Electronic Supplemantary Information

The reductive aromatization of naphthalene diimide: A versatile platform for 2,7-diazapyrenes

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Instrumentation and Materials

¹H NMR (500 MHz), ¹³C NMR (126 MHz), and ¹⁹F NMR (470 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer, and chemical shifts were reported as the delta scale in ppm relative to CDCl₃ (δ = 7.260 ppm) and CD₂Cl₂ (δ = 5.330) for ¹H NMR, CDCl₃ (δ = 77.16 ppm) and CD₂Cl₂ (δ = 53.52) for ¹³C NMR, and hexafluorobenzene (δ = -164.90 ppm, external standard) for ¹⁹F NMR respectively. UV/vis absorption spectra were recorded on a JASCO V670 spectrometer. Emission spectra were recorded using a JASCO FP-6500 spectrometer, and absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. Fluorescence lifetimes were also measured on HAMAMATSU Photonics Quantaurus-Tau C11367-25. Mass spectra were recorded on a Bruker microTOF using positive mode for acetonitrile solutions with ESI-TOF methods. Redox potentials were measured by cyclic voltammetry method on an ALS electrochemical analyzer model 612C. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. All of reactions were conducted under Ar atmosphere. Naphthalene diimide and 5-Methyl-2-thiopheneboronic acid were prepared according to the literature proceedure.^{81, 82}

Synthesis of naphthalene diimide

In a 300 mL three-necked flask were placed 1,4,5,8-naphthalenetetracarboxylic dianhydride (5.37 g, 20 mmol) and 28 % NH_3 (aq) (100 mL) under Ar. Then, the reaction mixture was stirred for 24 h at room temperature. After the suspention was filtrated, the obtained solid was washed with water and acetone. The corresponding naphthalene dimide was obtained as a brown solid (4.64 g, 17.4 mmol, 87% yield).^{S1}

Reductive Aromatization of 2a



In a 50 mL J-Young tube were placed naphthalene diimide (266 mg, 1.0 mmol), Zn (1.05 g, 16 mmol), pivalic anhydride (3.25 mL, 16 mmol), and 1,4-dioxane (10 mL) under Ar. The reaction mixture was stirred for 24 h at 120 °C. The suspension was filtrated through celite. After the solution was concentrated in *vacuo*, the remaining solid was washed with hexane. The residue was purified by column chromatography (SiO₂) with CH₂Cl₂ as an eluent. After recrystallization from CH₂Cl₂/hexane, **1b** (512 mg, 0.85 mmol, 85% yield) was obtained.

1b: A white solid, m.p. 194.9 °C (decomp.). ¹H NMR (CDCl₃): δ 7.98 (s, 4H), 1.55 (s, 36H). ¹³C NMR (CDCl₃): δ 176.6, 150.3, 132.1, 122.4, 117.9, 39.8, 27.4. HRMS(ESI) Calcd. For C₃₄H₄₁N₂O₈ [M+H]: 605.2857. Found: 605.2858.

Nickel-Catalyzed Cross-Coupling Reaction of 1b.



Typical procedure for nickel-catalyzed cross-coupling reaction of **1b** with a arylboronic acid is described below. In a 50 mL J-Young tube was placed K_3PO_4 (340 mg, 1.6 mmol). After drying of K_3PO_4 heating under the reduced pressure (120 °C, 1.0 Torr) for 1 h, **1b** (60.4 mg, 0.10 mmol) and 4-*tert*-butylphenylboronic acid (284.5 mg, 1.6 mmol) were added to the tube, and then Ni(cod)₂ (11.1 mg, 0.040 mmol), tricyclohexylphosphine (22.3 mg, 0.080 mmol), and toluene (3 mL) were added to the reaction container in the globe box. The rection mixture was stirred for 18 h at 60 °C. 10% Aquous solution of ethylene diamine (3 mL) was added to the reaction mixture and the resulting solution was extracted with CHCl₃ (30 mL × 3). The combined organic layer was dried over Na₂SO₄ and concentrated in *vacuo*. The residue was purified by column chromatography (SiO₂) with CHCl₃/hexane (1/3) to give **1c** (43.3 mg, 0.059 mmol, 59% yield)

1c: A yellow solid, m.p. 209.9 °C (decomp.). ¹H NMR (CDCl₃): δ 8.36 (s, 4H), 7.89 (d, 8H, J = 8.5 Hz), 7.60 (d, 8H, J = 8.5 Hz), 1.42 (s, 36H). ¹³C NMR (CDCl₃): δ 153.4, 151.7, 137.2, 130.7, 129.7, 126.2, 125.6, 122.6, 34.9, 31.5.

HRMS(ESI) Calcd. For C54H57N2 [M+H]: 733.4516. Found: 733.4512.

Isolated yields and spectroscopic data of other products are as follows:

$$\begin{array}{c} \text{Ar} & \text{N} & \text{Ar} \\ \hline & \text{Id}: \text{Ar} = 4 \text{-} \text{MeO-C}_6 \text{H}_4 \\ \hline \text{Ar} & \text{N} & \text{Ar} \end{array}$$

1d: 50% yield (Purified by column chromatography (SiO₂) with CHCl₃ and recrystallization from CHCl₃/hexane). A yellow solid, m.p. 219.1 °C (decomp.). ¹H NMR (CDCl₃): δ 8.30 (s, 4H), 7.90 (d, 8H, *J* = 8.8 Hz), 7.12 (d, 8H, *J* = 8.8 Hz), 3.92 (s, 12H). ¹³C NMR (CDCl₃): δ 160.2, 152.9, 132.6, 132.3, 129.9, 126.0, 122.3, 114.1, 55.6. HRMS(ESI) Calcd. For C₄₂H₃₃N₂O₄ [M+H]: 629.2435. Found: 629.2429.



1e: 18% yield (Purified by column chromatography (SiO₂) with CHCl₃ and recrystallization from CHCl₃/hexane). A yellow solid, m.p. 151.0 °C (decomp.). ¹H NMR (CDCl₃): δ 8.36 (s, 4H), 8.08 (d, 8H, *J* = 8.1 Hz), 7.88 (d, 8H, *J* = 8.1 Hz). ¹⁹F NMR (CDCl₃): δ -65.76. HRMS(ESI) Calcd. For C₄₂H₂₁F₁₂N₂ [M+H]: 781.15131. Found: 781.15166.



1f: 30 % yield (at 70 °C) (Purified by column chromatography (SiO₂) with CHCl₃ and recrystallization from CHCl₃/hexane). A red solid, m.p. 110.1 °C (decomp.). ¹H NMR (CDCl₃): δ 8.63 (s, 4H), 7.62 (d, 4H, *J* = 3.6 Hz), 6.93 (dd, 4H, *J* = 3.6, 1.0 Hz), 3.92 (s, 12H). ¹³C NMR (CDCl₃): δ 146.1, 143.9, 141.8, 130.4, 129.1, 126.6, 125.6, 120.9, 15.8. HRMS(ESI) Calcd. For C₃₄H₂₅N₂S₄ [M+H]: 589.0895. Found: 589.0880.

Desulfurization of 1f



In a 50 mL Schlenk flask were placed Raney Nickel (3.52 g), toluene (5 ml), and **1f** (59.1 mg, 0.10 mmol). The solution was stirred at 60 °C till all starting compound was consumed (about for 5 h, checked by TLC and MALDI-TOF MS) and the insoluble solid was filtered through a short pad of Celite with toluene, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (SiO₂) with the eluent CHCl₃ to give **1g** (37.5 mg, 0.077 mmol, 77% yield).

1g: A pale yellow solid, m.p. 62.6-64.4 °C. ¹H NMR (CDCl₃): δ 8.19 (s, 4H), 3.45 (t, 8H, J = 8.0 Hz) 1.92 (quin, 8H, J = 7.6 Hz) 1.52–1.39 (m, 16H), 0.91 (t, 12H J = 7.2 Hz). ¹³C NMR (CDCl₃): δ 155.4, 128.8, 123.5, 122.2, 35.7, 32.2, 30.8, 22.8, 14.2. HRMS(ESI) Calcd. For C₃₄H₄₉N₂ [M+H]: 485.38903. Found: 485.38956.

Synthesis of 1,3,6,8-tetrakismethylthienylpyrene.



In a 50 mL J-Young tube were placed 1,4-dioxane (5 mL), K_2CO_3 (1.11 g, 8.0 mmol), 1,3,6,8-tetrabromopyrene (259 mg, 0.50 mmol), 5-methyl-2-thiopheneboronic acid (426 mg, 3.0 mmol), and Pd(PPh₃)₄ (9.23 mg, 8.0 µmol) under Ar. The reaction mixture was stirred for 24 h at 85 °C. The resulting solution was quenched by 2N HCl (aq) and extracted with CH₂Cl₂ (50 mL × 3). The combined organic layer was dried over Na₂SO₄ and concentrated in *vacuo*. The residue was purified by recrystallization from CH₂Cl₂/EtOH, **3a** (201 mg, 0.34 mmol, 68% yield) was obtained as an orange solid.⁸³

3a: An orange solid, m.p. 200.9 °C (decomp.). ¹H NMR (CDCl₃): δ 8.53 (s, 4H), 8.17 (s, 2H), 7.18 (d, 4H, J = 3.4 Hz), 6.90 (dd, 4H, J = 3.4, 1.1 Hz), 2.61 (d, 12 H, J = 1.1 Hz). ¹³C NMR (CDCl₃): δ 141.2, 139.9, 131.0, 130.1, 128.9, 128.3, 126.2, 125.9, 125.7, 15.6. HRMS(ESI) Calcd. For C₃₆H₂₆S₄ [M]: 586.09173. Found: 586.08972.

Desulfurization of 3b



In the 50 mL shlenk, Raney Nickel (4.19 g), toluene (10 ml), and **3a** (87.8 mg, 0.15 mmol) was added. The solution was stirred at 70 °C till all starting compound was consumed (about for 5 h, checked by TLC and MALDI) and the insoluble solid was filtered through a short pad of Celite with toluene, and the solvent was removed in *vacuo*. The residue was purified by column chromatography (SiO₂) with the eluent hexane to give **3b** (37.5 mg, 0.078 mmol, 52% yield).

3b: A pale yellow solid, m.p. 54.1-56.4 °C.¹H NMR (CDCl₃): δ 8.19 (s, 4H), 7.68 (s, 2H), 3.29 (t, 8H, *J* = 8.0 Hz), 1.85 (quin, 8H, *J* = 7.3 Hz), 1.49-1.39 (m, 16 H), 0.92 (t, 12 H *J* = 7.0 Hz). ¹³C NMR (CDCl₃): δ 136.3, 128.9, 127.3, 126.6, 122.4, 33.9, 32.2, 31.7, 22.8, 14.3. HRMS(ESI) Calcd. For C₃₆H₅₀ [M]: 482.39125. Found: 482.39019.

Synthesis of 4.



In the screw bial were added **1g** (4.85 mg, 0.010 mmol), *p*-toluenesulfonic acid (4.20 mg, 0.020 mmol), and CHCl₃ (1 mL). The mixture was stirred for 10 minutes at room temperature. Then the solvent was evaporated in *vacuo*. The residue was purified by recrystallization from CHCl₃/hexane to give **4** (7.7mg, 0.0098 mmol, 98% yield).

4: A yellow solid, m.p. 85.0 °C (decomp.).¹H NMR (CD₂Cl₂): δ 8.58 (s, 4H), 7.82 (d, 4 H, *J* = 8.0 Hz), 7.26 (d, 4H, *J* = 8.0 Hz), 3.94 (t, 8 H, *J* = 7.9 Hz) 2.41 (s, 6 H), 1.98 (quintet, 8 H *J* = 7.6 Hz), 1.49 (quintet, 8 H, *J* = 7.0 Hz), 1.38 (sextet, 8H, *J* = 7.6 Hz), 0.90 (t, 12 H, *J* = 7.3 Hz). ¹³C NMR (CD₂Cl₂): δ 154.0, 143.0, 140.4, 129.6, 128.9, 126.2, 126.0, 125.7, 31.8, 31.5, 31.0, 22.5, 21.2, 13.8.

X-Ray Diffraction Analysis

Crystals suitable for X-ray analysis of 1c, 1f and 1g were obtained by recrystalization from toluene/acetonitrile, chlorobenzene/diethyl ether/acetonitrile and acetonitrile, respectively. X-ray diffraction data for 1c was taken on a Bruker D8 QUEST X-ray diffractometer equipped with PHOTON 100 CMOS active pixel sensor detector and I μ S microfocus source using Mo-K α radiation ($\lambda = 0.71073$ Å). X-ray diffraction data for 1f and 1g were taken on a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-K α radiation ($\lambda = 0.71075$ Å). All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions and refined as rigid atoms with the relative isotropic displacement parameters. Crystallographic data for the structures of 1c, 1f and 1g have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1816896(1c), CCDC-1816897(1f) and CCDC-1816898(1g). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystallographic Data for 1c, 1f, and 1g.

Compound	1c	1f	1g
Formula	$C_{54}H_{56}N_2$	$C_{34}H_{24}N_2S_4$	$C_{34}H_{48}N_2$
Formula weight (M_w)	733.01	588.79	484.74
Crystal system	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> –1	<i>P</i> 2/c	$Pna2_1$
Crystal color	Yellow	orange	colorless
Crystal description	Prism	Prism	Prism
<i>a</i> [Å]	7.2959 (4)	15.9885 (7)	21.6241 (8)
<i>b</i> [Å]	10.3488 (6)	6.2625 (3)	4.7229 (3)
<i>c</i> [Å]	14.0322 (7)	14.7453 (6)	27.9845 (9)
α [°]	96.970 (2)	90	90
β[°]	98.0126 (2)	111.597 (5)	90
γ [°]	100.566 (2)	90	90
V[Å ³]	1019.50 (10)	1372.77 (12)	2858 (2)
Ζ	1	2	4
$d_{\rm calcd} [{ m g \ cm}^{-3}]$	1.194	1.424	1.127
$R1 \ (I > 2\sigma(I))$	0.0444	0.0461	0.0675
<i>R</i> w (all data)	0.1235	0.1250	0.1878
GOF	1.042	1.098	1.053
Temperature [K]	101	93	93
Structure solution	SHELXT-2014/7	SHELXT-2014/7	SIR-97
	(Sheldrick, 2014)	(Sheldrick, 2014)	
Structure refinement	SHELXL-2014/7	SHELXL-2014/7	SHELXL-2014/7
	(Sheldrick, 2014)	(Sheldrick, 2014)	(Sheldrick, 2014)



Fig. S1. X-ray crystal structure of **1f** (a) top, and (b) side views. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

Theoretical Calculations

All calculations were performed using the Gaussian 09 program.^{S4} Initial geometry of the model compound for **1a** ($C_{14}H_8N_2$) and **1c** ($C_{54}H_{56}N_2$) were obtained calculated from the X-ray structure of **1g** and **1c**. Full optimization was performed without any symmetric restriction with Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional (B3LYP)^{S5} and the 6-31G+(d,p) basis set for C, H, and N atoms. The oscillator strengths of the model compound for **1a** and **1c** were calculated by the TD DFT method at the B3LYP/6-31G+ (d, p) level.



Fig. S2. Absorption spectrum of 1g and oscillator strengths of the model compound for 1a $(C_{14}H_8N_2)$ obtained by TD-DFT calculation at the B3LYP/6-31G+ (d, p) level of theory.

wavelength (nm)	oscillator strength (f)	Conditions
344.13	0.1019	49 -> 54 (-0.21056) 53 -> 55 (0.67272)
342.09	0.4354	49 -> 55 (0.16532) 53 -> 54 (0.68644)
295.82	0.0000	52 -> 54 (0.69901)
284.55	0.0000	50 -> 54 (-0.15197) 53 -> 56 (0.68913)
284.01	0.0000	51 -> 54 (0.69607) 53 -> 56 (-0.11848)
272.38	0.0042	51 -> 59 (0.10504) 52 -> 55 (0.69604)
268.72	0.0000	50 -> 54 (-0.15197) 53 -> 56 (0.68913)
263.44	0.0000	51 -> 55 (0.69151) 52 -> 59 (0.11027)
254.12	0.2599	49 -> 54 (0.66114) 50 -> 57 (0.10274) 53 -> 55 (0.19725)
249.06	0.0000	48 -> 54 (0.33028) 49 -> 56 (0.13499) 50 -> 55 (-0.41123) 53 -> 57 (0.44882)
245.84	0.0000	48 -> 54 (0.20554) 49 -> 56 (-0.14385) 50 -> 55 (0.53660) 53 -> 57 (0.38381)

Table S2. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions of the model compound for 1a (C₁₄H₈N₂) calculated at the B3LYP/6-31G+ (d, p) level of theory

225.96	0.8260	49 -> 55 (0.66335) 50 -> 56 (0.17187) 53 -> 54 (-0.14688)
225.49	0.0001	53 -> 58 (0.69882)
223.27	0.0000	46 -> 54 (0.14810) 48 -> 55 (0.66406) 49 -> 57 (0.18577)
220.64	0.0000	48 -> 54 (0.57764) 53 -> 57 (-0.37316)
217.20	0.0000	52 -> 56 (0.70025)
211.18	0.0000	46 -> 54 (0.16149) 49 -> 57 (0.13438) 53 -> 59 (0.66703)
211.13	0.0007	53 -> 60 (0.69960)
210.03	0.0000	53 -> 61 (0.70236)
209.66	0.0003	51 -> 56 (0.70133)



Fig. S3. MO diagrams of the model compound for 1a ($C_{14}H_8N_2$).



Fig. S4. Absorption spectrum of 1c and Oscillator strengths of the model compound for 1c ($C_{54}H_{56}N_2$) obtained by TD-DFT calculation at the B3LYP/6-31G+ (d, p) level of theory.

wavelength (nm)	oscillator strength (f)	Conditions
439.54	1.1680	197 ->198 (0.70013)
395.40	0.2547	185 ->198 (0.012869)
327.03	0.0000	194 -> 198 (0.12869) 197 -> 201 (0.64868)
323.42	0.0000	195 -> 198 (0.57822) 197 -> 200 (0.64868)
322.74	0.6034	196 -> 198 (0.69806)
319.43	0.0000	194 -> 198 (0.66013) 197 -> 201 (0.23758)
310.74	0.0063	188 -> 198 (-0.45089) 192 -> 198 (0.52553)

Table S3. Selected wavelengths, oscillator strengths, and compositions of major electronic transitions ofthe model compound for 1c ($C_{54}H_{56}N_2$) calculated at the B3LYP/6-31G+ (d, p) level of theory

308.84	0.0000	186 -> 198 (-0.22877) 193 -> 198 (0.49701) 195 -> 198 (-0.23332) 197 -> 200 (0.36030)
303.30	0.0000	186 -> 198 (0.13183) 193 -> 198 (-0.41064) 195 -> 198 (-0.32231) 197 -> 200 (0.44795)
296.77	0.0000	191 -> 198 (0.68445
295.38	0.0044	190 -> 198 (0.68946
291.96	0.0065	188 -> 198 (0.50293) 189 -> 198 (-0.12545) 192 -> 198 (0.44409) 197 -> 203 (0.14343)
		105 > 100 (0.70(7))
287.10	0.0000	$193 \rightarrow 199 (0.07967)$ $197 \rightarrow 202 (0.13499)$
283.85	0.0000	189 -> 198 (0.32015) 196 -> 199 (0.62292)
283.66	0.0000	186 -> 198 (0.58924) 193 -> 198 (0.22700) 194 -> 199 (-0.12254) 197 -> 204 (-0.25163)
282.61	0.0000	187 -> 198 (0.60088) 195 -> 199 (0.12324) 197 -> 202 (-0.32304)
281.51	0.0000	187 -> 198 (0.34163) 197 -> 202 (0.58350) 197 -> 207 (-0.12530)
281.19	0.0000	186 -> 198 (0.10744) 194 -> 199 (0.68983)

280.45	0.0096	188 -> 198 (0.16262) 189 -> 198 (0.49639) 196 -> 199 (-0.24798) 197 -> 203 (-0.34493) 197 -> 208 (0.15621)
279.37	0.00256	185 -> 198 (0.16308) 188 -> 199 (-0.41251) 189 -> 199 (0.11313) 192 -> 199 (0.42220) 197 -> 205 (-0.29577)







Fig. S5. MO diagrams of the model compound for 1c ($C_{54}H_{56}N_2$).

Electrochemical Measurement

Electrochemical measurements were recorded on ALS electrochemical analyser 612C. Measurements were performed in THF and CH2Cl2 which was dehyderated by distillation with tetrabutylammonium hexafluorophosphate as an electrolyte (0.1 M). A glassy carbon electrode, a platinum wire and Ag/AgClO₄ were used as working, conter, and reference electrodes, respectively. The scan rate was 100 mVs⁻¹ in **Figure S7-S9**, and 200 mVs⁻¹ in **Figure S6**. The mesurment was performed under nitrogen atmosphere. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.



Fig. S6. Cyclic voltammogram of 1g in CH₂Cl₂.



Fig. S7. Cyclic voltammogram of 1g in THF.



Fig. S8. Cyclic voltammogram of 3b in CH_2Cl_2 .



Fig. S9. Cyclic voltammogram of 3b in THF.

Compound	E _{red}	E _{ox}
1g	-2.56	0.83
3b		0.53

Table S4. Redox potentials (V vs Fc/Fc+).

Absorption and Fluorescence Spectra.

250 300

400

600

500

 λ / nm

700

800

UV/vis absorption and fluorescence spectra were recorded on a JASCO V670 spectrometer and a JASCO FP-6500 spectrometer respectively, and absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. Dilute solutions in distilled solvent in a 1 cm square quartz cuvette were used for the absorption and fluorescence measurements.



S20

250 300

400

500

 λ / nm

600

700



Fig. S10. Absorption (blue line), fluorescence in CH_2Cl_2 (red line) and fluorescence in solid (red dash line) spectra of 1b, 1c, 1d, 1e, 1f, and 1g.

Compound	$\lambda_{\mathrm{ex}} (\mathrm{nm})$	$\boldsymbol{\Phi}(\text{in CH}_2\text{Cl}_2 \text{ solution})$	 𝖗(Solid)
1b	360	0.43	0.41
1c	400	0.38	0.12
1d	400	0.36	0.28
1e	400	0.32	0.22
1f	450	0.13	0.01
1g	360	0.47	0.08

Table S5. Excited wavelength and absolute fluorescence quantum yields of 1b, 1c, 1d, 1e, 1f, and 1g in CH_2Cl_2 and solid.



Fig. S11. Absorption spectra of 4 (blue line) and 1g with 1132 equivalent of TFA (red line).

Protonation Behavior

Ttifluoroacetic acid (TFA) was added to CH_2Cl_2 solution of **1g**. UV/vis absorption and fluorescence spectra were recorded on a JASCO V670 spectrometer and a JASCO FP-6500 spectrometer respectively, and absolute fluorescence quantum yields were measured by the photon-counting method using an integration sphere. Dilute solutions in distilled solvent in a 1 cm square quartz cuvette were used for the absorption and fluorescence measurements. Equilibrium constants were obtained by fitting.



Fig. S12. Spectral changes in absorption spectra of 1g on the addition of TFA into a dichloromethane solution of 1g.



Fig. S13. Spectral changes in fluorescence spectra of 1g on the addition of TFA into a dichloromethane solution of 1g.

Table S6. Equilibrium constants

<i>K</i> ₁	2.7 × 10 ⁵ M ^{−1}
<i>K</i> ₂	$1.2 \times 10^3 \mathrm{M}^{-1}$

Preparation process of MIS devices

The metal-insulator-semiconductor (MIS) devices were fabricated as follows: (1) On a quartz substrate ($4.9 \times 50 \text{ mm}^2$, 1 mm thick), 5 nm thick Ti for adhesion and 30 nm thick Au for gate electrode were deposited by direct-current sputtering and thermal vacuum deposition, respectively; (2) For insulating layers, a 300 nm thick SiO₂ layer was deposited by radio-frequency sputtering and a 250 nm thick PMMA (Aldrich) layer was deposited by spin-coating from 3 wt % PMMA solution in toluene; (3) To remove toluene, 1 h thermal annealing was done at 100 °C; (4) the target organic semiconducting layer was spin-coated from 2 wt% hexane solution at 1000 rpm for 30 s; (5) A 30 thick top Au electrode was deposited by vacuum deposition.

FI-TRMC Measurements

The schematic diagram of FI-TRMC was described in our previous reports. The microwave circuit was constructed using a waveguide system with a homodyne setup and a resonant cavity in which a MIS device was loaded. Microwave at around 9 GHz was generated from a signal generator (SMF 100A; Rohde & Schwarz). Pulse gate voltages at an interval of 50 ms was applied to the loaded MIS device in the cavity by a multifunction generator (WF 1973; NF Corporation). The flowing current was monitored by a digital phosphor oscilloscope (MDO 3022; Tektronix, while the reflected microwave from the MIS device was first amplified with high gain FET amplifier (Gain 30 dB, 8–12 GHz; Ciao CA812-304), picked up by a Schottky diode, and observed by the oscilloscope.



Fig. S14. X-ray diffraction patterns of 1g-based MIS device used in FI-TRMC measurements. The estimated *d* values from the three peaks were $d_{001} = 14.4$ Å, $d_{002} = 7.2$ Å, and $d_{003} = 4.8$ Å.



Fig. S15. (a) Typical time profiles of the flowed electric current in **1g**-based MIS device by injecting electrons. (b) Typical time profiles of amount of accumulated charges by electron injection in **1g**-based device. The charge amount was calculated from integration of the value of flowed current.



Fig. S16. Typical time profiles of change in reflected microwave power by electron injection in **1g**-based MIS device.



Fig. S17. Correlation between pseudo-electrical conductivity $(N_h\mu_h)$ and the number (N_h) of injected holes in **3**-based MIS device.

References

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S30



S31





S33



ppm

¹H-NMR

ppm



S35



Т ppm



¹H-NMR

¹³C-NMR

