43. IR spectrum of 4
Figure S44. IR spectrum of BAzDI-1
Figure S45. IR spectrum of 12
Figure S46. IR spectrum of BAzDI-2