Supporting Information for

Azulene-Bridged Coordinated Framework Based Quasi-Molecular Rectifier

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Experimental Section

General: Unless specified otherwise, all the chemicals were purchased from Sigma-Aldrich and used without further treatment. Au wires (Φ=17 µm) were purchased from Beijing Xinxing Braim Technology Co., Ltd. Silver paste was purchased from Adamas. Dichloromethane, dimethylsulfoxide (DMSO) and trimethylamine were distilled over CaH₂. After purification, all distilled solvents were stored under dry nitrogen. All reactions were carried out under nitrogen atmosphere by standard Schlenk-line technique.

¹H NMR and ¹³C NMR spectra were obtained using a Mercury Plus 400 (400 MHz for proton, 100 MHz for carbon) spectrometer with tetramethylsilane as the internal reference. A HITACHI U-4100 spectrophotometer was employed to measure UV/Vis absorption spectral. Reflection–absorption infrared spectroscopy (RAIRS) was conducted using a Polarization Modulation Infrared Reflection Absorption Spectrometer (KSV NIMA, Sweden). Before acquiring the spectrum of sample, a background spectrum was collected using a freshly cleaned bare gold substrate. All samples were grown on thin film of 100 nm Au with a 5 nm Cr adhesion layer on silicon wafer. One thousand scans from 800 to 4000 cm⁻¹ at 4 cm⁻¹ resolution were collected for each background/sample pair. Fourier transform infrared (FTIR) spectra were recorded using Spectrum 100 spectrophotometer (Perkin Elmer, Inc., USA). X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250Xi (Thermo Fisher) with Al Kα radiation as X-ray source for radiation. MALDI-TOF-MS spectra were obtained using a SCIEX MALDI-TOF 4800 plus instrument with a laser repetition frequency of 200 Hz. 2,5-Dihydroxybenzoic acid was used as the matrix for MALDI-TOF spectrometry. ToF-SIMS analysis was performed using ToF-SIMS V (ION-TOF GmbH, Germany) equipment with a 30 KeV Bi⁺ Primary ion gun and a 500 eV Cs⁺ sputter gun. Scanning electron microscopy (SEM) measurements along with elemental analysis were performed on JEOL JSM-7800F Prime (SEM) with Thermo Scientific NORAN System 7 (EDS). Transmission electron microscopy (TEM) characterizations were conducted using a JEM-2100 (JEOL Ltd., Japan) with an accelerating voltage of 200KV. A Bruker made Bio-Fast Scan Scanning Probe Microscope (F-SPM) equipped with a conducting tip coated with Pt was employed for the C-AFM measurements. Current-Voltage (I-V) characters of all samples were measured by using an Agilent 4200 semiconductor parameter analyzer.

7-oxocyclohepta-1,3,5-trienyl-4-methylbenzenesulfonate (1), 2-amino-1,3,diethoxycarbonyl azulene (2), 2-amino-6-bromo-1,3-diethoxycarbonyl azulene (3), 2,2'-diamino-1,1'3,3'-tetraethoxycarbonyl-6,6'-biazulene (4), 2,2'-diformamido-1,1'3,3'-tetraethoxycarbonyl-6,6'-biazulene (5) and 2-diformamido-1,3-diethoxycarbonyl azulene (5') were synthesized according to previous literature. ¹,² 2,2'-diisocyano-1,1'3,3'-tetraethoxycarbonyl-6,6'-biazulene (DIBA), 2-isocyano-1,3,-diethoxycarbonyl azulene (IBA), [CoCl₂]₄(µ-DIBA) (PDIBA) and [CoCl₂]₄(µ-IBA) (PIBA) were synthesized by using modified literature methods. ¹,⁴

Synthesis of 7-oxocyclohepta-1,3,5-trienyl-4-methylbenzenesulfonate (1)

To a 500 ml round-bottomed flask, 2-hydroxycyclohepta-2,4,6-trienone (tropolone) (10.6 g, 86 mmol) and 4-methylbenzene-1-sulfonyl chloride (tosyl chloride) (16.4 g, 86 mmol) were added sequentially. Then, 120 ml of anhydrous methylene chloride (CH₂Cl₂) was added into the same round-bottomed flask at room temperature. The mixture was stirring with a
magnetic stir bar to dissolve the tropolone and tosyl chloride. Then, triethylamine (12 ml, 86 mmol) was added dropwise to the stirring CH$_2$Cl$_2$ through a glass syringe. This should result in a yellow slurry. Another 120 ml of CH$_2$Cl$_2$ was added because of increased viscosity of the reaction mixture. The mixture was stirring at room temperature for 32 h under nitrogen and quenched with 250 ml deionized water. The reaction mixture was transferred into a 500-ml separation funnel and extracted with CH$_2$Cl$_2$ (3 × 250 ml). Combine the organic extracts and dry using MgSO$_4$ for 5 min. Filter and concentrate the dried extracts with a rotary evaporator to yield a tan-colored solid. The solid was used for next step without further purification (yield: 98%).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 2.44 (s, 3H, CH$_3$), 6.97 (t, 1H), 7.07 (t, 1H, H$_6$), 7.15 (d, 1H, H$_5$-$7$), 7.20 (m, 1H), 7.32 (d, 2H), 7.45 (d, 1H), 7.91 (d, 2H). MS (ESI): calculated for C$_{14}$H$_{12}$O$_4$S: (M$^+$+1): 277.05, found: 277.11.

Synthesis of 2-amino-1,3-diethoxycarbonyl azulene (2)

7-oxocyclohepta-1,3,5-trienyl 4-methylbenzenesulfonate (1) (11.8 g, 43 mmol) and ethyl cyanoacetate (9.7 g 86 mmol) was transferred into an oven-dried 250 ml round-bottomed flask, flask A, which has been flushed with argon and equipped with a Teflon-coated magnetic stir bar. Weigh 5.8 g (86 mmol) of sodium ethoxide and quickly transfer the powder into an oven-dried 100 ml round-bottomed flask, flask B. Then, add 50 ml of anhydrous ethanol to the powder. Cool the flask A to 0 °C by immersing into an ice water bath and add the contents of the flask B into the flask A dropwise through a 10 ml glass syringe over 15 min. Once the addition is complete, put the flask A into the ice water bath (0 °C) for 6 h, and then slowly allow the reaction mixture to warm to room temperature overnight. Then, deionized water (100 ml) was poured into the reaction mixture. The resulting yellow suspension was extracted with chloroform (3 × 100 ml). The combined organic extracts was dried and evaporated to give an orange solid. The crude product was purified by chromatography with CH$_2$Cl$_2$/petroleum ether (1:1) as eluent to yield 2-amino-1,3-diethoxycarbonyl azulene (2) as yellow solid (yield: 85%).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 1.46 (t, 6H, CH$_3$), 4.45 (q, 4H, CH$_2$), 7.43 (q, 1H, H$_6$), 7.54 (t, 2H, H$_5$-$7$), 7.78 (s, 2H, NH$_2$), 9.13 (d, 2H, H$_4$-$8$). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 14.69 (CH$_3$), 59.85 (CH$_2$), 99.75, 131.41, 132.63, 132.88, 146.13, 162.47, 166.57 (CO$_2$Et). MS (ESI): calculated for C$_{16}$H$_{17}$NO$_4$ (M$^+$+1): 288.12, found: 288.14.

Synthesis of 2-amino-6-bromo-1,3-diethoxycarbonyl azulene (3)

Bromine (3.84 g, 24.0 mmol) was added dropwise to a chilled (0 °C) solution of 2-amino-1,3-diethoxycarbonyl azulene (2) (6.9 g, 24.0 mmol) in 250 ml of chloroform with vigorous stirring over a period of 20 min. The ice bath was then removed, and the reaction mixture was allowed to warm to room temperature. After 30 min of stirring at room temperature, formation of an orange precipitate was observed. The mixture was stirred for an additional 30 min and then poured into 500 ml of distilled water. The organic layer was separated and the aqueous layer was extracted with 100 ml of chloroform. The organic fractions were combined and dried over anhydrous MgSO$_4$. Filtration followed by solvent removal under vacuum provided dark organic residue. The crude product was purified by a column chromatography using hexane/CH$_2$Cl$_2$ (1:1) as eluent to yield 3 as orange powder (yield: 76%).

$^1$H NMR (CDCl$_3$, 400 MHz): δ 1.46 (t, 6H, CH$_3$), 4.43 (q, 4H, CH$_2$), 7.76 (d, 2H, H$_5$-$7$), 7.80 (s, 2H, NH$_2$), 8.79 (d, 2H, H$_4$-$8$). $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 14.85 (CH$_3$), 60.29 (CH$_2$), 101.17, 128.58, 129.65, 135.52, 144.51, 162.53 (azulenic C), 166.45 (CO$_2$Et). MS (MALDI-TOF): calculated for C$_{16}$H$_{16}$BrNO$_4$ (M$^+$): 365.03, found: 365.18.
Synthesis of 2,2'-diamino-1,1'3,3'-tetraethoxycarbonyl-6,6'-biazulenyl (4)

2-amino-6-bromo-1,3-diethoxycarbonyl azulene (3) (0.15 g, 0.41 mmol), Pd(dppf)Cl₂ (dppf: bis(diphenylphosphino) ferrocene), (0.034 g, 0.042 mmol), bis(pinacolato)diboron (0.027 g, 0.107 mmol) and potassium acetate (0.131 g, 1.329 mmol) were put into a 100 ml round-bottomed flask equipped with a Teflon-coated magnetic stir bar and a reflux condenser. To this mixture, distilled DMSO (45 ml) was then added. The resulting deep orange solution was stirred at 105 °C for 5 hours. Then, the reaction mixture was cooled to room temperature and quenched with 30 ml deionized water. The content of the flask was transferred into a 500 ml separation funnel and diluted with additional 150 ml of H₂O. The mixture was extracted with CH₂Cl₂ (3 × 50 ml). The organic extracts were combined, washed thoroughly with deionized water (3 × 200 ml) to remove any remaining DMSO, and dried over anhydrous Na₂SO₄. The drying agent was then filtered off. Then, the filtrate was concentrated to about 20 ml, layer with 50 ml of hexane, and kept at -35 °C for 13 hours. The product (4) was finally obtained as a brick-red powder (yield: 80%).

1H NMR (CDCl₃, 400 MHz): δ 1.49 (t, 3H, CH₃), 4.47 (q, 2H, CH₂), 7.79 (d, 1H, H₅,₅',₇,₇'), 7.86 (s, 1H, NH₂), 9.14 (d, 1H, H₄,₄',₈,₈'). 13C NMR (CDCl₃, 100 MHz): δ 14.91 (CH₃), 60.21 (CH₂), 100.56, 130.71, 133.59, 145.11, 148.57, 162.95 (CO₂Et), 166.71. MS (MALDI-TOF): calculated for C₃₂H₃₂N₂O₈ (M⁺): 572.22, found: 572.19

Synthesis of 2,2'-diformamido-1,1'3,3'-tetraethoxycarbonyl-6,6'-biazulene (5)

A mixture of acetic anhydride (14.9 ml, 0.158 mol) and formic acid (11.9 ml, 0.315 mol) was heated at 60 °C for 2.5 hours with stirring. To this in-situ formed acetic-formic anhydride, a solution of 4 (0.9 g, 1.575 mmol) in a minimum amount of CH₂Cl₂ was added, along with additional formic acid (11.9 ml, 0.315 mol). The dark red mixture was stirred at 60 °C for 18 hours while gradually turning chestnut in color. The mixture was cooled to room temperature, quenched with 10% aqueous Na₂CO₃, and extracted with CH₂Cl₂ (3 × 100 ml). The organic extracts were combined, washed with 100 ml H₂O, and dried over anhydrous Na₂SO₄. The chestnut-colored solution was filtered to remove the drying agent and the filtrate was concentrated on a rotary evaporator. Adding of hexane to the concentrated solution caused the precipitation of chestnut-colored solid, which was filtered off and dried in vacuum to give 5 (79%). 1H NMR (CDCl₃, 400 MHz): δ 1.47 (t, 6H, CH₃), 4.50 (q, 4H, CH₂), 7.94 (d, 2H, H₅,₅',₇,₇'), 8.69 (s, 1H, NH), 9.49 (d, 2H, H₄,₄',₈,₈'). 13C NMR (CDCl₃, 100 MHz): δ 14.91 (CH₃), 60.21 (CH₂), 100.56, 130.71, 133.59, 145.11, 148.57, 162.95 (CO₂Et), 166.71. MS (MALDI-TOF): calculated for C₃₄H₃₂N₂O₁₀ (M⁺+1): 629.21, found: 629.08.

5' was synthesized by using the similar synthesis procedure for 5 (yield: 51%).

Synthesis of 2,2'-diisocyano-1,1'3,3'-tetraethoxycarbonyl-6,6'-biazulene (DIBA)

To a solution of 5 (2.04 g, 3.24 mmol) and trimethylamine (19.7 ml, 141.9 mmol), POCl₃ (0.6 ml, 6.45 mmol) was added slowly to this mixture at room temperature under nitrogen atmosphere. The resulting mixture was stirred for 1 hour and then quenched with 100 ml of 10 % Na₂CO₃. The organic fraction was separated and the aqueous fraction was extracted with additional CH₂Cl₂ (3 × 50 ml). All organic extracts were combined and the resulting solution was washed with 100 ml H₂O, and dried over anhydrous Na₂SO₄. The solution was filtered to remove the drying agent and the filtrate was concentrated using a rotary evaporator. The crude product was purified by a column chromatography by using CH₂Cl₂/ethyl acetate (100:3) as eluent to yield DIBA as lavender powder (yield: 34%). 1H NMR (CDCl₃, 400 MHz): δ 1.53 (t, 3H, CH₃), 4.53 (q, 2H, CH₂), 8.03 (d, 1H, H₅,₅',₇,₇'), 9.91 (d, 1H, H₄,₄',₈,₈'). 13C NMR (CDCl₃, 100 MHz): δ 14.2 (CH₃), 61.3 (CH₂), 113.7, 131.9, 132.4, 140.2, 140.6, 156.5 (aromatic C), 163.1
\( \text{CO}_2\text{Et} \), 178.6 (CNR). MS (MALDI-TOF): calculated for \( \text{C}_{34}\text{H}_{28}\text{N}_2\text{O}_8 \) (M\(^{+1}\)): 593.18, found: 593.19.

**IBA** was synthesized by using the similar method for synthesis of **DIBA**.

### Synthesis of PDIBA powders

To a solution of DIBA (2 mM, in CHCl\(_3\)), CoCl\(_2\) aqueous solution (1 mM) was slowly layered. PDIBA powders were prepared in situ by coordination of DIBA and Co (II). No stirring was needed during the whole process. After 12 h, flocculent powder was precipitated, filtrated and washed by acetone and CHCl\(_3\) for three times. PDIBA powders were finally obtained as deep violet-red powders (yield: 60%).

**PIBA** was synthesized by stirring the acetone solution of IBA and CoCl\(_2\) for 12 h at room temperature. After 12 h, the mixture was evaporated to remove the solvent under vacuum. The residue was chromatographed on Al\(_2\)O\(_3\) by using hexane/Et\(_2\)O (4:1) as eluent. A deep violet-red band was collected to give PIBA with yield of 78%. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta \) 1.51 (t, 6H, CH\(_3\)), 4.15 (q, 4H, CH\(_2\)), 7.88 (dd, 2H, H\(_5\), H\(_7\)), 8.13 (d, 1H, H\(_6\)), 9.75 (d, 2H, H\(_4\), H\(_8\)). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \( \delta \) 14.4 (CH\(_3\)), 60.8 (CH\(_2\)), 112.6, 132.5, 132.9, 140.9, 141.1, 142.7 (aromatic C), 162.9 (CO\(_2\)Et), 165.6 (CNR). MS (MALDI-TOF): calculated for \( \text{C}_{68}\text{H}_{60}\text{N}_4\text{O}_{16}\text{Co} \) [PIBA-Cl\(_2\)]\(^{2+}\): 1247.32, found: 1247.44

### Preparation of Au@PDIBA-n

The commercial gold wires (Φ=17 µm) were cleaned with Piranha solution, then rinsed thoroughly with large volumes of deionized water, CHCl\(_3\) and acetone. After drying with a stream of nitrogen gas, the gold wires were immersed into DIBA solution (10mM in CHCl\(_3\)) for 24 h. Then, the as-prepared DIBA-coated Au wire was immersed into CoCl\(_2\) aqueous for 15 min and washed by deionized water to produce end capped DIBA-coated Au wire (denoted as Au@DIBA-Co, step i). After this, Au@DIBA-Co was immersed into DIBA solution again for 15 min and washed by fresh CHCl\(_3\) to produce defined one-layered BCCF-coated Au wire (denoted as Au@PDIBA-1, step iii). After n cycles of step ii and iii, n-layered BCCF-coated Au wires (denoted as Au@PDIBA-n, n=1-5) and Co-capped Au@PDIBA-n (denoted as Au@PDIBA-n-Co, n=1-4) can be easily produced. Then, a “float-on” strategy was adopted to fabricate the sandwich-like junction Au@PDIBA@Au. As shown in Scheme S2, the naked Au wire was firstly fixed onto arbitrary substrate (e.g., glass, wafer or PET) using silver paste. And then, buffer liquid (deionized water) was dropped onto this Au wire. After that, cable-like Au@PDIBA-5 was carefully floated onto this system. PDIBA-5 was electrically contacted to Au electrodes with minimal damage after slowly evaporation of buffer liquid at room temperature. No precautions to exclude air or ambient laboratory light were taken during this procedure. A home-made sandwich-like Au/PDIBA-5/Au diode was fabricated without the aid of complicate procedure, nanotechnologies and extra equipment.

### Preparation of PDIBA-LB

A polytetrafluoroethylene Langmuir tank (375 mm × 75 mm × 5 mm) was filled with \( 4 \times 10^{-4} \) M CoCl\(_2\) aqueous solution as the subphase. The surface of this subphase was carefully cleaned by surface-touch vacuuming. Then, DIBA solution (\( 1 \times 10^{-4} \) M in CHCl\(_3\), 24 µl) was carefully spread onto the surface of CoCl\(_2\) aqueous solution using a micro-syringe. Surface-
pressure/area isotherm measurements were also performed by using a KSV system (pressing speed: 10 mm min\(^{-1}\)). Single-layered PDIBA-LB was transferred onto transparent quartz substrate at a surface pressure of 8.9 mN \(\cdot\) m\(^{-1}\) by the vertical dipping method at room temperature. Different layered PDIBA-LB can be easily obtained by transferring single-layered PDIBA-LB onto the quartz substrate for several times.

Scheme S1. a) TsCl, TEA, CH\(_2\)Cl\(_2\), RT, 32 h; b) ethyl cyanacetate, absolute ethanol, EtONa, 0 °C, overnight; c) Br\(_2\), 0 °C, 2 h; d) B\(_2\)pin\(_2\) (0.26 equiv), 10 mol% Pd(dppf)Cl\(_2\), KOAc, DMSO, 100 °C; e) HC(O)OAc, 50 °C; f) POCl\(_3\), Et\(_3\)N, 20 °C.

Scheme S2. Illustration of the fabrication process of Au/PDIBA-n/Au diode and its optical image. By riding Au@PDIBA-5 on top of another naked Au wire, a home-made sandwich-like Au/PDIBA-5/Au diode was fabricated. This “soft” method provides us an easy and reliable preparation procedure for molecular electronics without the aid of complicate procedure, nanotechnologies and extra equipment.
Fig. S1. Analysis of BCCF formation procedure using TOF-SIMS. Illustration of BCCF formation procedure (a) on Au surface and the TOF-SIMS spectra of Au@DIBA (b), Au@PDIBA-1 (c) and Au@PDIBA-5 (d). The TOF-SIMS spectrum of Au@DIBA presents the characteristic molecular peak of [C_{34}H_{28}N_{2}O_{8}Au]^+ due to cationization by Au^+. For Au@PDIBA-1, the TOF-SIMS spectrum also presented the quasi-molecular peak of [C_{136}H_{112}N_{8}O_{32}Co]^+ (4DIBA-Co). Similarly, the peak of [C_{136}H_{112}N_{8}O_{32}CoAu]^+ (Au-4DIBA-Co) also appears because of cationization by Au^+. The TOF-SIMS spectrum of Au@PDIBA-5 shows the molecular peak of [C_{34}H_{28}N_{2}O_{8}Co]^+ (DIBA-Co). As the reaction proceeding, the intensity of [C_{34}H_{28}N_{2}O_{8}Au]^+ (Au@DIBA) peak decreased sharply, whereas the intensity of the complex-related ([C_{34}H_{28}N_{2}O_{8}Co]^+) (DIBA-Co) peak increased. This change implied that Co atom can effectively react with isocyanide group of DIBA to form BCCF after LbL procedure.

Scheme S3. Synthesis of PIBA. a) TsCl, TEA, CH₂Cl₂, RT, 32 h; b) ethyl cyanacetate, ethanol, EtONa, 0 °C, overnight; c) HC(O)OAc, 50 °C; d) POCl₃, Et₃N, 20 °C; e) CoCl₂, RT, 12 h.
Fig. S2. $^1$H NMR (a) and $^{13}$C NMR (b) spectra of IBA.
**Fig. S3. Structure analysis of PIBA.** $^1$H NMR (a), $^{13}$C NMR (b) and MALDI-TOF mass (c) spectra of PIBA. As depicted in the MALDI-TOF mass spectrum, a (quasi)molecular peak appeared at 1247.44 (C$_{68}$H$_{60}$H$_{16}$O$_{16}$Co, calculated: 1247.32, found: 1247.44), implying that each Co (II) ion was bound to four IBA ligands. Thus, DIBA can connect to Co (II) ions in similar way, ultimately forming biazulene-bridged cobalt coordinated framework (BCCF) in this work.
**Fig. S4.** FTIR spectra of IBA, DIBA, PIBA and PDIBA powders. The stretching band for isocyano bond of PIBA, PDIBA showed a blue-shift in comparison with that of IBA and DIBA.

**Fig. S5.** XPS spectra of PDIBA-5. (A) XPS survey and the C1s (B), N1s (C), Co2p (D), Cl 2p (E) and O1s (F) core level spectra of Au@PDIBA-5. As shown in Fig. S5d, the Co 2p core level spectrum can be fitted into two spin orbit peaks (2p 1/2|2p 3/2) at 796.6|780.9 eV and 803.4|784.9 eV, corresponding to N≡C-Co₆ and Co satellite,⁴ respectively. In general, the splitting between Co 2p 1/2 and Co 2p 3/2 peaks was depended on oxidation state of cobalt.⁴ In our case, the 2p 3/2 - 2p 1/2 separation was 15.7 eV, similar to those observed for paramagnetic Co (II) complex.⁴,⁶ Besides, Co satellites can't be observed in diamagnetic Co (III) complexes, further indicating the cobalt existed in the 2⁺ oxidation state in our work. And according to Vernon's prediction,⁷ strong, well-defined electron “shake-up” satellites at 784.9 eV and 803.4 eV hinted probably charge transfer event between ligand and metal centers in PDIBA.
Fig. S6. Cross-section SEM images and the corresponding elemental mapping images of Au@PDIBA-5 profile. From the cross section image of Au@PDIBA-5, it can be seen that carbon apparently distributed along the marginal of gold wire, demonstrating the cable-like structure of Au@PDIBA-5.

Scheme S4. Schematic illustration of the fabrication procedure for single layer PDIBA (denoted as PDIBA-LB) via LB method.
Fig. S7. UV-Vis absorption spectra of DIBA and PDIBA-5 films. As depicted in the UV/Vis spectra for DIBA, the strong absorption peak at 320 nm can be attributed to S₀ → S₂ transition of azulene block.¹ After the formation of PDIBA-5, this peak red-shifted to 350 nm due to the extension of conjugated system. In addition, the newly generated peak at 452 nm for PDIBA-5, which can be attributed to the metal-to-ligand charge transfer (MLCT), was also observed.³ Such peak clearly indicated that the π-electronic system of ligand was coupled with d-orbitals of metal centers.⁸

Fig. S8. The I–V curves for Au/DIBA/Au and Au/PDIBA-n/Au (n=1-5) junctions (a) and ln I versus height of PDIBA-n (n=1-5) (b). In this work, tunneling mechanism was determined to dominate the charge transfer process.⁹ Thus, the current decay exponentially with the molecular length, as described by the following equation:¹⁰

\[ I = I₀e^{βd} \]

where, \( d \) is the molecular length and \( β \) is the decay factor, which is the intrinsic property of molecule. According to Fig. S8b, the \( β \) is determined to be 0.41 nm⁻¹.
Fig. S9. XPS survey (a) and the C1s (b), N1s (c), and O1s (d) core level spectra of DIBA.

Fig. S10. Cyclic voltammetry curves of as-synthesized compounds.
Table S1. Elemental analysis of Au supported PDIBA-5 based on XPS results.

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Table S2. The electrochemical data of as-synthesized compounds.

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<tr>
<td>PDIBA-5</td>
<td>0.97</td>
<td>0.27</td>
<td>-5.1</td>
<td>-4.4</td>
<td>5.36</td>
<td>4.66</td>
<td>0.7</td>
</tr>
<tr>
<td>IBA</td>
<td>0.75</td>
<td>-0.35</td>
<td>-4.88</td>
<td>-3.78</td>
<td>5.14</td>
<td>4.04</td>
<td>1.1</td>
</tr>
<tr>
<td>PIBA</td>
<td>0.89</td>
<td>-0.2</td>
<td>-5.02</td>
<td>-3.93</td>
<td>5.28</td>
<td>4.19</td>
<td>1.09</td>
</tr>
</tbody>
</table>

a) By adding 0.29 V, all the electrochemical data versus Ag/Ag$^+$ can be converted to the corresponding potentials versus a saturated calomel electrode (SCE).
**Table S3.** The performance of reported molecular rectifiers.

<table>
<thead>
<tr>
<th>Active materials</th>
<th>RR&lt;sup&gt;a)&lt;/sup&gt;</th>
<th>Voltage</th>
<th>Cycling stability</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Dipyrimidinyl-diphenyl diblock</td>
<td>~5</td>
<td>1.5 V</td>
<td>~50</td>
<td><em>Nature Chem.</em> 2009, 1, 635-641.</td>
</tr>
<tr>
<td>4 Five-coordinate iron(III) phenolate complex</td>
<td>4.5-12</td>
<td>-2 V</td>
<td>decay to 1 after multiple scan</td>
<td><em>Angew. Chem. Int. Ed.</em> 2013, 52, 13346-13350.</td>
</tr>
<tr>
<td>5 Stilbene</td>
<td>1.7</td>
<td>0.85 V</td>
<td>~5000</td>
<td><em>Nano Lett.</em> 2013, 13, 6233-6237.</td>
</tr>
<tr>
<td>6 Hetero π-stacked complex</td>
<td>1.38</td>
<td>1 V</td>
<td>500</td>
<td><em>J. Am. Chem. Soc.</em> 2015, 137, 5939-5947</td>
</tr>
<tr>
<td>7 Thiophene-1,1-dioxide oligomer</td>
<td>4-200&lt;sup&gt;b)&lt;/sup&gt;</td>
<td>≤0.6 V</td>
<td>≤1000</td>
<td><em>Nature Nanotechnol.</em> 2015, 10, 522-527</td>
</tr>
<tr>
<td>8 Poly(ethylene oxide) block copolymers</td>
<td>~1.5</td>
<td>1 V</td>
<td>~</td>
<td><em>Adv. Mater.</em> 2016, 28, 757-763</td>
</tr>
<tr>
<td>9 Azulene-based coordinated framework</td>
<td>~6.5</td>
<td>1 V</td>
<td>≥300</td>
<td>This work</td>
</tr>
</tbody>
</table>

<sup>a)</sup>RR: rectification ratio; <sup>b)</sup>Rectification effect is obtained when polar solvent or ionic liquid is added. RR varies when applied voltage and repeating unit of oligomer changes.

**References**