Supporting Information

A 2-to-2' 18-to18' doubly linked Ni(II) norcorrole dimer: an effectively conjugated antiaromatic dyad

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Instrumentation and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) spectra were recorded on a Bruker AVANCE III HD spectrometer. Chemical shifts were reported as the delta scale in ppm relative to $CHCl_3$ (δ = 7.260 ppm) for ^{1}H NMR and $CDCl_3$ (δ = 77.16 ppm) for ^{13}C NMR. UV/vis/NIR absorption spectra were recorded on a Shimadzu UV-2550 or JASCO V670 spectrometer. High-resolution electrospray ionization time-of-flight (ESI-TOF) mass spectra were taken on a Bruker micrOTOF instrument. 3-Bromonorcorrole and 2-bromonorcorrole were synthesized according to the literature.[1] Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Synthetic Procedure and Characterizations of Compounds

Synthesis of 3-to-3' singly linked Ni(II) norcorrole dimer 7

A Schlenk flask containing Ni(II) 3-bromo-5,15-dimesitylnorcorrole **6** (12.73 mg, 19.4 μmol), Ni(cod)$_2$ (10.67 mg, 38.8 μmol), and dry THF (2 mL) was prepared in argon-filled glove box. The solution was stirred at 60 °C for 2 h. The resulting mixture was passed through a short pad of alumina with CHCl$_3$. The solution concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (hexane/CH$_2$Cl$_2$ = 2/1 as an eluent). The solvent was removed *in vacuo*. The residue was further purified by silica-gel column chromatography (hexane/CH$_2$Cl$_2$ = 5/1 as an eluent). The collected brown band was concentrated. Recrystallization from CHCl$_3$/MeOH afforded **7** (5.44 mg, 4.72 μmol, 49%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.05 (s, 4H, Mes), 6.17 (s, 4H, Mes), 3.20 (s, 12H, *o*-Me), 2.71 (s, 12H, *o*-Me), 2.27 (s, 6H, *p*-Me), 1.76 (s, 6H, *p*-Me), 1.53 (d, J = 4.5 Hz, 2H, β-H), 1.45 (d, J = 4.0 Hz, 2H, β-H), 1.44 (d, J = 4.0 Hz, 2H, β-H), 1.36 (d, J = 4.0 Hz, 2H, β-H), 1.32 (d, J = 4.0 Hz, 2H, β-H), 0.83 (d, J = 4.5 Hz, 2H, β-H), –1.57 (s, 2H, β-H) ppm; ^{13}C NMR (500 MHz, CDCl$_3$): δ = 169.1, 167.4, 166.5, 165.6, 158.0, 157.4, 149.7, 148.0, 147.5, 145.7, 137.2, 136.7, 136.1, 133.7, 133.3, 129.7, 129.2, 128.2 (overlap), 127.9, 126.5, 125.9, 114.8, 114.4, 113.8 (overlap), 21.0, 20.5, 18.4, 17.4 ppm; UV/vis (CH$_2$Cl$_2$): λ_{max} (ε [M^{-1} cm^{-1}]) = 438 (59000), 529 (28079) nm; ESI-MS: *m/z* = 1152.3447, calcd for (C$_{72}$H$_{58}$N$_8$Ni$_2$)$^+$ = 1152.3447 [M$^+$].

Synthesis of 2-to-2' singly linked Ni(II) norcorrole dimer 9

A Schlenk flask containing Ni(II) 2-bromo-5,15-dimesitylnorcorrole **8** (26.42 mg, 40.2 µmol), Ni(cod)$_2$ (22.11 mg, 80.4 µmol), and dry THF (5 mL) was prepared in argon-filled glove box. The solution was stirred at 60 °C for 2 h. The resulting mixture was passed through a short pad of alumina with $CHCl_3$. The solution was concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (hexane/CH_2Cl_2 = 2/1 as an eluent). The solvent was removed *in vacuo*. The residue was further purified by silica-gel column chromatography (hexane/CH_2Cl_2 = 5/1 as an eluent). The collected red band was concentrated. Recrystallization from CH_2Cl_2/MeOH afforded **9** (15.98 mg, 13.9 µmol, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.20 (s, 4H, Mes), 5.79 (s, 4H, Mes), 2.80 (s, 12H, *o*-Me), 2.44 (s, 12H, *o*-Me), 1.79 (s, 6H, *p*-Me), 1.49 (s, 6H, *p*-Me), 1.38 (d, J = 4.5 Hz, 2H, β-H), 1.22 (d, J = 4.0 Hz, 4H, β-H), 1.10 (d, J = 4.5 Hz, 2H, β-H), 1.03 (d, J = 4.0 Hz, 2H, β-H), 0.38 (d, J = 4.0 Hz, 2H, β-H), –1.07 (s, 2H, β-H) ppm; ^{13}C NMR (500 MHz, $CDCl_3$): δ = 169.9, 167.9, 166.1, 165.3, 158.5, 157.3, 148.6, 148.5, 148.2, 146.3, 136.9, 136.6, 133.4, 132.6, 130.4, 128.9, 128.2, 128.1, 127.7, 125.5, 124.7, 120.7, 120.5, 115.3, 115.2, 114.8, 20.6, 20.4, 17.5, 17.1 ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 442 (73014), 562 (48675) nm; ESI-MS: m/z = 1152.3439, calcd for $(C_{72}H_{58}N_8Ni_2)^+$ = 1152.3447 [M^+].

Synthesis of 2-to-2' 18-to-18' doubly linked Ni(II) norcorrole dimer 10

A three-necked flask containing 2-to-2' singly linked norcorrole dimer **9** (20.0 mg, 17.4 μmol) was evacuated and then refilled with N_2. To the flask, CH_2Cl_2 (350 mL) was added. A solution of silver hexafluorophosphate (8.80 mg, 34.8 μmol) in THF (5 mL) was added dropwise. The mixture was stirred at room temperature for 2 h. Aqueous $Na_2S_2O_4$ solution was added to the mixture. Organic materials were extracted with CH_2Cl_2. The combined organic layers were washed with water and dried over Na_2SO_4. After removing the solvent *in vacuo*, the residue was purified by silica-gel column chromatography (hexane/CH_2Cl_2 = 5/1 as an eluent). The collected green band was concentrated. Recrystallization from $CHCl_3$/MeOH afforded **10** (4.00 mg, 3.48 μmol, 20%). ^{1}H NMR (500 MHz, $CDCl_3/CS_2$ = 1/1): δ = 5.76 (s, 8H, Mes), 2.64 (s, 24H, *o*-Me), 1.45 (s, 12H, *p*-Me), 0.09 (d, J = 4.5 Hz, 4H, β-H), 0.05 (d, J = 4.5 Hz, 4H, β-H), –1.85 (s, 4H, β-H) ppm; UV/vis (CH_2Cl_2): λ_{max} (ε [M^{-1} cm^{-1}]) = 448 (48399), 651 (60055) nm; ESI-MS: *m/z* = 1150.3316, calcd for $(C_{72}H_{56}N_8Ni_2)^+$ = 1150.3316 [M^+]. (The ^{13}C NMR spectrum of **10** was not obtained because of the low solubility.)

^{1}H and ^{13}C NMR Spectra of Compounds

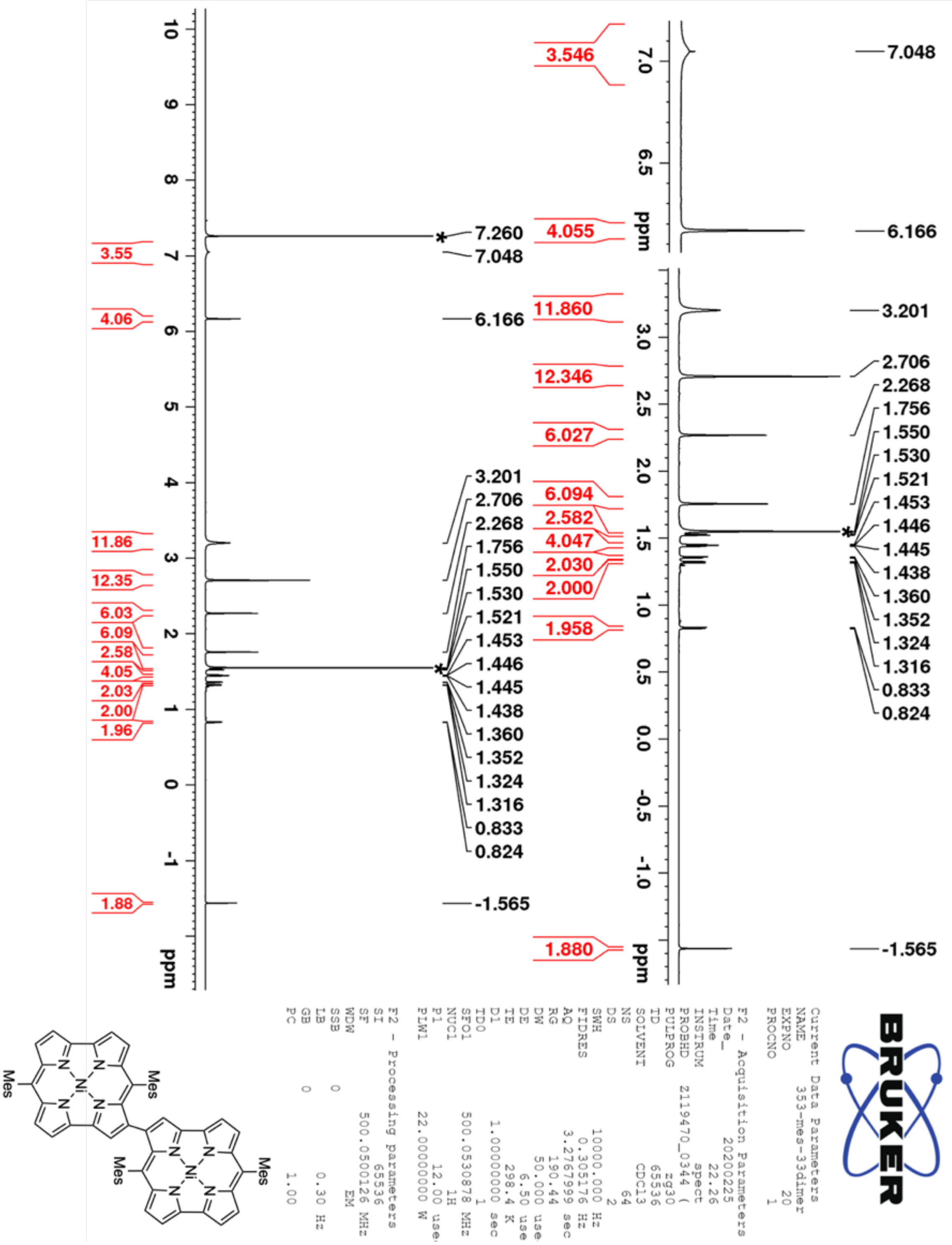

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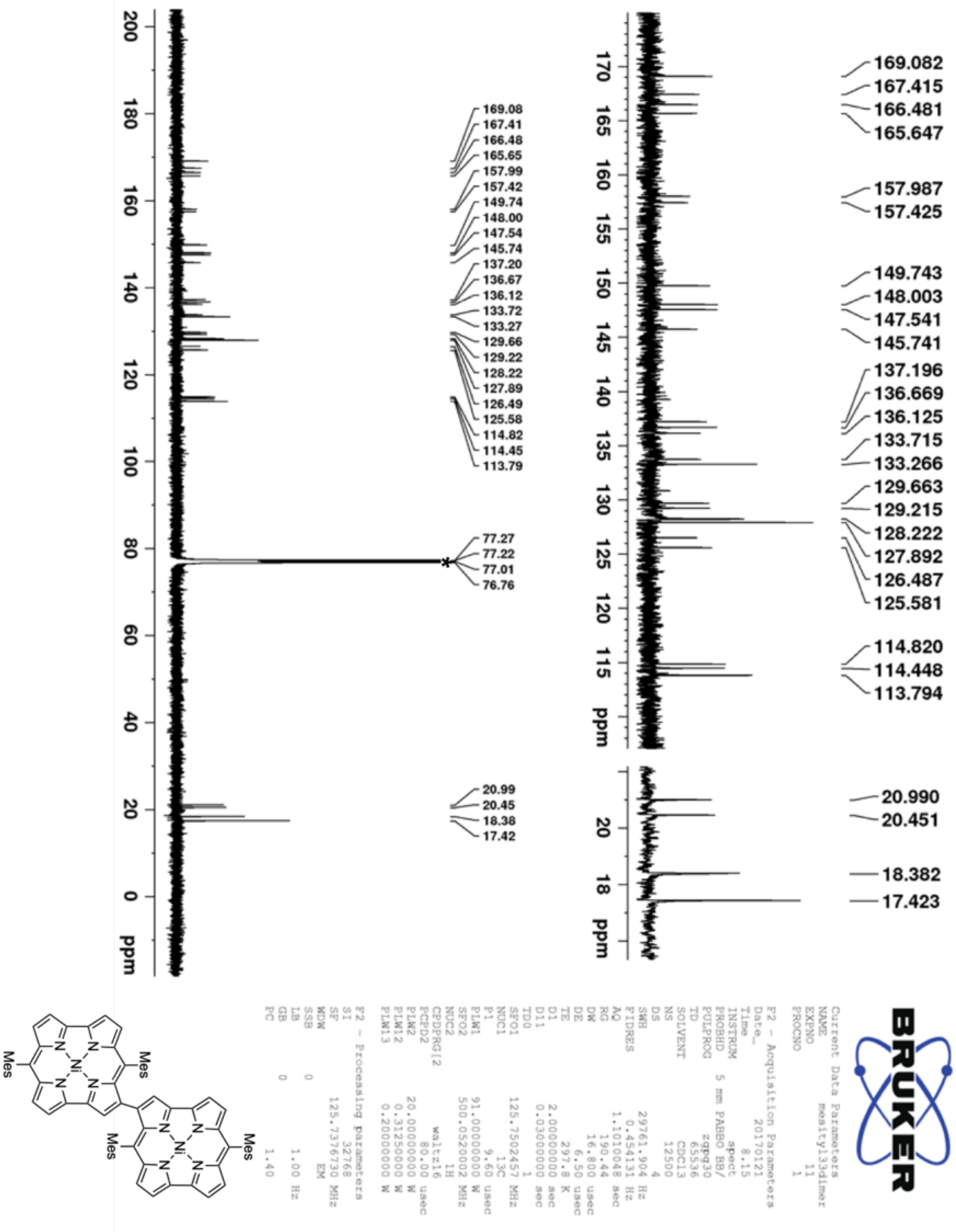
Figure S1. ^{1}H NMR spectrum of **7** in $CDCl_3$ at 25 °C. *Solvent peaks.



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NUC2                   1H
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Figure S2. ^{13}C NMR spectrum of **7** in $CDCl_3$ at 25 °C. *Solvent peaks.

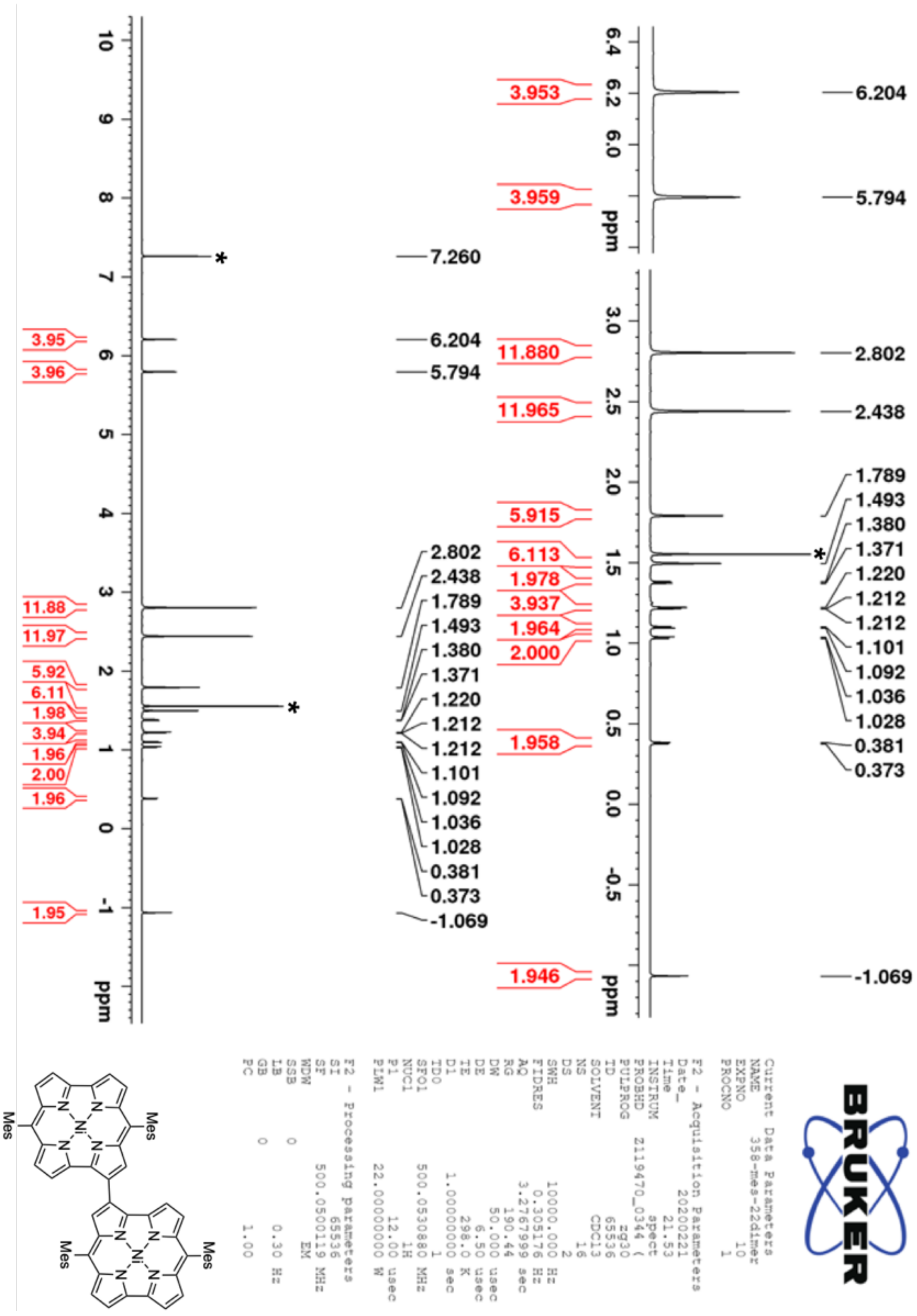

Figure S3. ^{1}H NMR spectrum of **9** in $CDCl_3$ at 25 °C. *Solvent peaks.

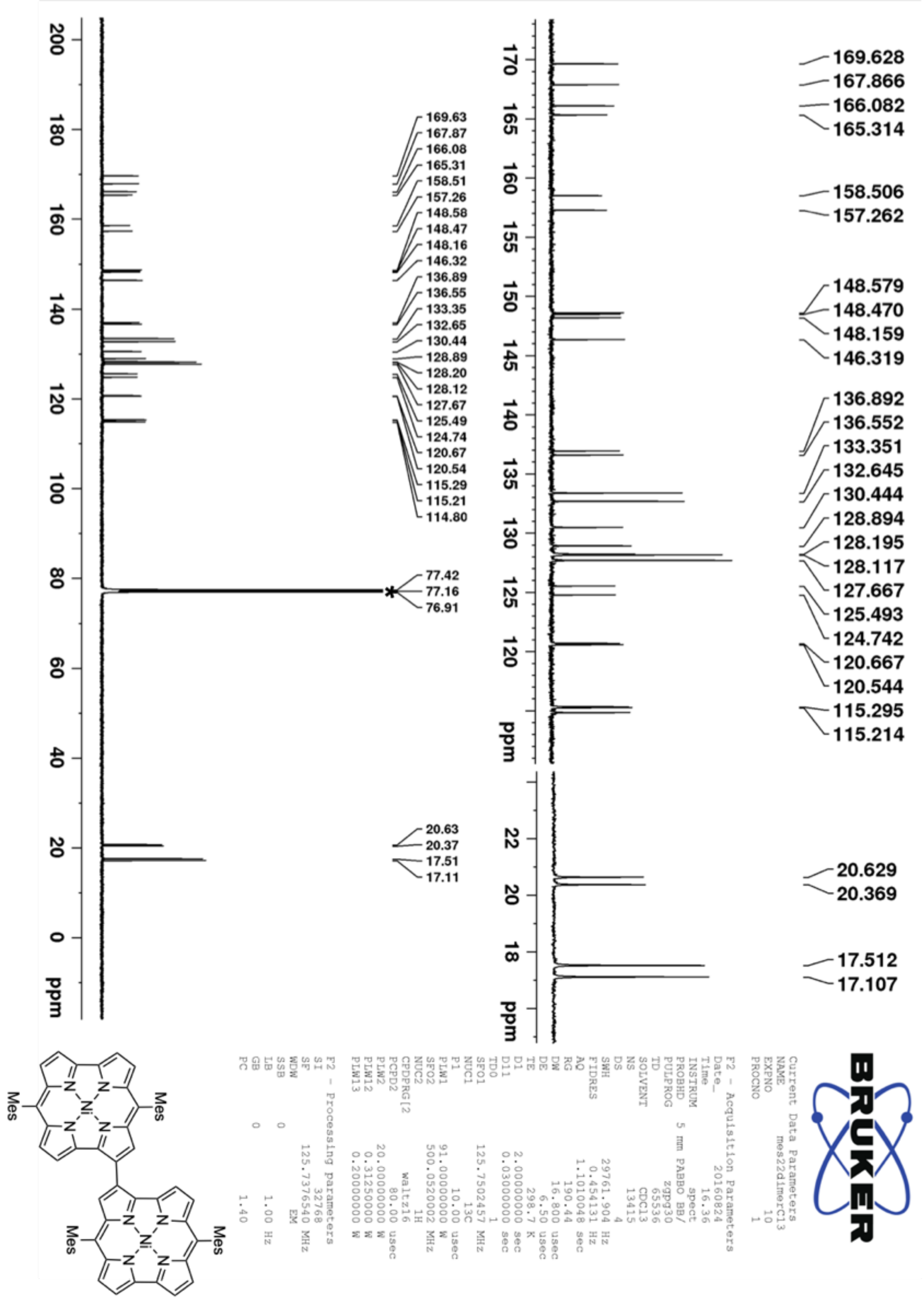

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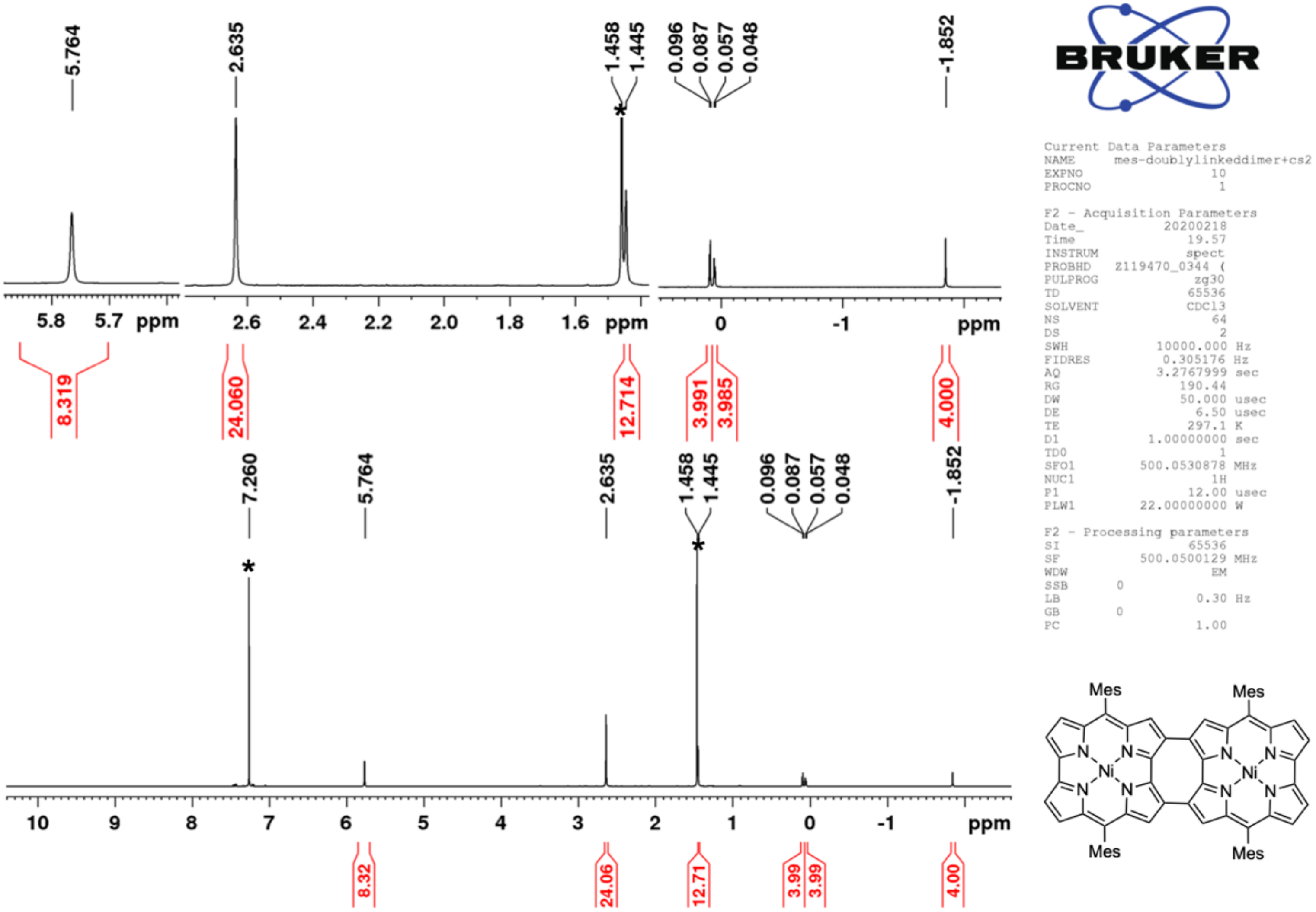
Figure S4. ^{13}C NMR spectrum of **9** in $CDCl_3$ at 25 °C. *Solvent peaks.



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TD                     65536
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DS                         2
SWH            10000.000 Hz
FIDRES          0.305176 Hz
AQ             3.2767999 sec
RG                    190.44
DW                50.000 usec
DE                  6.50 usec
TE                 297.1 K
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NUC1                      1H
P1                 12.00 usec
PLW1         22.00000000 W

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WDW                       EM
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GB           0
PC                      1.00
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Figure S5. ^{1}H NMR spectrum of **10** in $CDCl_3/CS_2$ = 1/1 at 25 °C. *Solvent peaks.

X-ray Diffraction Analysis

X-ray data of **7**, **9**, and **10** were taken on a Rigaku CCD diffractometer (Saturn 724 with MicroMax-007) with Varimax Mo optics using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å). Crystallographic details are given in CIF files. Fine crystals of **7** suitable for the X-ray diffraction analysis were obtained by the vapor diffusion of methanol into its 1,2-dichloroethane solution. Fine crystals of **9** suitable for the X-ray diffraction analysis were obtained by the vapor diffusion of ethanol into its chloroform solution. Fine crystals of **10** suitable for the X-ray diffraction analysis were obtained by the vapor diffusion of methanol into its 1,1,2,2-tetrachloroethane solution. Crystallographic data for **7**, **9**, and **10** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1991857, 1991856, and 1991855, respectively.

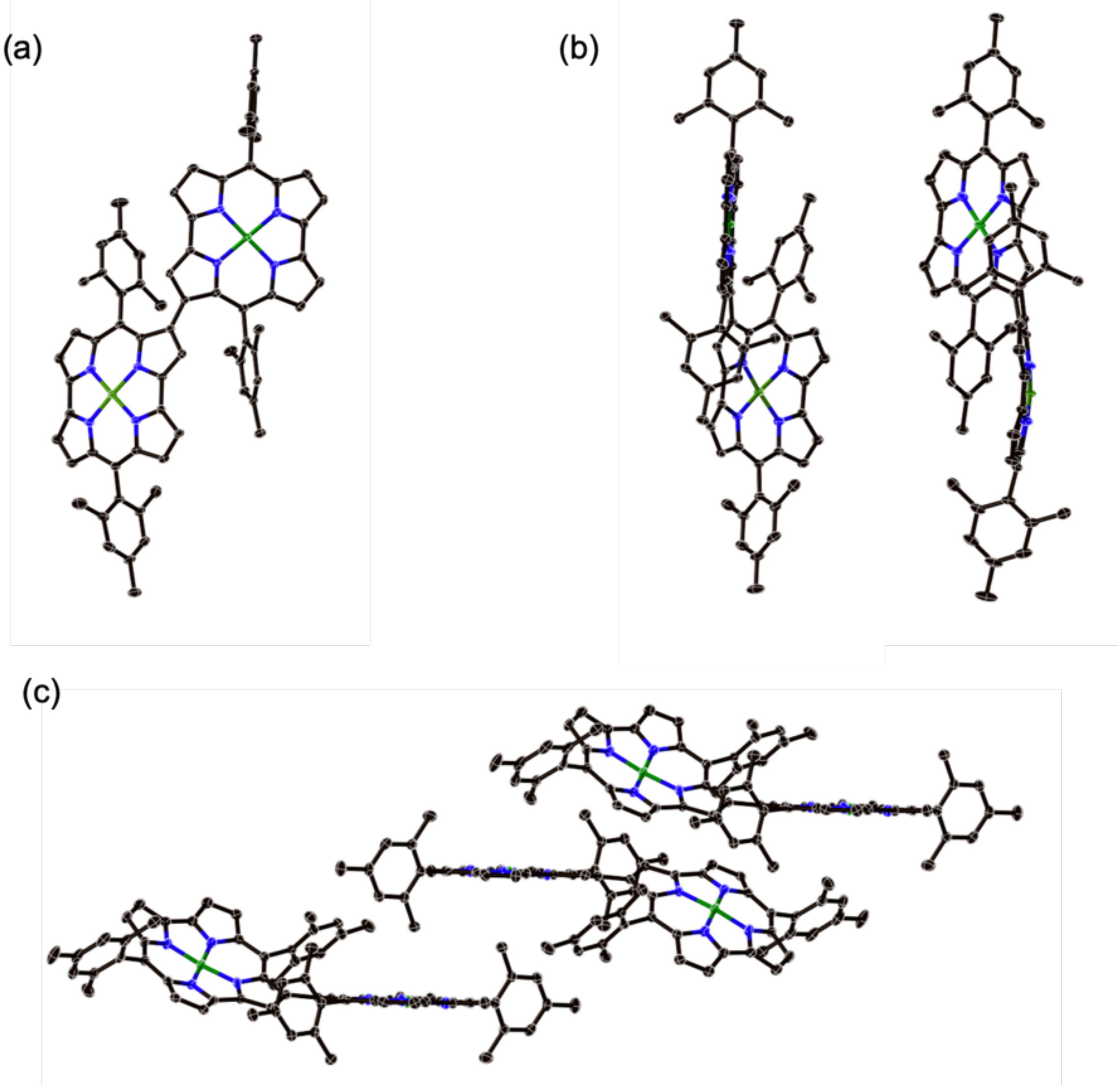


Figure S6. X-ray crystal structure of **7**. (a) Top view, (b) side view, and (c) packing structure. The hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

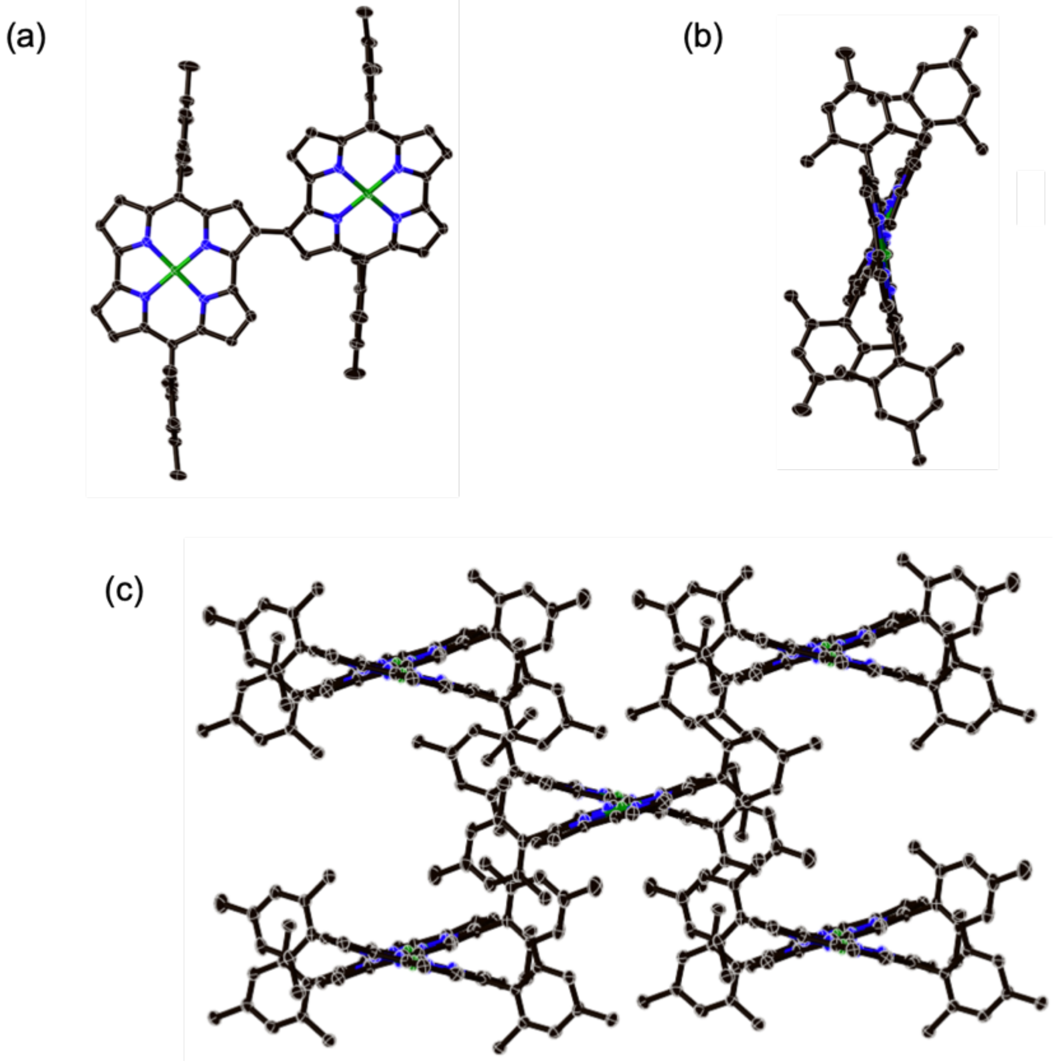


Figure S7. X-ray crystal structure of **9**. (a) Top view, (b) side view, and (c) packing structure. The hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

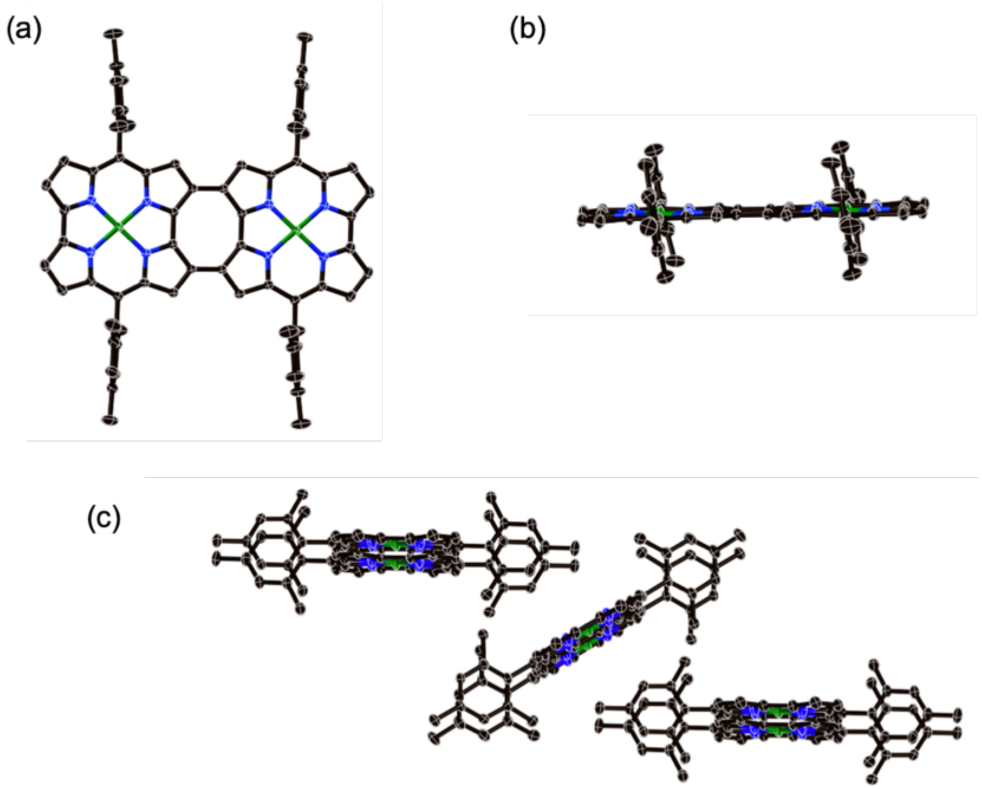


Figure S8. X-ray crystal structure of **10**. (a) Top view, (b) side view, and (c) packing structure. The hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled at 50% probability level.

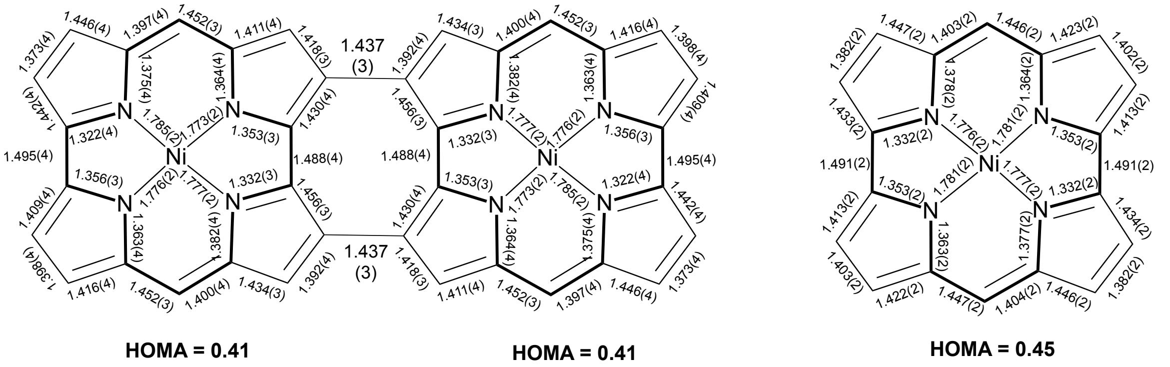


Figure S9. Bond lengths in crystal structure of **10** (left) and **1** (right).[2] *meso*-Mesityl substituents are omitted.

Table S1. Crystal data and structure refinements for **7**, **9**, and **10**.

Compound	**7**	**9**	**10**
Empirical Formula	$C_{72}H_{58}N_8Ni_2$ $2(C_2H_4Cl_2)$	$0.5(C_{72}H_{58}N_8Ni_2)$ $2(CHCl_3)$	$0.5(C_{72}H_{56}N_8Ni_2)$ $2(C_2H_2Cl_4)$
Mw	1350.58	815.08	911.00
Crystal System	triclinic	monoclinic	monoclinic
Space Group	*P*–1 (No. 2)	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)
a	12.0197(3) Å	35.3376(6) Å	17.4782(4) Å
b	15.4760(7) Å	11.9482(2) Å	12.6007(2) Å
c	18.5471(7) Å	17.8205(3) Å	17.9057(3) Å
α	72.164(4)°	—	—
β	77.709(3)°	102.422(2)°	98.164(2)°
γ	86.387(3)°	—	—
Volume	3209.0(2) Å^3	7348.0(2) Å^3	3903.54(13) Å^3
Z	2	8	4
Density (calcd.)	1.398 g/cm^3	1.474 g/cm^3	1.550 g/cm^3
Completeness	0.750	0.991	0.951
Goodness-of-Fit	1.029	1.018	1.005
R_1 [$I>2\sigma(I)$]	0.0638	0.0901	0.0536
wR_2 (all data)	0.1612	0.2828	0.1588
Temperature [K]	93(2)	93(2)	93(2)

Electrochemical Analysis

Cyclic voltammograms of **1**, **7**, **9**, and **10** were recorded on ALS electrochemical analyzer 612C. Measurements were performed in freshly distilled dichloromethane with tetrabutylammonium hexafluorophosphate as electrolyte. A three electrodes system was used and consisted of a grassy carbon working electrode, a platinum wire and Ag/AgNO$_3$ as the reference electrode. All potentials are referenced to the potential of ferrocene/ferrocenium cation couple.

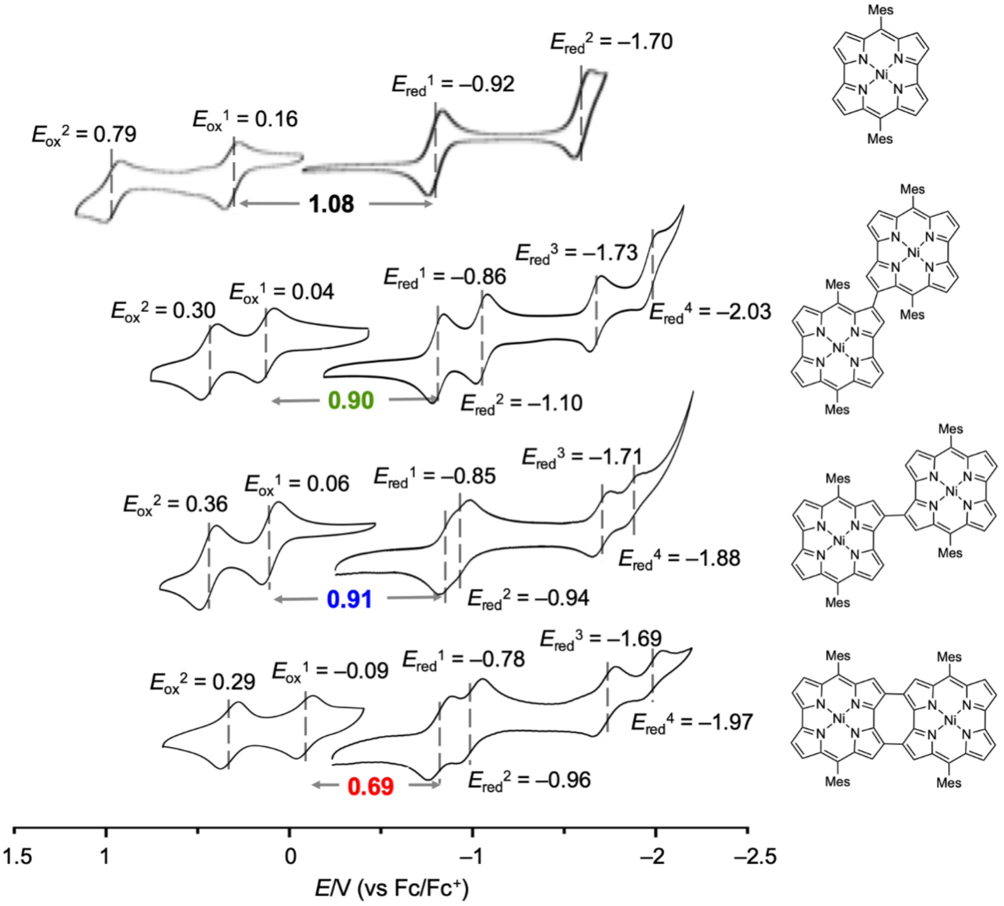


Figure S10. Cyclic voltammograms of **1**, **7**, **9**, and **10**.

Theoretical Calculations

All calculations were carried out using the *Gaussian 09* program.[3] Initial geometries of the model compounds were obtained from their X-ray structures. Full optimizations were performed with Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP)[4] and a basis set consisting of SDD[5] for Ni and 6-31G(d) for the rest. The calculated oscillator strengths were obtained with the TD-DFT method at the CAM-B3LYP[6]/6-31G(d)+SDD level.

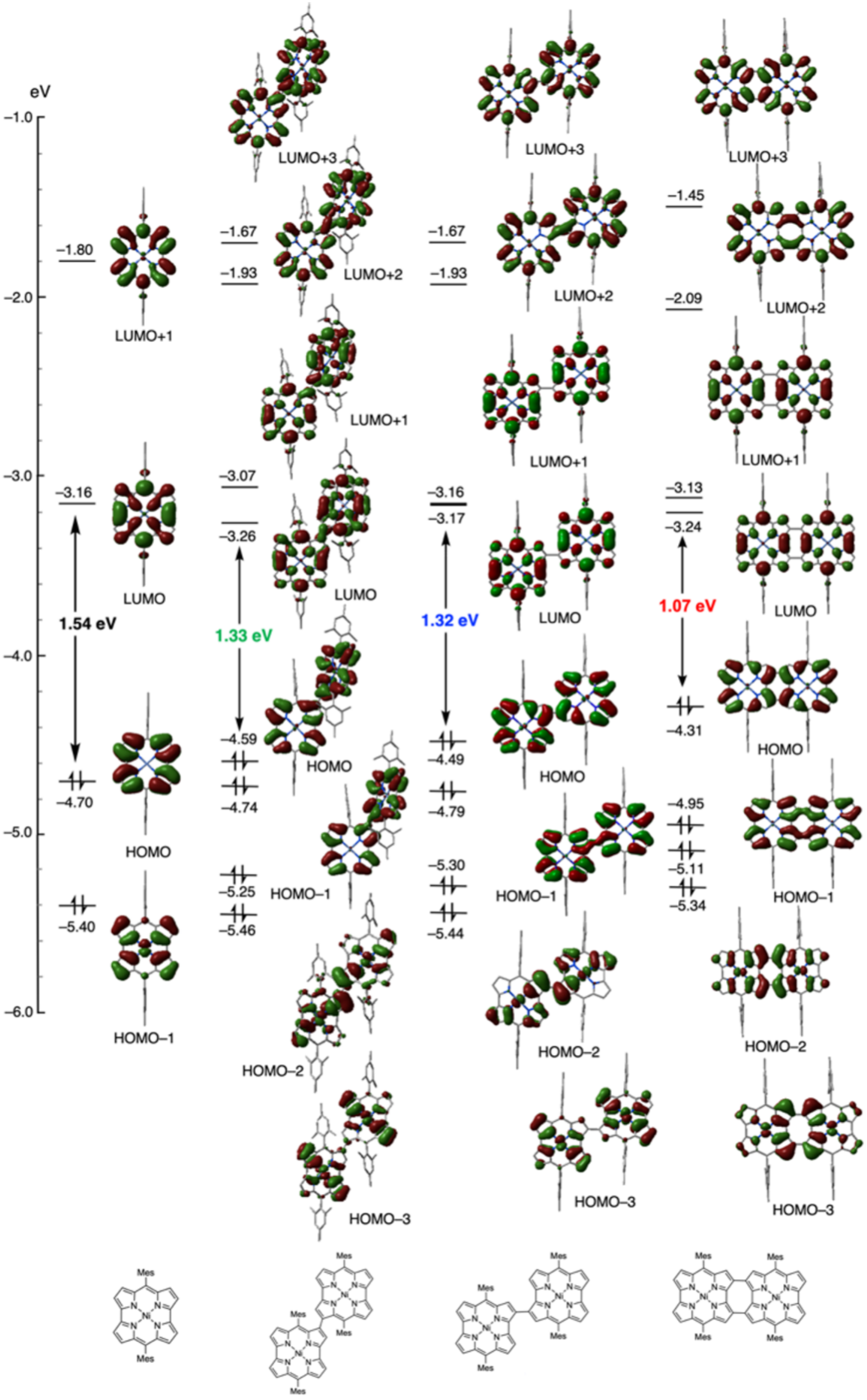


Figure S11. Calculated energy diagrams and molecular orbitals of **1**, **7**, **9**, and **10**.

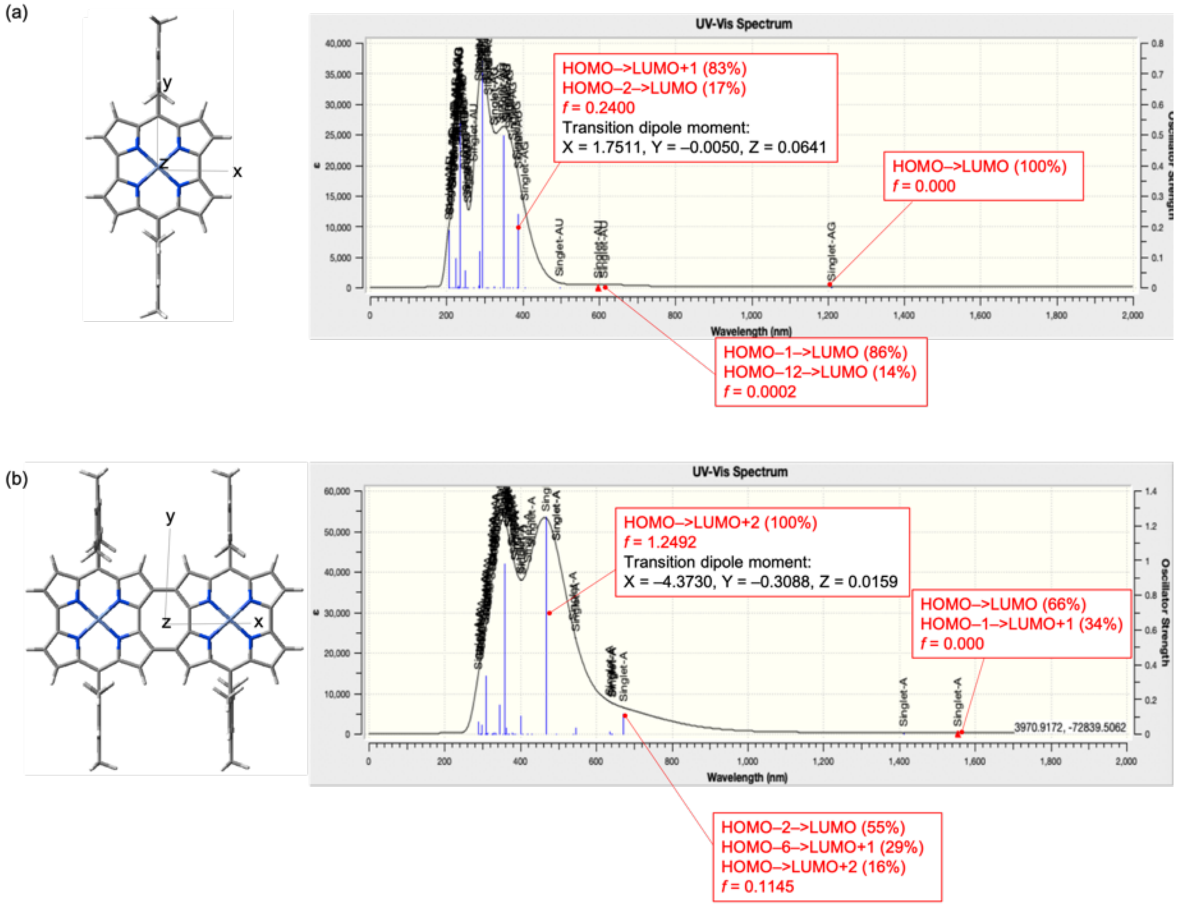


Figure S12. Simulated absorption spectra of (a) **1** and (b) **10**.

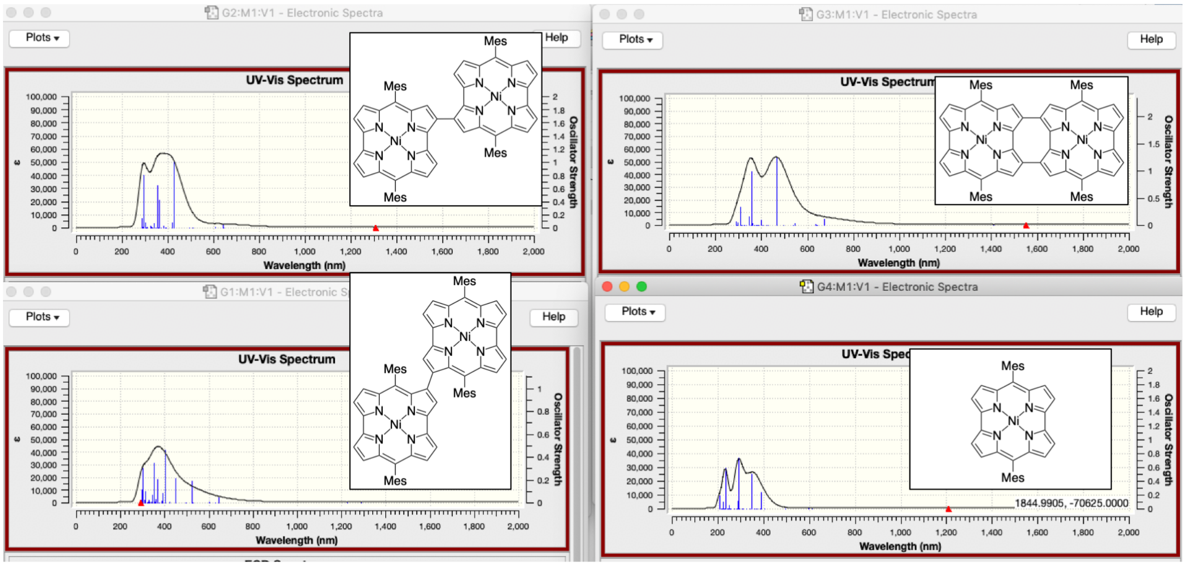
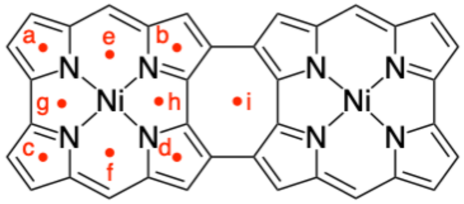


*Figure S13***.** Comparison of simulated absorption spectra of **1**, **7**, **9**, and **10**.

	A		B	
	NICS(0)	NICS(1)	NICS(0)	NICS(1)
a	5.9	5.0	11.3	9.9
b	5.9	5.0	12.6	11.3
c	5.9	5.0	11.3	9.9
d	5.9	5.0	12.6	11.3
e	45.6	38.5	67.4	56.7
f	45.6	38.5	67.4	56.7
g	46.0	40.1	70.6	59.9
h	46.0	40.1	61.2	52.6
i			-17.5	-14.8

A



B

Figure S14. NICS(0) and NICS(1) values of monomer **A** and doubly linked dimer **B**. Calculations were carried out at the B3LYP/6-31G(d)+SDD level of theory. Mesityl groups were replaced with hydrogen atoms to simplify the calculations.

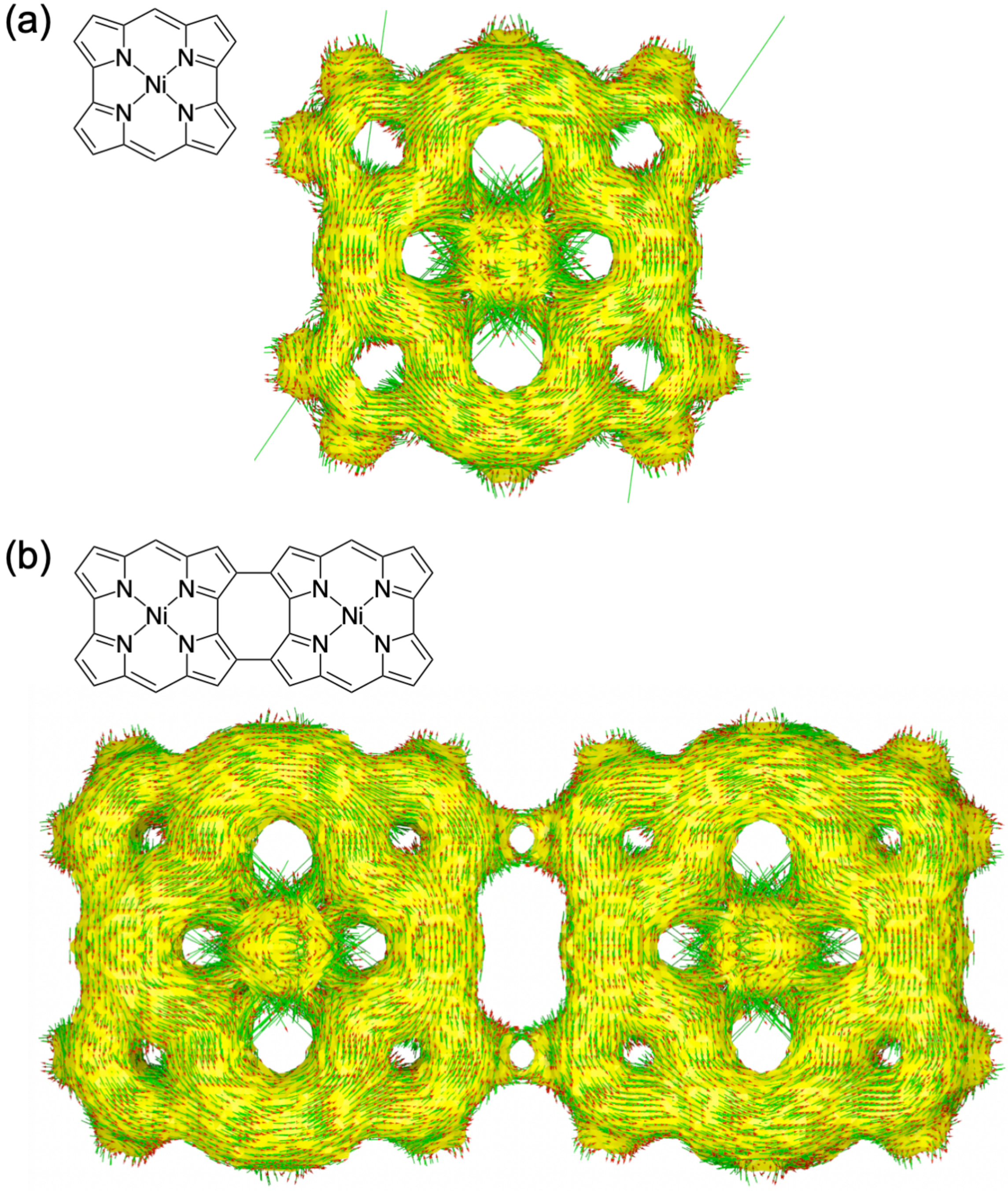


Figure S15. ACID plots of (a) monomer **A** and (b) doubly linked dimer **B**. Calculations were carried out at the B3LYP/6-31G(d)+SDD level of theory. Mesityl groups were replaced with hydrogen atoms to simplify the calculations.

References

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2) Ito, T.; Hayashi, Y.; Shimizu, S.; Shin, J. Y.; Kobayashi, N.; Shinokubo, H. *Angew. Chem. Int. Ed.* **2012**, *51*, 8542.

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