

CHEMISTRY

A **European** Journal

Supporting Information

Boron Arylations of Subporphyrins with Aryl Zinc Reagents

Ryota Kotani, Kota Yoshida, Eiji Tsurumaki, and Atsuhiko Osuka^{*[a]}

chem_201504719_sm_miscellaneous_information.pdf

Supporting Information

Contents

1. Experimental procedure
2. NMR spectra
3. HR-APCI-TOF mass spectra
4. Absorption and emission spectra
5. DFT calculations
6. X-Ray crystal analysis
7. Cyclic voltammograms
8. Supporting references

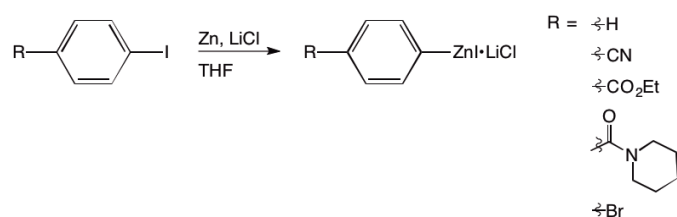
1. Experimental procedure

Methoxo(5,10,15-triphenylsubporphyrinato)boron(III) (1)

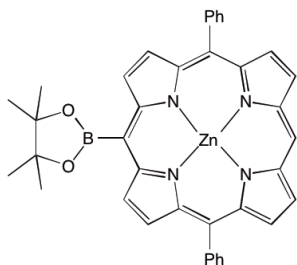
Subporphyrin 1 was prepared according to ref [S1].

General procedure for the preparation of aryl zinc reagents.

Aryl zinc reagents were prepared according to ref [S2]. The concentration of the solution was determined by titration with I_2 in a THF solution before use.

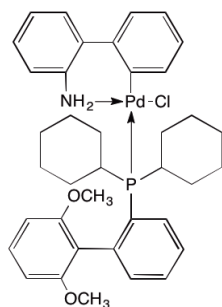


[5-(4',4',5',5'-Tetramethyl[1',3',2']dioxaborolan-2'-yl)-10,20-diphenylporphinato]zinc(II)



This compound was synthesized according to ref [S3].

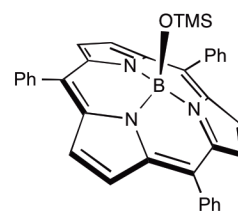
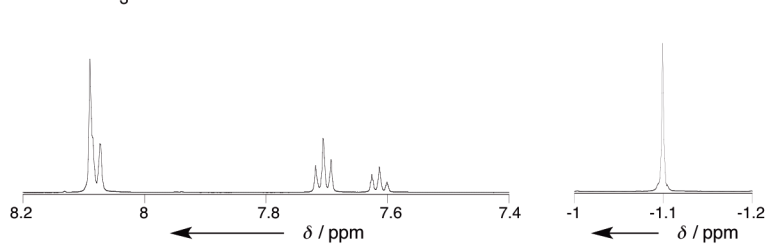
SPhos Pd G2



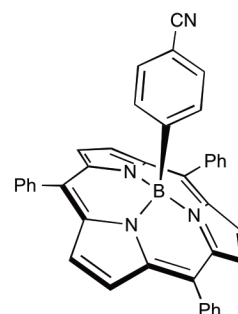
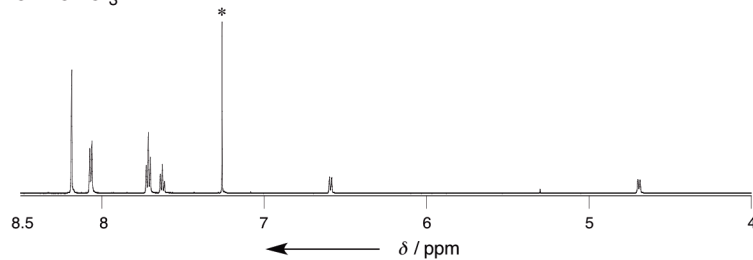
This compound was purchased from Sigma Aldrich.

2. NMR spectra

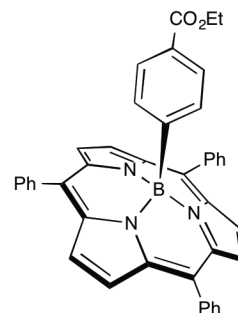
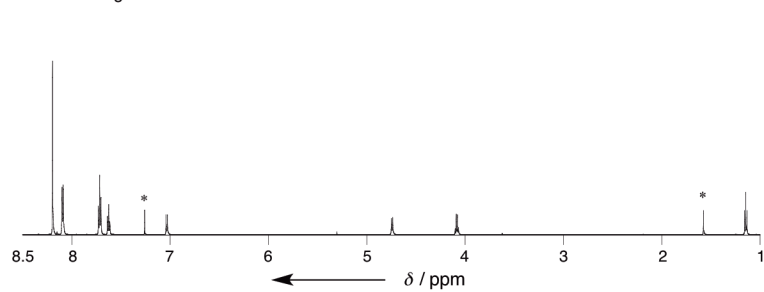
4 in CDCl₃



5 in CDCl₃



6 in CDCl₃



7 in CDCl₃

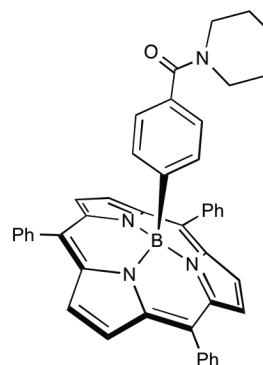
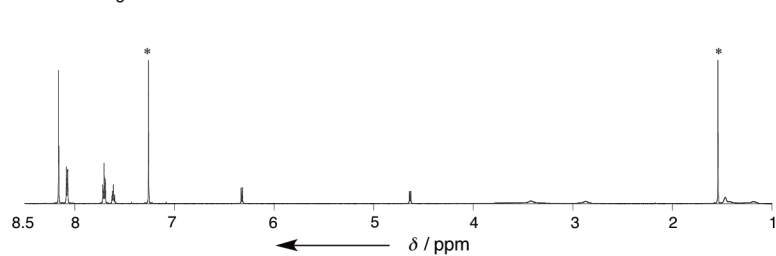


Figure S2-1. ¹H NMR spectra of 4-7 in CDCl₃ at room temperature. Peaks marked with * are due to residual solvents.

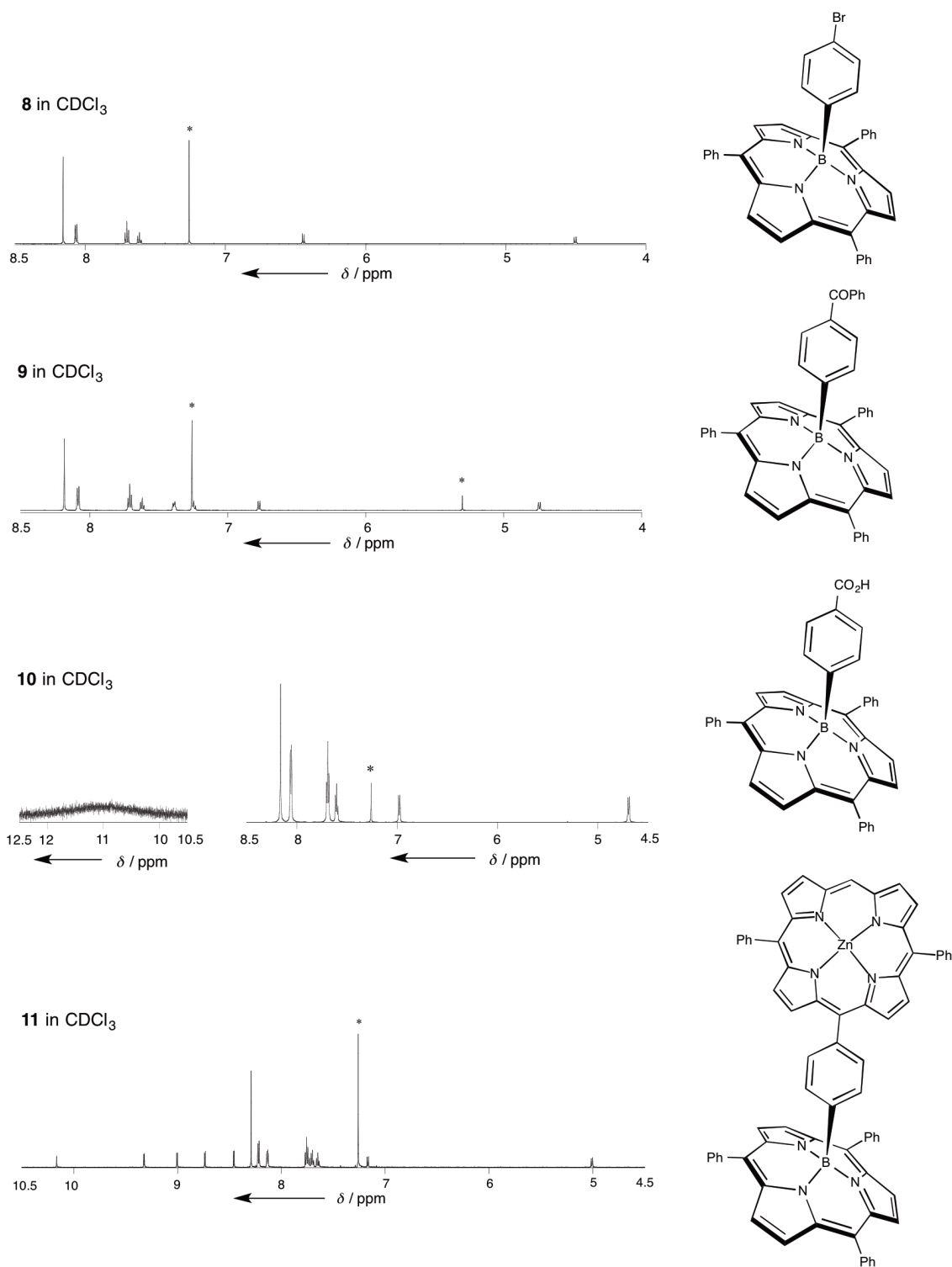


Figure S2-2. ¹H NMR spectra of 8-11 in CDCl₃ at room temperature. Peaks marked with * are due to residual solvents.

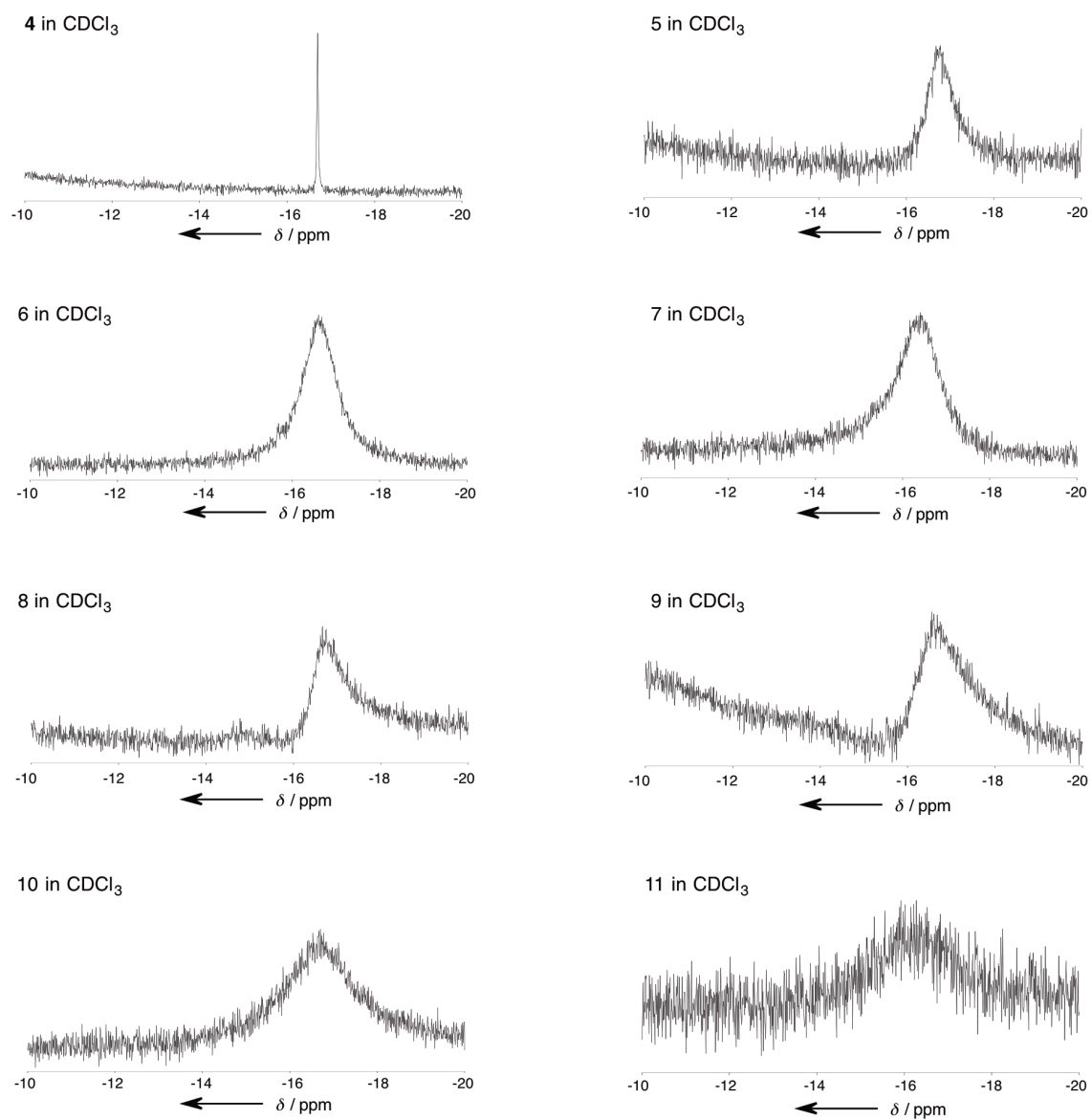


Figure S2-3. ^{11}B NMR spectra of 4-11 in CDCl_3 at room temperature.

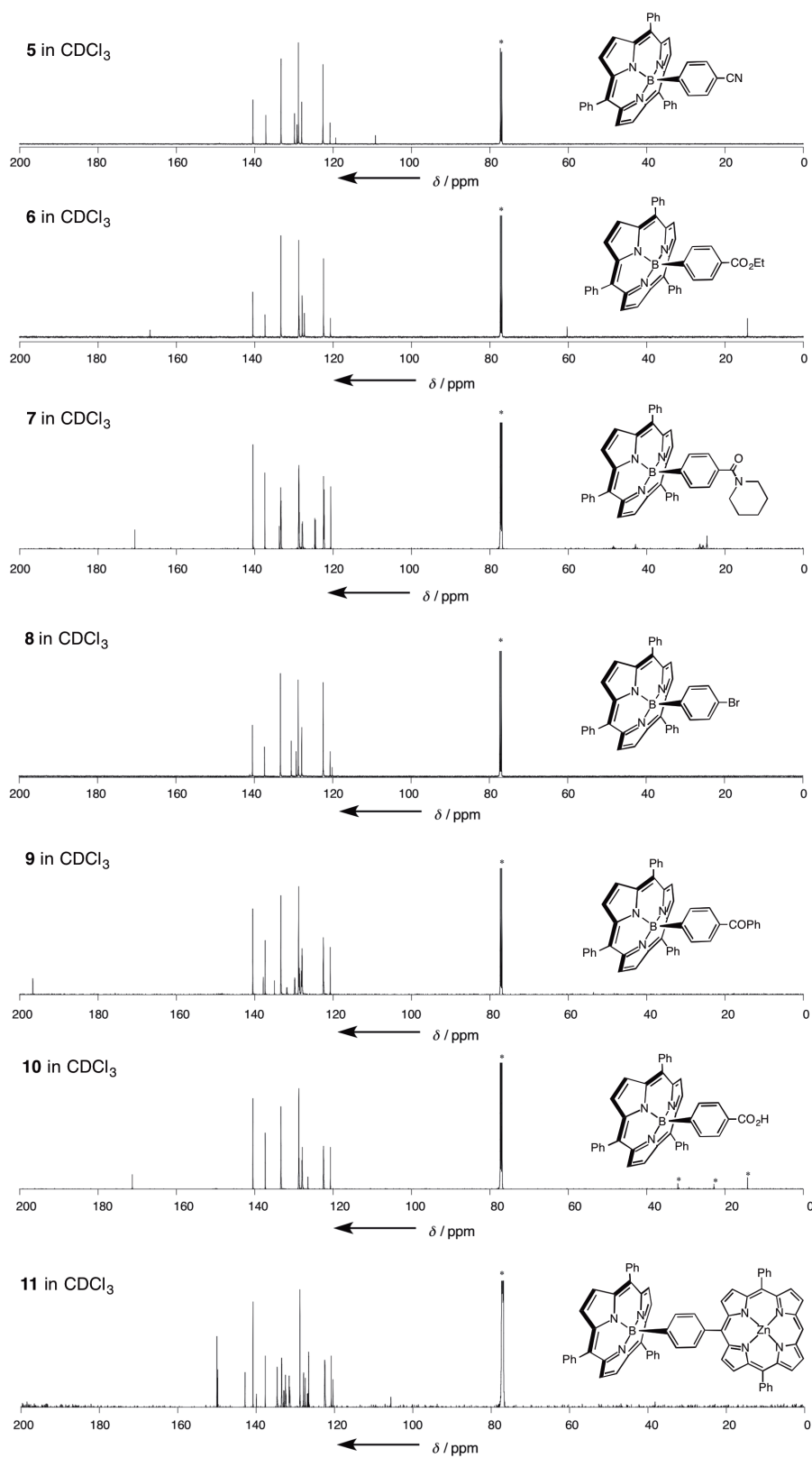
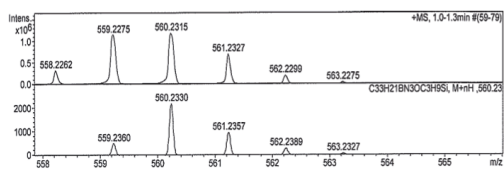
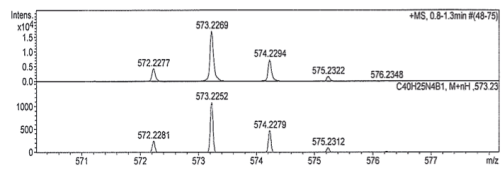


Figure S2-4. ^{13}C NMR spectra of 5-11 in CDCl_3 at room temperature. Peaks marked with * are due to residual solvents.

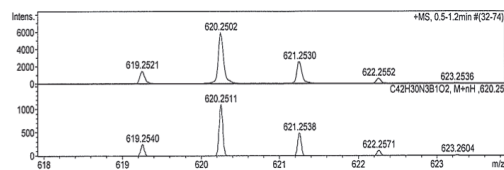
3. HR-APCI-TOF mass spectra



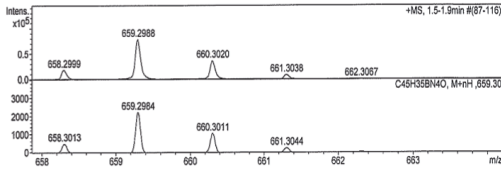
obsd for **4** (upper), calcd for **4** (lower); $C_{38}H_{20}N_3^{11}BOSi$ ($[M+H]^+$)
 $([M])^+$ was overlapped with $([M+H])^+$.



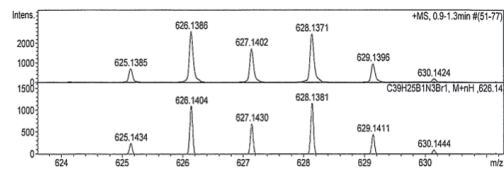
obsd for **5** (upper), calcd for **5** (lower); $C_{40}H_{25}N_4^{11}B$ ($[M+H]^+$)



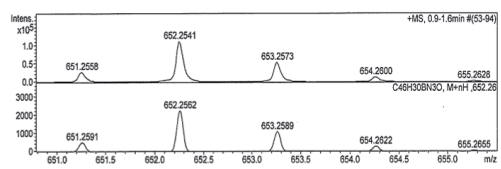
obsd for **6** (upper), calcd for **6** (lower); $C_{42}H_{30}N_3^{11}BO$ ($[M+H]^+$)



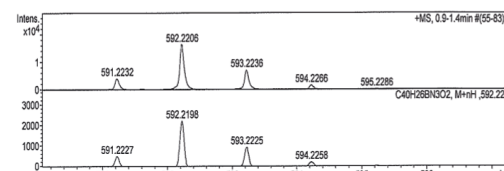
obsd for **7** (upper), calcd for **7** (lower); $C_{45}H_{35}N_4^{11}BO$ ($[M+H]^+$)



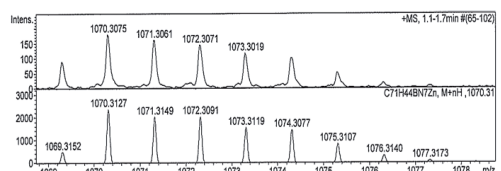
obsd for **8** (upper), calcd for **8** (lower); $C_{39}H_{25}N_3^{11}B^{79}Br$ ($[M+H]^+$)



obsd for **9** (upper), calcd for **9** (lower); $C_{46}H_{30}N_3^{11}BO$ ($[M+H]^+$)



obsd for **10** (upper), calcd for **10** (lower); $C_{40}H_{26}N_3^{11}BO_2$ ($[M+H]^+$)



obsd for **11** (upper), calcd for **11** (lower); $C_{71}H_{44}N_7^{11}B^{64}Zn$ ($[M+H]^+$)

Figure S3-1. HR-APCI-TOF mass spectra of **4-11**.

4. Absorption and emission spectra

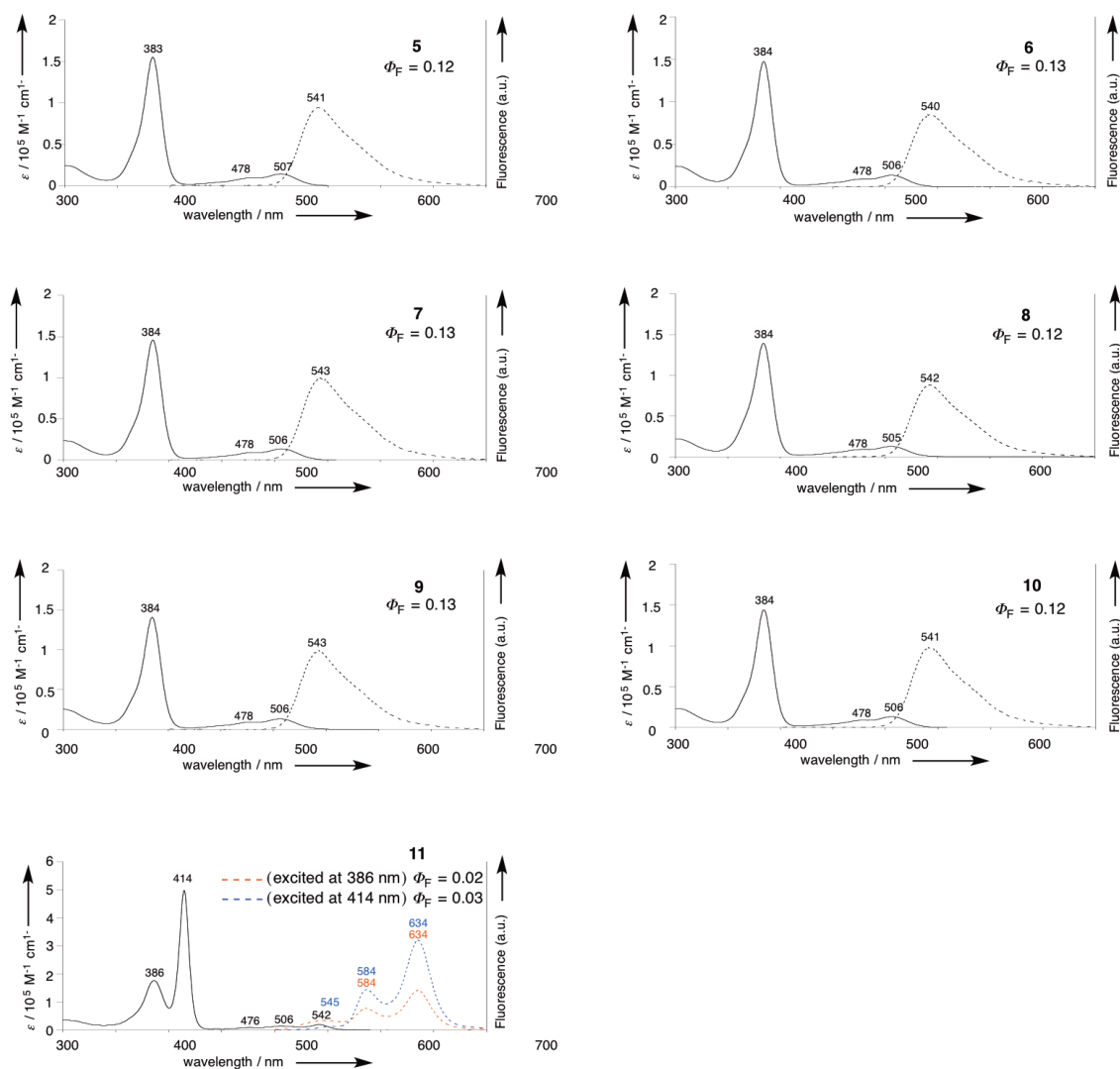


Figure S4-1. UV/Vis absorption (solid) and fluorescence (dashed) spectra of 5-11 in CH_2Cl_2 . Subporphyrins were excited at each Soret-like band absorption maxima.

5. DFT calculations

All calculations were carried out using the Gaussian 09 program.^[S4] Initial geometries were obtained from X-ray structures. All structures were fully optimized without any symmetry restriction. The calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional)level,^[S5,S6] employing a basis set 6-311G(d).

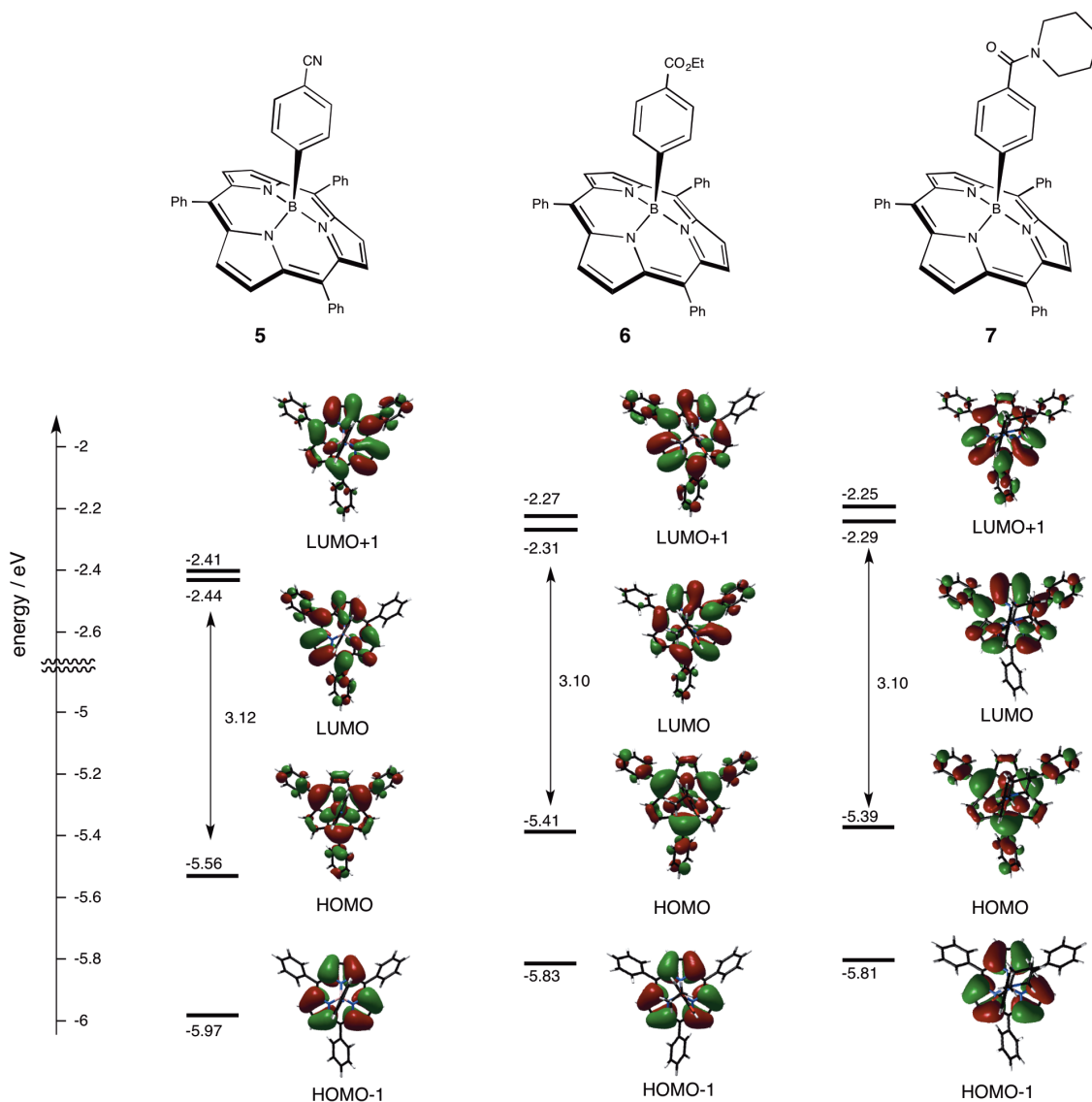


Figure S5-1. MO diagrams and energies of subporphyrins 5-7. (Each MO was visualized with cubegen program).

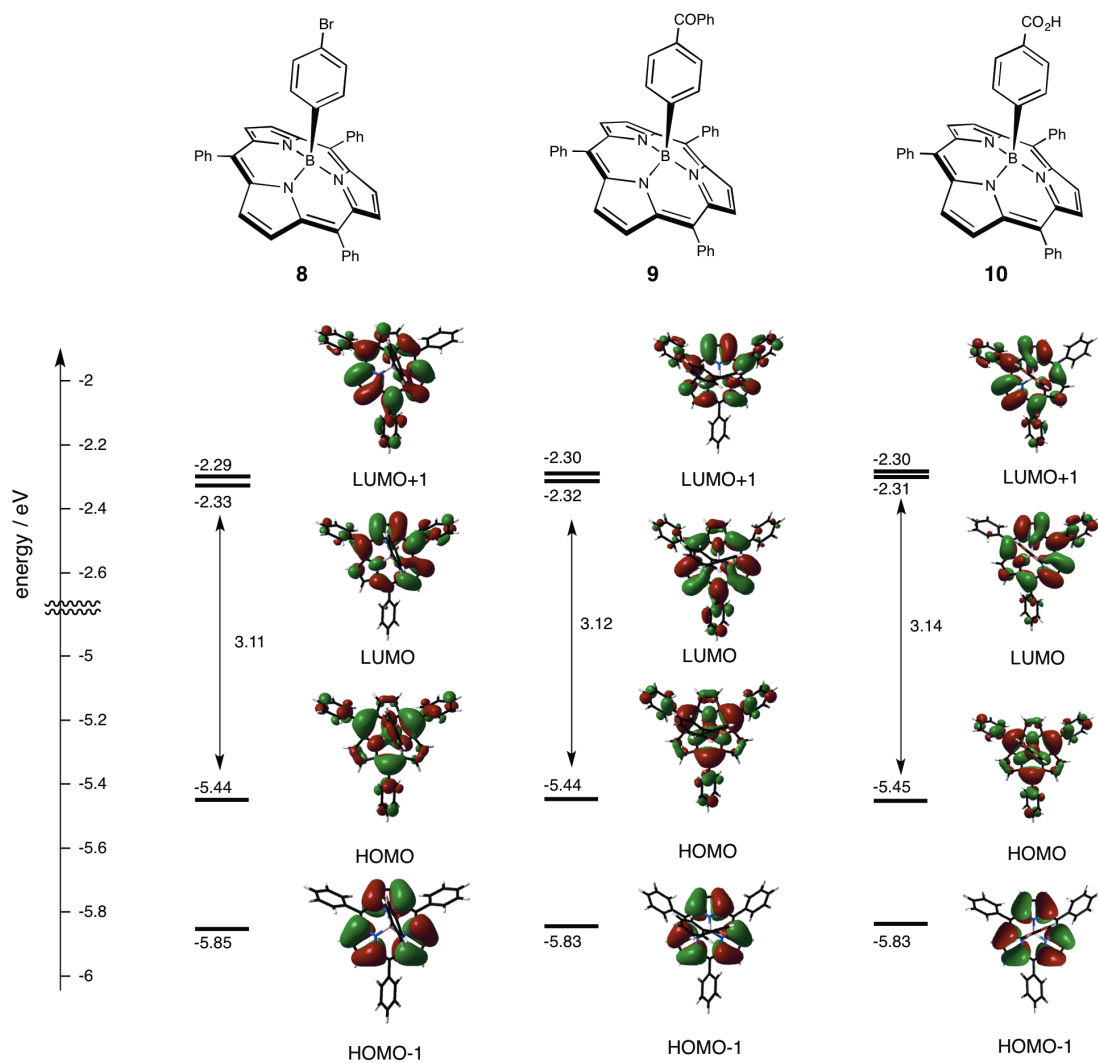


Figure S5-2. MO diagrams and energies of subporphyrins 8-10. (Each MO was visualized with cubegen program).

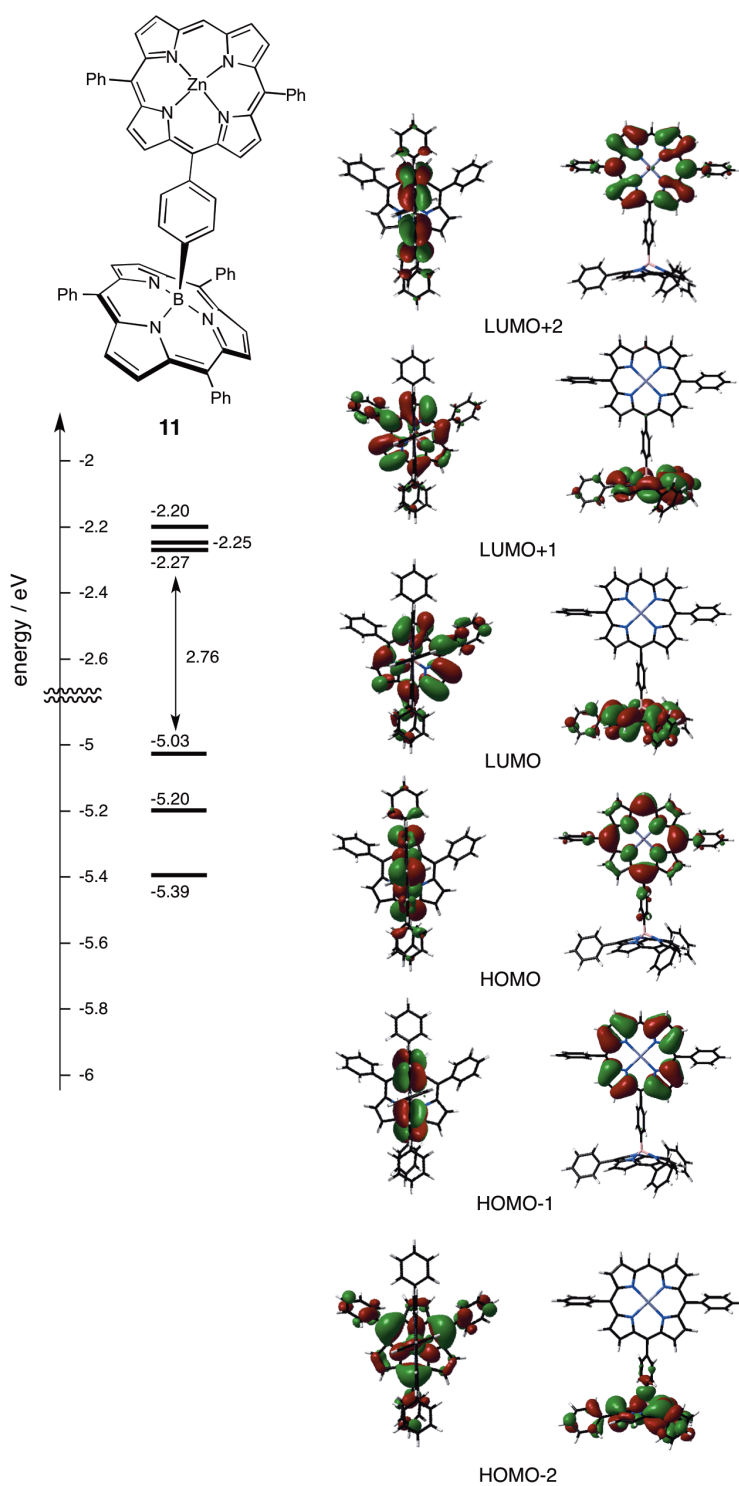


Figure S5-3. MO diagrams and energies of subporphyrin **11**. (Each MO was visualized with cubegen program).

6. X-Ray crystal analysis

X-Ray single crystal diffraction analyses were performed on a Rigaku XtaLAB P200 apparatus at $-180\text{ }^{\circ}\text{C}$ using two dimensional detector PILATUS 100K/R with $\text{CuK}\alpha$ radiation ($\lambda = 1.54187\text{ \AA}$). The structures were solved by direct method SIR-97^[57] or SHELXS-97 and refined by SHELXL-97 or SHELXL-2014/7 program.^[58]

Table S1. Crystal Data of 4-7.

Compound	4	5	6	7
Molecular formula	$2(\text{C}_{12}\text{H}_3\text{BN}_2\text{OSi})$	$\text{C}_{12}\text{H}_3\text{BN}_2$	$\text{C}_{12}\text{H}_3\text{BN}_2\text{O}_2$	$\text{C}_{12}\text{H}_3\text{BN}_2\text{O}$
Solvent system	Chloroform/ <i>n</i> -hexane	Dichloromethane/ methanol	Dichloromethane/ methanol	Benzene/ <i>n</i> -heptane
FW	1119.06	574.47	619.50	658.58
crystal system	triclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> -1 (No.2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> -1 (No.2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> (Å)	10.756(3)	12.2634(19)	10.3448(19)	11.3147(15)
<i>b</i> (Å)	14.406(4)	19.755(2)	19.709(3)	17.177(2)
<i>c</i> (Å)	20.456(6)	12.710(2)	14.032(3)	17.832(3)
α (deg)	103.709(4)	90	100.881(11)	90
β (deg)	97.794(13)	109.556(5)	96.135(5)	96.135(5)
γ (deg)	105.087(4)	90	93.769(5)	90
<i>V</i> (Å ³)	2096.7(14)	2901.5(8)	1653.2(6)	3373.0(8)
<i>D</i> (g cm ⁻³)	1.279	1.315	1.245	1.297
<i>Z</i>	2	4	2	4
<i>T</i> (K)	93	93	93	93
<i>R</i> , [<i>I</i> > 2.0 σ (<i>I</i>)]	0.0398	0.0449	0.0413	0.0387
<i>wR</i> , (all data)	0.1130	0.1202	0.1154	0.1005
GOF	1.014	1.067	1.037	1.024
CCDC	1438151	1438154	1438155	1438152

Table S2. Crystal Data of 8-11.

Compound	8	9	10	11
Moiety formula	3(C ₁₀ H ₁₂ BN.Br)	C ₁₀ H ₁₂ BN.O, CH ₂ Cl ₂	2(C ₁₀ H ₁₂ BN.O), 5(C ₂ H ₄)	C ₁₀ H ₁₂ BN.Zn, CHCl ₃
Solvent system	Dichloromethane/ methanol	Dichloromethane/ <i>n</i> -hexane	Benzene/ <i>n</i> -heptane	Chloroform/ <i>n</i> -hexane
FW	1878.99	736.47	1573.44	1190.70
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
<i>a</i> (Å)	14.1177(16)	10.525(3)	10.0530(19)	13.1938(6)
<i>b</i> (Å)	20.155(2)	13.202(5)	16.391(2)	13.8074(1)
<i>c</i> (Å)	31.338(4)	13.834(5)	26.731(5)	17.9912(16)
α (deg)	90	104.395(15)	80.213(13)	76.876(19)
β (deg)	101.286(5)	93.667(4)	89.64(2)	77.20(2)
γ (deg)	90	104.558(8)	77.889(17)	61.533(17)
<i>V</i> (Å ³)	8744.6(17)	1785.7(11)	4242.0(13)	2781.3(6)
<i>D</i> _c (g cm ⁻³)	1.427	1.370	1.232	1.422
<i>Z</i>	4	2	2	2
<i>T</i> (K)	93	93	93	93
<i>R</i> _i [<i>I</i> > 2.0 σ (<i>I</i>)]	0.0572	0.0705	0.0616	0.0666
<i>wR</i> _i (all data)	0.1519	0.1742	0.2033	0.2041
GOF	1.042	1.053	1.034	1.072
CCDC	1438153	1438157	1438156	1438158

Table S3. Selected bond lengths, bowl depths, and dihedral angles of **1** and **3-11**.

Compounds	N-B	B-X	dihedral angles (deg)	bowl depths (Å)
1	1.485, 1.500, 1.507	1.438	38.3, 45.7, 48.1	1.29
3	1.507, 1.509, 1.515	1.611	47.3, 46.5, 49.0	1.42
4	1.498, 1.502, 1.508	1.431	38.3, 46.2, 46.9	1.32
	1.500, 1.502, 1.506	1.430	45.5, 52.3, 58.9	1.36
5	1.497, 1.501, 1.512	1.625	46.1, 51.4, 54.5	1.42
6	1.494, 1.502, 1.512	1.616	42.6, 44.6, 47.0	1.32
7	1.494, 1.501, 1.502	1.619	41.9, 41.9, 45.8	1.31
	1.503, 1.505, 1.512	1.619	50.5, 50.8, 55.1	1.43
8	1.489, 1.502, 1.518	1.626	50.1, 52.7, 54.7	1.40
	1.496, 1.502, 1.514	1.628	48.0, 55.7, 55.7	1.41
9	1.500, 1.507, 1.508	1.613	41.4, 51.5, 58.7	1.40
	1.503, 1.504, 1.509	1.623	42.6, 46.2, 53.4	1.36
10	1.501, 1.502, 1.507	1.620	45.8, 47.4, 55.7	1.35
11	1.504, 1.504, 1.504	1.616	46.3, 47.0, 55.7	1.40

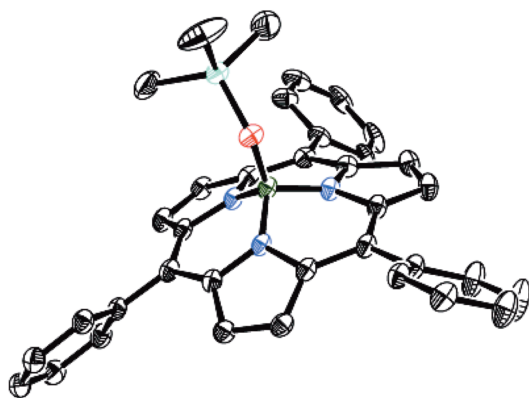


Figure S6-1. X-Ray crystal structure of **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 50% probability level.

7. Cyclic voltammograms

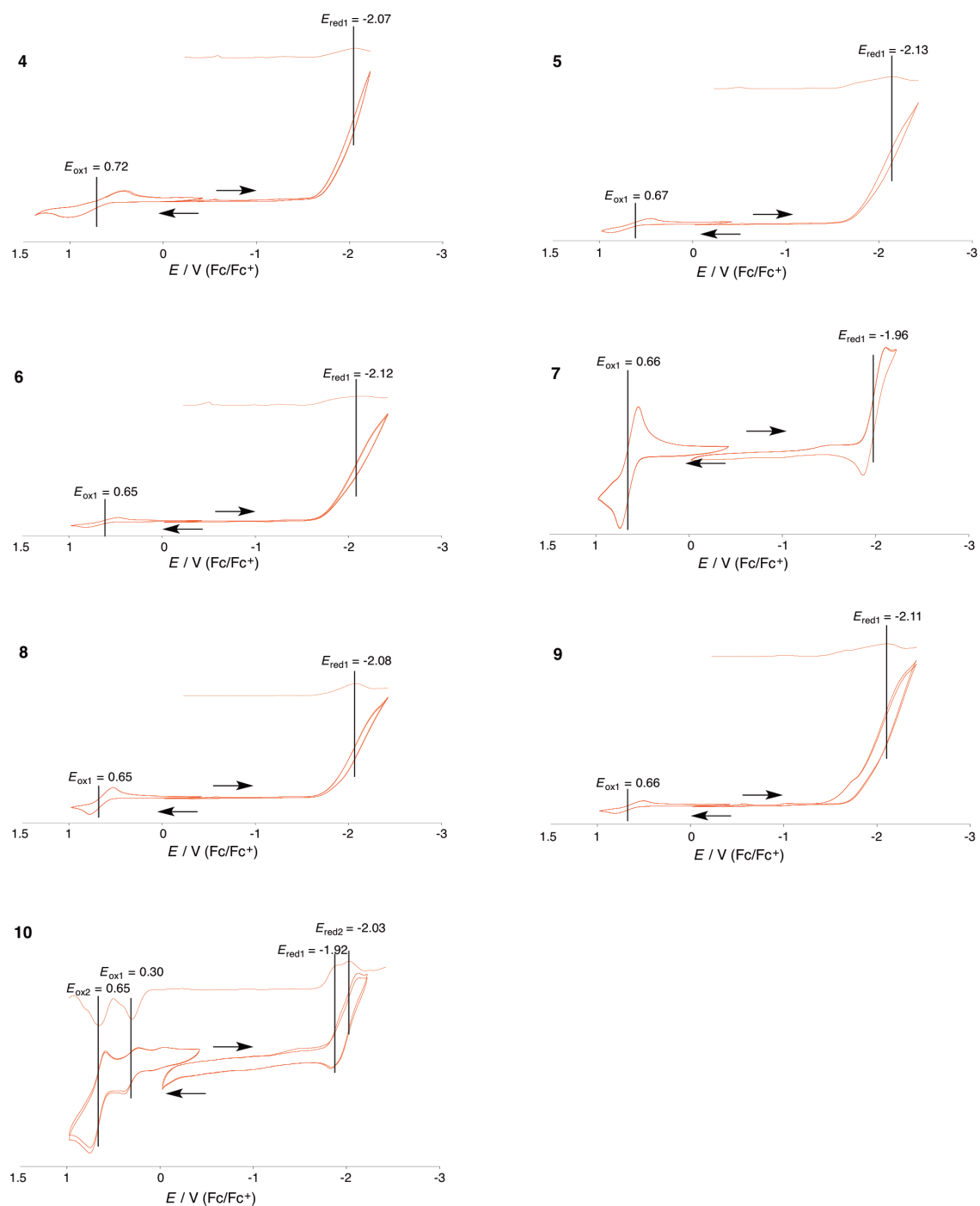


Figure S7-1. Cyclic voltammograms of **5-11** (in V vs. ferrocene / ferrocenium cation).

Measurement conditions; solvent: CH_2Cl_2 , supporting electrolyte: 0.10 M tetrabutylammoniumhexafluorophosphate, working electrode: glassy carbon rod, counter electrode: platinum wire, reference electrode: $\text{Ag} / 0.01 \text{ M AgClO}_4$, scan rate: 0.05 V / s.

8. Supporting references

- [S1] a) Y. Inokuma, Z. S. Yoon, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2007**, *129*, 4747; b) S.-y. Hayashi, E. Tsurumaki, Y. Inokuma, P. Kim, Y. M. Sung, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2011**, *133*, 4254.
- [S2] A. Krasovskiy, V. Malakhov, A. Gavryushin, P. Knochel, *Angew. Chem. Int. Ed.* **2006**, *45*, 6040; *Angew. Chem.* **2006**, *118*, 6186.
- [S3] A. G. Hyslop, M. A. Kellet, P. M. Iovine, M. J. Therien, *J. Am. Chem. Soc.* **1998**, *120*, 12676.
- [S4] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- [S5] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372.
- [S6] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1998**, *37*, 785.
- [S7] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115.
- [S8] SHELXS-97, SHELXL-97 and SHELXL-2014/7, programs for refinement of crystal structures from diffraction data, University of Goettingen, Goettingen (Germany); a) G. Sheldrick, T. Schneider, *Methods Enzymol.* **1997**, *277*, 319; b) G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.