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Supporting Information

Construction of Giant Porphyrin Macrorings Self-Assembled from Thiophenylene-Linked Bisporphyrins for Light-Harvesting Antennae

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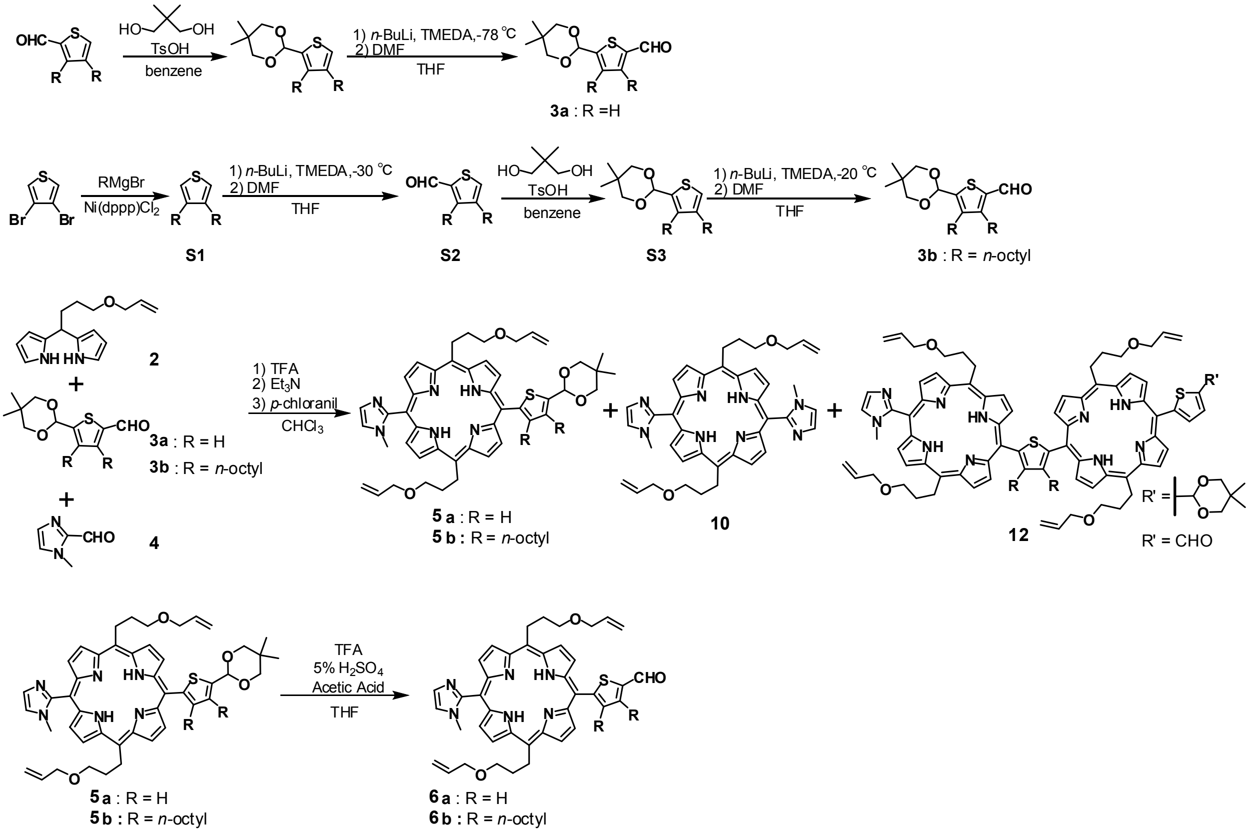
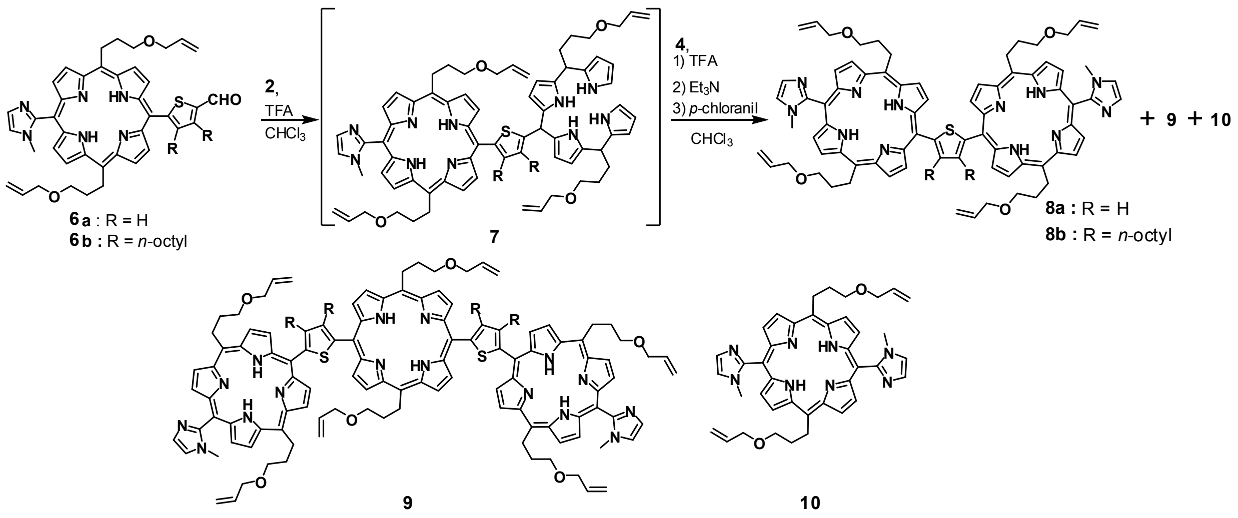
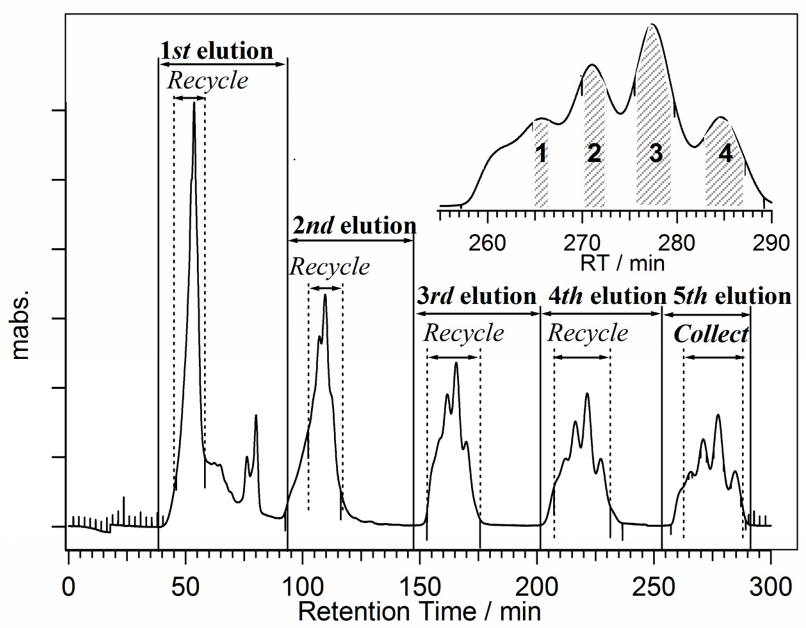
Scheme S1. Synthesis of thiophenylene-porphyrin **6a** and **6b**.



Scheme S2. Synthesis of thiophenylene-porphyrin **8a** and **8b**.



(a)



(b)

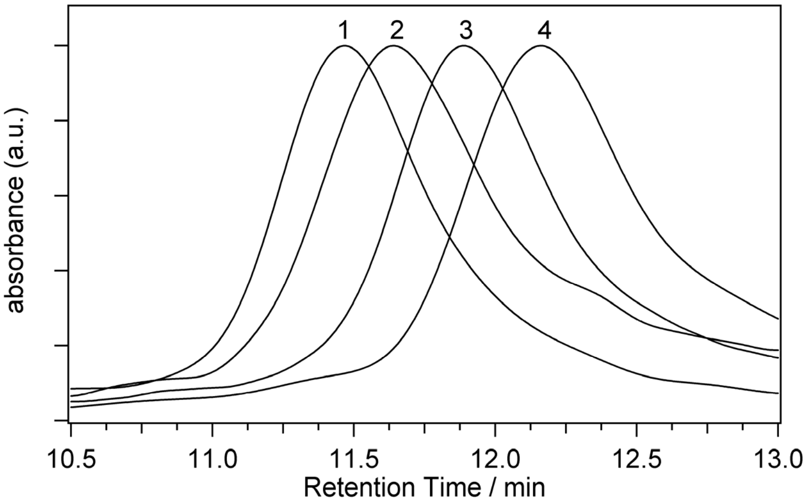


Figure S1. (a) Recycling GPC chromatogram of **C-(1b)$_{\mathbf{mix}}$**, inset: enlargement from 258 to 290 min, where fractions 1-4 were collected, column: Tosoh TSK-GEL G3000H$_{HR}$ (polystyrene, exclusion limit = 60,000 Da), eluent: pyridine, (b) analytical GPC chromatograms of fractions 1-4, conditions: same as Figure 3. The fractions 1-4 were assigned as 7-10 mers (**C-(1b)$_{\mathbf{7\text{-}10}}$**) by mass spectra in Figure 4.

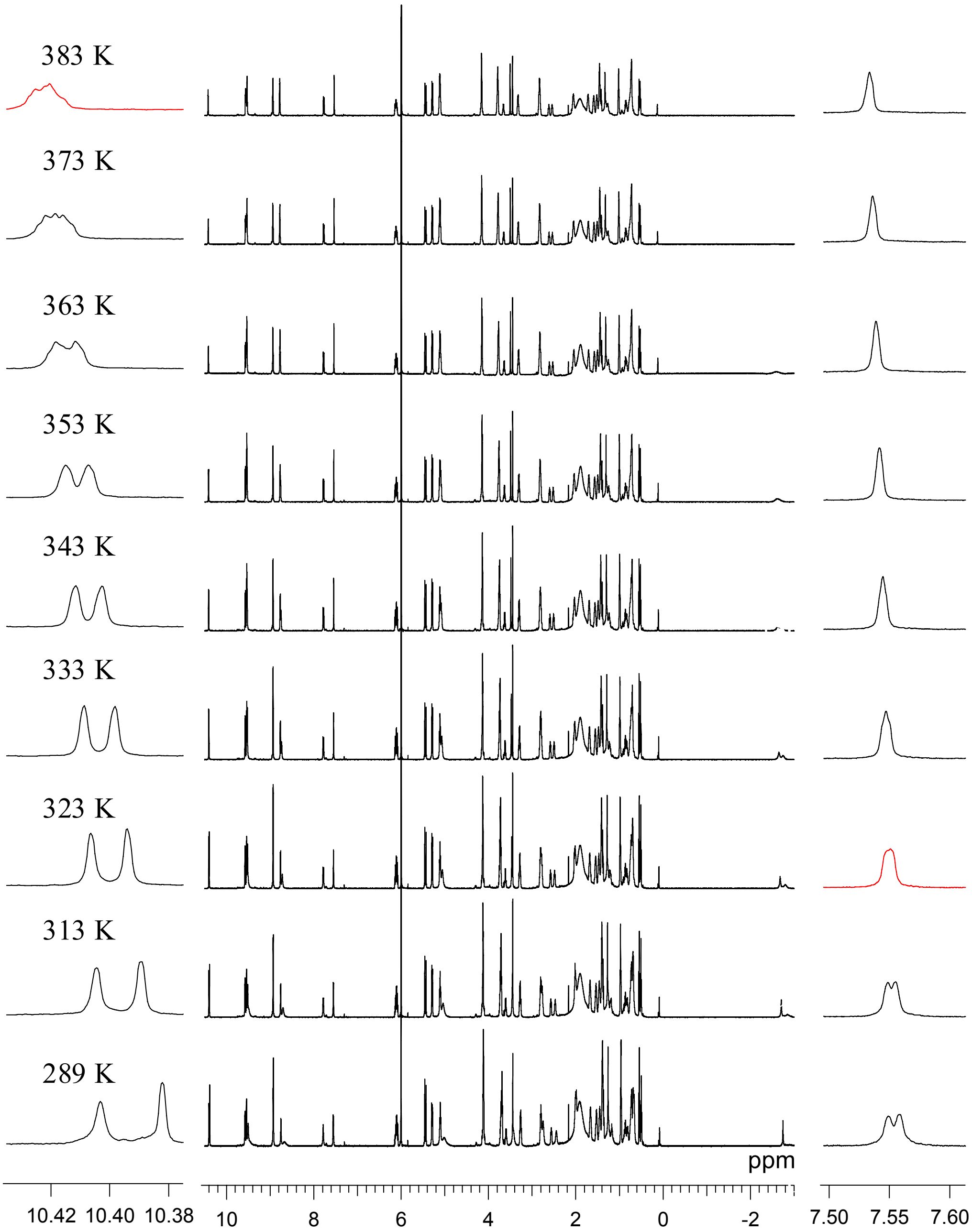


Figure S2. Variable-temperature ^{1}H NMR spectra of **6b** in $(CDCl_2)_2$. From Eyring plot for **6b**, the activation parameters, $\Delta H^{\ddagger}$ = 11.6 kJ mol^{-1} and $\Delta S^{\ddagger}$ = -0.19 kJ mol^{-1}K^{-1}, were obtained from the slope and the intercept (y = 1.03-1400x; $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$).

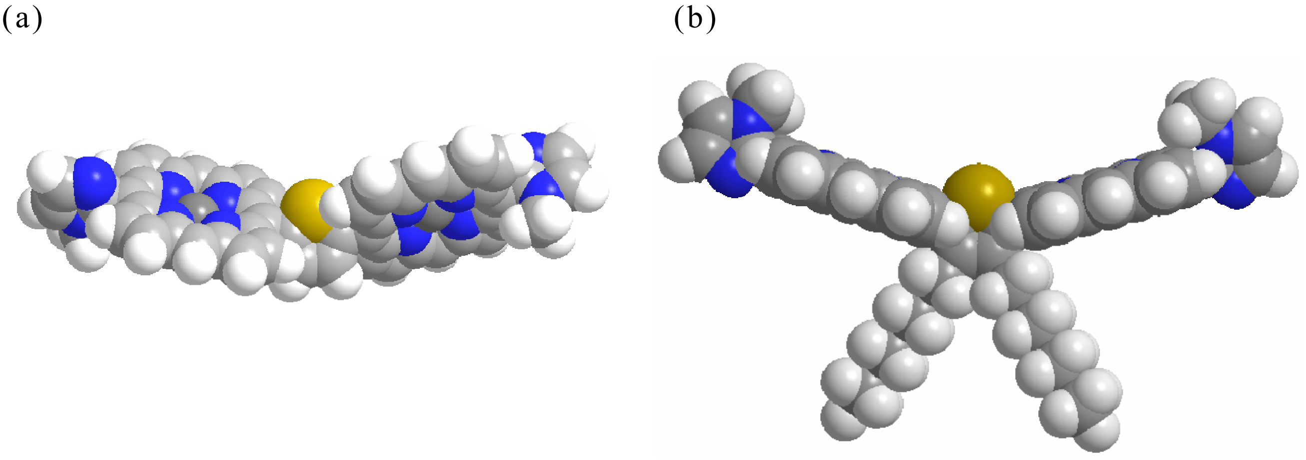


Figure S3. Local minimized structures of (a) **1a** and (b) **1b**. They were prepared by semiempirical MO method (AM1) on WinMOPAC Ver. 3.9 (Fujitsu Co. Ltd.). Allyloxy propyl groups at the *meso*-positions were replaced by hydrogen atoms for simplicity.

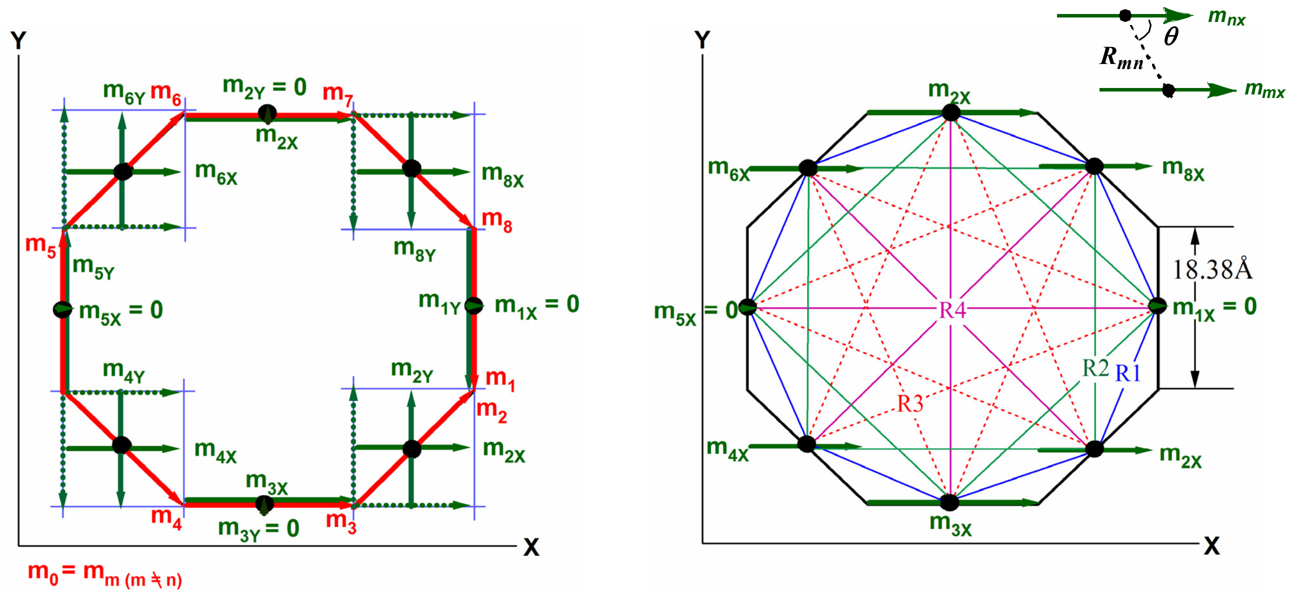


Figure S4. Definitions of dipole moments $m_{1\text{-}8}$, $m_{1x\text{-}8x}$ and $m_{1y\text{-}8y}$, distances $R_{1\text{-}4}$ and angle θ in 8 mer.

Table S1-1. Initial parameters used for the deconvolution analyses of the recycling GPC chart for **N-(1b)$_{\mathbf{mix}}$** obtained parameters.

	Initial parameters for fitting		Result (R^2 [d] = 1.00)		
	Function	HBW [b] / min			
N-(1b)$_{\mathbf{n}}$ [a]		Range	Area (%)	HBW [b] / min	RT [c] / min
n = 7	Gaussian	1.0 - 2.0	27	1.5	64.1
n = 8	Gaussian	1.0 - 2.0	36	1.2	62.9
n = 9	Gaussian	1.0 - 2.0	18	1.2	61.7
n = 10	Gaussian	1.0 - 2.0	11	1.7	60.5
n = 11	Gaussian	1.0 - 2.0	7	2.0	58.8

[a] Determined from the calibration plots in Figure 5, [b] Half-band width, [c] Retention Time, [d] Coefficient of determination.

Table S1-2. Initial parameters used for the deconvolution analyses of the recycling GPC chart for **N-(1a)$_{\mathbf{mix}}$** obtained parameters.

	Initial parameters for fitting		Result (R^2 [d] =0.98)		
	Function	HBW [b] / min			
N-(1a)$_{\mathbf{n}}$ [a]		Range	Area (%)	HBW [b] / min	RT [c] / min
n = 7	Gaussian	1.0 - 3.5	12.6	3.5	147.9
n = 8	Gaussian	1.0 - 3.0	11.9	2.5	144.9
n = 9	Gaussian	1.0 - 3.0	13.3	2.3	142.5
n = 10	Gaussian	1.0 - 3.0	12.5	2.2	140.3
n = 11	Gaussian	1.0 - 3.0	11.4	2.2	138.3
n = 12	Gaussian	1.0 - 3.0	10.3	2.1	136.4
n = 13	Gaussian	1.0 - 3.0	9.0	2.1	134.7
n = 14	Gaussian	1.0 - 3.0	8.6	2.1	133.0
n = 15	Gaussian	1.0 - 3.0	8.0	2.0	131.3
n = 16	Gaussian	1.0 - 3.0	2.4	1.7	129.8

[a] Determined from the calibration plots in Figure 5, [b] Half-band width, [c] Retention Time, [d] Coefficient of determination.

Calculation for entropy and enthalpy values of cyclic *N* mer. The thermodynamic parameters were calculated by referring to the procedure described in the literature[57, 58 in the main text].

$\mathrm{E}_{\mathrm{molec}} = \sqrt[3]{97} = 4.6$ Å (For chloroform)

$$\mathrm{ISD} = \sqrt[3]{\frac{10^{27}}{[\mathrm{x}]\cdot \mathrm{N_A}}} = \sqrt[3]{\frac{10^{27}}{12.5\cdot \mathrm{N_A}}} = 5.1\ \text{Å}$$

$[\mathrm{x}] = 12.5$ mol / L

$$\mathrm{V_{free}} = 8(ISD - E_{molec})^3 = 8(5.1-4.6)^3 = 1.0\ \text{Å}^3$$

$V_{\mathrm{free}} = [\mathrm{x}]\cdot N_{\mathrm{A}}\cdot \mathrm{V_{free}} = 7.52 \times 10^{24}\,\text{Å}^3 = 0.0075$ L

$$S_N^{trans} = R\ln\left[\left(\frac{\boldsymbol{10}^{\frac{-15}{2}} V_{\mathrm{free}}}{N_A[\mathrm{A}]}\right)\cdot\left(\frac{2\pi MRT\mathrm{e}^{\frac{5}{3}}}{h^2}\right)\right] = \boldsymbol{11.1} + \boldsymbol{12.5}\ln(T) + \boldsymbol{12.5}\ln(M) + \boldsymbol{8.3}\ln V_{\mathrm{free}} \qquad \text{(S1)}$$

$$S_N^{rot} = R\ln\left[\pi^{\frac{1}{2}}\left(\frac{\boldsymbol{8}\pi^{2} RT\mathrm{e}}{h^2 N_A^{4}}\right)^{\frac{3}{2}} \cdot \left(\mathrm{I}\cdot M^{2}\right)^{\frac{3}{2}}\right] \qquad \text{(S2)}$$

$$\Delta S = \boldsymbol{8}\times\left(S_N^{trans} + S_N^{rot}\right) - N\times(S_{\boldsymbol{8}}^{trans} + S_{\boldsymbol{8}}^{rot}) \qquad \text{(S3)}$$

$$\Delta H = \boldsymbol{8}\times Hf_N - N\times Hf_{\boldsymbol{8}} \qquad \text{(S4)}$$

ISD: Intermolecular distance, [x]: Concentration of molecules, N_A: Avogadro number, $\mathrm{E}_{\mathrm{molec}}$: Edge length of a molecule (for chloroform), $\mathrm{V_{free}}$: Volume of cube defines motion of center of mass of a single molecule, V_{free}: Volume of cubes define motions of centers of masses of one mole of molecules, $S_N{}^{trans}$: transition entropy of *N* mer, $S_N{}^{rot}$: rotation entropy of *N* mer, [A]: the experimental concentration of analyte, *M*: Molecular weight, *T* : 320 K, *h* : plank constant, *R*: gas constant, I: moment of inertia/[molecular weight of unit porphyrin (1015.83)] = 1.2 × 10^{-42} kgm^2, S_N^{trans} : translation entropy of *N* mer, S_N^{rot} : rotation entropy of *N* mer, Hf_N: Heat of formation.

Table S2. Entropy and enthalpy value estimated form equation (S1-S4)

	equation	*MW of N mer*	S_N^{trans} / J [a]	S_N^{rot} / J [b]	*Hf* / kJ [c]	ΔH / kJ [d]	ΔS / $kJ \cdot K^{-1}$ [e]
a	8 mer $\rightleftharpoons$ 7 mer	7110.81	153	410	20348	185.0	0.53
	8 mer	8126.64	155	413	23229	0.0	0.00
b	8 mer $\rightleftharpoons$ 9 mer	9142.47	157	416	26123	-74.6	-0.54
c	8 mer $\rightleftharpoons$ 11 mer	11174.13	159	421	31921	-147.9	-1.61

[a] Estimated from equation (S1), [b] Estimated from equation (S2), [c] Estimated from equation (S3), [d] Heat of formation obtained by geometry optimization using the semiempirical MO calculation (AM130 method in WinMOPAC Ver. 3.9 (Fujitsu Co. Ltd.)), [e] Estimated from equation (S4).

Table S3. Orientation factors calculated from equation (2) and the excitonic coupling energy in 7 mer estimated from equation (1).

7 mer	θ [a]	cosθ	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}^3$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
1,2	64	0.43	0.44	R1	17	220	0.00 m_o [e]	0.78 m_o	0.00 m_o^2	0 m_o^2
1,3	39	0.78	-0.83	R2	30	38	0.00 m_o	0.97 m_o	0.00 m_o^2	0 m_o^2
1,4	13	0.97	-1.85	R3	37	19	0.00 m_o	0.43 m_o	0.00 m_o^2	0 m_o^2
1,5	13	0.97	-1.85	R4	37	19	0.00 m_o	0.43 m_o	0.00 m_o^2	0 m_o^2
1,6	39	0.78	-0.83	R5	30	38	0.00 m_o	0.97 m_o	0.00 m_o^2	0 m_o^2
1,7	64	0.43	0.44	R6	17	220	0.00 m_o	0.78 m_o	0.00 m_o^2	0 m_o^2
2,3	13	0.97	-1.85	R1	17	220	0.78 m_o	0.97 m_o	0.76 m_o^2	-622 m_o^2
2,4	13	0.97	-1.85	R2	30	38	0.78 m_o	0.43 m_o	0.34 m_o^2	-47 m_o^2
2,5	39	0.78	-0.83	R3	37	19	0.78 m_o	0.43 m_o	0.34 m_o^2	-11 m_o^2
2,6	64	0.43	0.44	R4	37	19	0.78 m_o	0.97 m_o	0.76 m_o^2	13 m_o^2
2,7	90	0.00	1.00	R5	30	38	0.78 m_o	0.78 m_o	0.61 m_o^2	46 m_o^2
3,4	39	0.78	-0.83	R1	17	220	0.97 m_o	0.43 m_o	0.42 m_o^2	-155 m_o^2
3,5	64	0.43	0.44	R2	30	38	0.97 m_o	0.43 m_o	0.42 m_o^2	14 m_o^2
3,6	90	0.00	1.00	R3	37	19	0.97 m_o	0.97 m_o	0.95 m_o^2	37 m_o^2
3,7	64	0.43	0.44	R4	37	19	0.97 m_o	0.78 m_o	0.76 m_o^2	13 m_o^2
4,5	90	0.00	1.00	R1	17	220	0.43 m_o	0.43 m_o	0.19 m_o^2	83 m_o^2
4,6	64	0.43	0.44	R2	30	38	0.43 m_o	0.97 m_o	0.42 m_o^2	14 m_o^2
4,7	39	0.78	-0.83	R3	37	19	0.43 m_o	0.78 m_o	0.34 m_o^2	-11 m_o^2
5,6	39	0.78	-0.83	R1	17	220	0.43 m_o	0.97 m_o	0.42 m_o^2	-155 m_o^2
5,7	13	0.97	-1.85	R2	30	38	0.43 m_o	0.78 m_o	0.34 m_o^2	-47 m_o^2
6.7	13	0.97	-1.85	R1	17	220	0.97 m_o	0.78 m_o	0.76 m_o^2	-622 m_o^2
Total										-1451 m_o^2

[a] Angle between center of dipole moment $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [b] Orientation factor of $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [c] Center-to-center distance between $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [d] X-components of the transition dipole moments of m-th and n-th complementary dimer units, [e] $|\boldsymbol{m}_m|$.

Table S4. Orientation factors calculated from equation (2) and the excitonic coupling energy in 8 mer estimated from equation (1).

8 mer	θ [a]	$\cos\theta$	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}^{3}$	dipole moment [d]			E
m, n					Å	$\times 10^6$	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	$\times 10^6$
1,2	68	0.38	0.56	R1	17	204	0.00 m_o [e]	0.00 m_o	0.00 m_o^2	0 m_o^2
1,3	45	0.71	-0.50	R2	31	32	0.00 m_o	0.71 m_o	0.00 m_o^2	0 m_o^2
1,4	23	0.92	-1.56	R3	41	15	0.00 m_o	1.00 m_o	0.00 m_o^2	0 m_o^2
1,5	90	0.00	1.00	R4	44	11	0.00 m_o	0.71 m_o	0.00 m_o^2	0 m_o^2
1,6	23	0.92	-1.56	R3	41	15	0.00 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
1,7	45	0.71	-0.50	R2	31	32	0.00 m_o	0.71 m_o	0.00 m_o^2	0 m_o^2
1,8	68	0.38	0.56	R1	17	204	0.00 m_o	1.00 m_o	0.00 m_o^2	0 m_o^2
2,3	23	0.92	-1.56	R1	17	204	0.71 m_o	1.00 m_o	0.71 m_o^2	-451 m_o^2
2,4	0	1.00	-2.00	R2	31	32	0.71 m_o	0.71 m_o	0.50 m_o^2	-65 m_o^2
2,5	23	0.92	-1.56	R3	41	15	0.71 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
2,6	45	0.71	-0.50	R4	44	11	0.71 m_o	0.71 m_o	0.50 m_o^2	-6 m_o^2
2,7	68	0.38	0.56	R3	41	15	0.71 m_o	1.00 m_o	0.71 m_o^2	12 m_o^2
2,8	90	0.00	1.00	R2	31	32	0.71 m_o	0.71 m_o	0.50 m_o^2	32 m_o^2
3,4	23	0.92	-1.56	R1	17	204	1.00 m_o	0.71 m_o	0.71 m_o^2	-451 m_o^2
3,5	45	0.71	-0.50	R2	31	32	1.00 m_o	0.00 m_o	0.00 m_o^2	0
3,6	68	0.38	0.56	R3	41	15	1.00 m_o	0.71 m_o	0.71 m_o^2	12 m_o^2
3,7	90	0.00	1.00	R4	44	11	1.00 m_o	1.00 m_o	1.00 m_o^2	23 m_o^2
3,8	68	0.38	0.56	R3	41	15	1.00 m_o	0.71 m_o	0.71 m_o^2	12 m_o^2
4,5	68	0.38	0.56	R1	17	204	0.71 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
4,6	90	0.00	1.00	R2	31	32	0.71 m_o	0.71 m_o	0.50 m_o^2	32 m_o^2
4,7	68	0.38	0.56	R3	41	15	0.71 m_o	1.00 m_o	0.71 m_o^2	12 m_o^2
4,8	45	0.71	-0.50	R4	44	11	0.71 m_o	0.71 m_o	0.50 m_o^2	-6 m_o^2
5,6	68	0.38	0.56	R1	17	204	0.00 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
5,7	45	0.71	-0.50	R2	31	32	0.00 m_o	0.71 m_o	0.00 m_o^2	0 m_o^2
5,8	23	0.92	-1.56	R3	41	15	0.00 m_o	1.00 m_o	0.00 m_o^2	0 m_o^2
6,7	23	0.92	-1.56	R1	17	204	0.71 m_o	1.00 m_o	0.71 m_o^2	-451 m_o^2
6,8	0	1.00	-2.00	R2	31	32	0.71 m_o	0.71 m_o	0.50 m_o^2	-65 m_o^2
7,8	23	0.92	-1.56	R1	17	204	1.00 m_o	0.71 m_o	0.71 m_o^2	-451 m_o^2
Total										-1810 m_o^2

[a] Angle between center of dipole moment $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [b] Orientation factor of $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [c] Center-to-center distance between $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [d] X-components of the transition dipole moments of m-th and n-th complementary dimer units, [e] $|\boldsymbol{m}_{m}|$.

Table S5. Orientation factors calculated from equation (2) and the excitonic coupling energy in 9 mer estimated from equation (1).

9 mer	θ [a]	cosθ	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}^3$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
1,2	70	0.34	0.65	R1	17	194	0.00 m_o[e]	0.64 m_o	0.00 m_o^2	0 m_o^2
1,3	50	0.64	-0.24	R2	32	29	0.00 m_o	0.98 m_o	0.00 m_o^2	0 m_o^2
1,4	30	0.87	-1.25	R3	44	12	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
1,5	10	0.98	-1.91	R4	50	8	0.00 m_o	0.34 m_o	0.00 m_o^2	0 m_o^2
1,6	10	0.98	-1.91	R4	50	8	0.00 m_o	0.34 m_o	0.00 m_o^2	0 m_o^2
1,7	30	0.87	-1.25	R3	44	12	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
1,8	50	0.64	-0.24	R2	32	29	0.00 m_o	0.98 m_o	0.00 m_o^2	0 m_o^2
1,9	70	0.34	0.65	R1	17	194	0.00 m_o	0.64 m_o	0.00 m_o^2	0 m_o^2
2,3	30	0.87	-1.25	R1	17	194	0.64 m_o	0.98 m_o	0.63 m_o^2	-307 m_o^2
2,4	10	0.98	-1.91	R2	32	29	0.64 m_o	0.87 m_o	0.56 m_o^2	-62 m_o^2
2,5	10	0.98	-1.91	R3	44	12	0.64 m_o	0.34 m_o	0.22 m_o^2	-10 m_o^2
2,6	30	0.87	-1.25	R4	50	8	0.64 m_o	0.34 m_o	0.22 m_o^2	-4 m_o^2
2,7	50	0.64	-0.24	R4	50	8	0.64 m_o	0.87 m_o	0.56 m_o^2	-2 m_o^2
2,8	70	0.34	0.65	R3	44	12	0.64 m_o	0.98 m_o	0.63 m_o^2	10 m_o^2
2,9	90	0.00	1.00	R2	32	29	0.64 m_o	0.64 m_o	0.41 m_o^2	24 m_o^2
3,4	10	0.98	-1.91	R1	17	194	0.98 m_o	0.87 m_o	0.85 m_o^2	-632 m_o^2
3,5	30	0.87	-1.25	R2	32	29	0.98 m_o	0.34 m_o	0.34 m_o^2	-25 m_o^2
3,6	50	0.64	-0.24	R3	44	12	0.98 m_o	0.34 m_o	0.34 m_o^2	-2 m_o^2
3,7	70	0.34	0.65	R4	50	8	0.98 m_o	0.87 m_o	0.85 m_o^2	9 m_o^2
3,8	90	0.00	1.00	R4	50	8	0.98 m_o	0.98 m_o	0.97 m_o^2	16 m_o^2
3,9	70	0.34	0.65	R3	44	12	0.98 m_o	0.64 m_o	0.63 m_o^2	10 m_o^2
4,5	50	0.64	-0.24	R1	17	194	0.87 m_o	0.34 m_o	0.30 m_o^2	-28 m_o^2
4,6	70	0.34	0.65	R2	32	29	0.87 m_o	0.34 m_o	0.30 m_o^2	11 m_o^2
4,7	90	0.00	1.00	R3	44	12	0.87 m_o	0.87 m_o	0.75 m_o^2	18 m_o^2
4,8	70	0.34	0.65	R4	50	8	0.87 m_o	0.98 m_o	0.85 m_o^2	9 m_o^2
4,9	50	0.64	-0.24	R4	50	8	0.87 m_o	0.64 m_o	0.56 m_o^2	-2 m_o^2
5,6	90	0.00	1.00	R1	17	194	0.34 m_o	0.34 m_o	0.12 m_o^2	45 m_o^2
5,7	70	0.34	0.65	R2	32	29	0.34 m_o	0.87 m_o	0.30 m_o^2	11 m_o^2
5,8	50	0.64	-0.24	R3	44	12	0.34 m_o	0.98 m_o	0.34 m_o^2	-2 m_o^2
5,9	30	0.87	-1.25	R4	50	8	0.34 m_o	0.64 m_o	0.22 m_o^2	-4 m_o^2
6,7	50	0.64	-0.24	R1	17	194	0.34 m_o	0.87 m_o	0.30 m_o^2	-28 m_o^2
6,8	30	0.87	-1.25	R2	32	29	0.34 m_o	0.98 m_o	0.34 m_o^2	-25 m_o^2
6,9	10	0.98	-1.91	R3	44	12	0.34 m_o	0.64 m_o	0.22 m_o^2	-10 m_o^2
7,8	10	0.98	-1.91	R1	17	194	0.87 m_o	0.98 m_o	0.85 m_o^2	-632 m_o^2
7,9	10	0.98	-1.91	R2	32	29	0.87 m_o	0.64 m_o	0.56 m_o^2	-62 m_o^2
8,9	30	0.87	-1.25	R1	17	194	0.98 m_o	0.64 m_o	0.63 m_o^2	-307 m_o^2
Total										-1981 m_o^2

[a] Angle between center of dipole moment $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [b] Orientation factor of $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [c] Center-to-center distance between $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [d] X-components of the transition dipole moments of m-th and n-th complementary dimer units, [e] $|\boldsymbol{m}_m|$.

Table S6-1. Orientation factors calculated from equation (2) and the excitonic coupling energy in 10 mer estimated from equation (1).

10 mer	θ [a]	$\cos\theta$	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}^{3}$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
1,2	72	0.31	0.71	R1	17	187	0.00 m_o[e]	0.59 m_o	0.00 m_o^2	0 m_o^2
1,3	54	0.59	-0.04	R2	33	27	0.00 m_o	0.95 m_o	0.00 m_o^2	0 m_o^2
1,4	36	0.81	-0.96	R3	46	10	0.00 m_o	0.95 m_o	0.00 m_o^2	0 m_o^2
1,5	18	0.95	-1.71	R4	54	6	0.00 m_o	0.59 m_o	0.00 m_o^2	0 m_o^2
1,6	0	1.00	-2.00	R5	57	6	0.00 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
1,7	18	0.95	-1.71	R4	54	6	0.00 m_o	0.59 m_o	0.00 m_o^2	0 m_o^2
1,8	36	0.81	-0.96	R3	46	10	0.00 m_o	0.95 m_o	0.00 m_o^2	0 m_o^2
1,9	54	0.59	-0.04	R2	33	27	0.00 m_o	0.95 m_o	0.00 m_o^2	0 m_o^2
1,10	72	0.31	0.71	R1	17	187	0.00 m_o	0.59 m_o	0.00 m_o^2	0 m_o^2
2,3	36	0.81	-0.96	R1	17	187	0.59 m_o	0.95 m_o	0.56 m_o^2	-202 m_o^2
2,4	18	0.95	-1.71	R2	33	27	0.59 m_o	0.95 m_o	0.56 m_o^2	-52 m_o^2
2,5	0	1.00	-2.00	R3	46	10	0.59 m_o	0.59 m_o	0.35 m_o^2	-14 m_o^2
2,6	18	0.95	-1.71	R4	54	6	0.59 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
2,7	36	0.81	-0.96	R5	57	6	0.59 m_o	0.59 m_o	0.35 m_o^2	-4 m_o^2
2,8	54	0.59	-0.04	R4	54	6	0.59 m_o	0.95 m_o	0.56 m_o^2	0 m_o^2
2,9	72	0.31	0.71	R3	46	10	0.59 m_o	0.95 m_o	0.56 m_o^2	8 m_o^2
2,10	90	0.00	1.00	R2	33	27	0.59 m_o	0.59 m_o	0.35 m_o^2	19 m_o^2
3,4	0	1.00	-2.00	R1	17	187	0.95 m_o	0.95 m_o	0.90 m_o^2	-677 m_o^2
3,5	18	0.95	-1.71	R2	33	27	0.95 m_o	0.59 m_o	0.56 m_o^2	-52 m_o^2
3,6	36	0.81	-0.96	R3	46	10	0.95 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
3,7	54	0.59	-0.04	R4	54	6	0.95 m_o	0.59 m_o	0.56 m_o^2	0 m_o^2
3,8	72	0.31	0.71	R5	57	6	0.95 m_o	0.95 m_o	0.90 m_o^2	7 m_o^2
3,9	90	0.00	1.00	R4	54	6	0.95 m_o	0.95 m_o	0.90 m_o^2	12 m_o^2
3,10	72	0.31	0.71	R3	46	10	0.95 m_o	0.59 m_o	0.56 m_o^2	8 m_o^2

Table S6-2 (continued). Orientation factors calculated from equation (2) and the excitonic coupling energy in 10 mer estimated from equation (1).

10 mer	θ [a]	$\cos\theta$	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}{}^3$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
4,5	36	0.81	-0.96	R1	17	187	0.95 m_o[e]	0.59 m_o	0.56 m_o^2	-202 m_o^2
4,6	54	0.59	-0.04	R2	33	27	0.95 m_o	0.00 m_o	0.00 m_o^1	0 m_o^1
4,7	72	0.31	0.71	R3	46	10	0.95 m_o	0.59 m_o	0.56 m_o^2	8 m_o^2
4,8	90	0.00	1.00	R4	54	6	0.95 m_o	0.95 m_o	0.90 m_o^2	12 m_o^2
4,9	72	0.31	0.71	R5	57	6	0.95 m_o	0.95 m_o	0.90 m_o^2	7 m_o^2
4,10	54	0.59	-0.04	R4	54	6	0.95 m_o	0.59 m_o	0.56 m_o^2	0 m_o^2
5,6	72	0.31	0.71	R1	17	187	0.59 m_o	0.00 m_o	0.00 m_o^1	0 m_o^1
5,7	90	0.00	1.00	R2	33	27	0.59 m_o	0.59 m_o	0.35 m_o^2	19 m_o^2
5,8	72	0.31	0.71	R3	46	10	0.59 m_o	0.95 m_o	0.56 m_o^2	8 m_o^2
5,9	54	0.59	-0.04	R4	54	6	0.59 m_o	0.95 m_o	0.56 m_o^2	0 m_o^2
5,10	36	0.81	-0.96	R5	57	6	0.59 m_o	0.59 m_o	0.35 m_o^2	-4 m_o^2
6,7	72	0.31	0.71	R1	17	187	0.00 m_o	0.59 m_o	0.00 m_o^2	0 m_o^2
6,8	54	0.59	-0.04	R2	33	27	0.00 m_o	0.95 m_o	0.00 m_o^2	0 m_o^2
6,9	36	0.81	-0.96	R3	46	10	0.00 m_o	0.95 m_o	0.00 m_o^2	0 m_o^2
6,10	18	0.95	-1.71	R4	54	6	0.00 m_o	0.59 m_o	0.00 m_o^2	0 m_o^2
7,8	36	0.81	-0.96	R1	17	187	0.59 m_o	0.95 m_o	0.56 m_o^2	-202 m_o^2
7,9	18	0.95	-1.71	R2	33	27	0.59 m_o	0.95 m_o	0.56 m_o^2	-52 m_o^2
7,10	0	1.00	-2.00	R3	46	10	0.59 m_o	0.59 m_o	0.35 m_o^2	-14 m_o^2
8,9	0	1.00	-2.00	R1	17	187	0.95 m_o	0.95 m_o	0.90 m_o^2	-677 m_o^2
8,10	18	0.95	-1.71	R2	33	27	0.95 m_o	0.59 m_o	0.56 m_o^2	-52 m_o^2
9,10	36	0.81	-0.96	R1	17	187	0.95 m_o	0.59 m_o	0.56 m_o^2	-202 m_o^2
Total										-2299 m_o^2

[a] Angle between center of dipole moment $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [b] Orientation factor of $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [c] Center-to-center distance between $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [d] X-components of the transition dipole moments of m-th and n-th complementary dimer units, [e] $|\boldsymbol{m}_{m}|$.

Table S7-1. Orientation factors calculated from equation (2) and the excitonic coupling energy in 11 mer estimated from equation (1).

11 mer	θ [a]	cosθ	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}^{3}$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
1,2	74	0.28	0.76	R1	18	182	0.00 m_o[e]	0.54 m_o	0.00 m_o^2	0 m_o^2
1,3	57	0.54	0.12	R2	34	26	0.00 m_o	0.91 m_o	0.00 m_o^2	0 m_o^2
1,4	41	0.76	-0.71	R3	47	9	0.00 m_o	0.99 m_o	0.00 m_o^2	0 m_o^2
1,5	25	0.91	-1.48	R4	57	5	0.00 m_o	0.76 m_o	0.00 m_o^2	0 m_o^2
1,6	8	0.99	-1.94	R5	62	4	0.00 m_o	0.28 m_o	0.00 m_o^2	0 m_o^2
1,7	8	0.99	-1.94	R5	62	4	0.00 m_o	0.28 m_o	0.00 m_o^2	0 m_o^2
1,8	25	0.91	-1.48	R4	57	5	0.00 m_o	0.76 m_o	0.00 m_o^2	0 m_o^2
1,9	41	0.76	-0.71	R3	47	9	0.00 m_o	0.99 m_o	0.00 m_o^2	0 m_o^2
1,10	57	0.54	0.12	R2	34	26	0.00 m_o	0.91 m_o	0.00 m_o^2	0 m_o^2
1,11	74	0.28	0.76	R1	18	182	0.00 m_o	0.54 m_o	0.00 m_o^2	0 m_o^2
2,3	41	0.76	-0.71	R1	18	182	0.54 m_o	0.91 m_o	0.49 m_o^2	-128 m_o^2
2,4	25	0.91	-1.48	R2	34	26	0.54 m_o	0.99 m_o	0.54 m_o^2	-41 m_o^2
2,5	8	0.99	-1.94	R3	47	9	0.54 m_o	0.76 m_o	0.41 m_o^2	-15 m_o^2
2,6	8	0.99	-1.94	R4	57	5	0.54 m_o	0.28 m_o	0.15 m_o^2	-3 m_o^2
2,7	25	0.91	-1.48	R5	62	4	0.54 m_o	0.28 m_o	0.15 m_o^2	-2 m_o^2
2,8	41	0.76	-0.71	R5	62	4	0.54 m_o	0.76 m_o	0.41 m_o^2	-2 m_o^2
2,9	57	0.54	0.12	R4	57	5	0.54 m_o	0.99 m_o	0.54 m_o^2	1 m_o^2
2,10	74	0.28	0.76	R3	47	9	0.54 m_o	0.91 m_o	0.49 m_o^2	7 m_o^2
2,11	90	0.00	1.00	R2	34	26	0.54 m_o	0.54 m_o	0.29 m_o^2	15 m_o^2
3,4	8	0.99	-1.94	R1	18	182	0.91 m_o	0.99 m_o	0.90 m_o^2	-637 m_o^2
3,5	8	0.99	-1.94	R2	34	26	0.91 m_o	0.76 m_o	0.69 m_o^2	-69 m_o^2
3,6	25	0.91	-1.48	R3	47	9	0.91 m_o	0.28 m_o	0.26 m_o^2	-7 m_o^2
3,7	41	0.76	-0.71	R4	57	5	0.91 m_o	0.28 m_o	0.26 m_o^2	-2 m_o^2
3,8	57	0.54	0.12	R5	62	4	0.91 m_o	0.76 m_o	0.69 m_o^2	1 m_o^2
3,9	74	0.28	0.76	R5	62	4	0.91 m_o	0.99 m_o	0.90 m_o^2	6 m_o^2
3,10	90	0.00	1.00	R4	57	5	0.91 m_o	0.91 m_o	0.83 m_o^2	9 m_o^2
3,11	74	0.28	0.76	R3	47	9	0.91 m_o	0.54 m_o	0.49 m_o^2	7 m_o^2

Table S7-2 (continued). Orientation factors calculated from equation (2) and the excitonic coupling energy in 11 mer estimated from equation (1).

11 mer	θ [a]	$\cos\theta$	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}^3$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
4,5	25	0.91	-1.48	R1	18	182	0.99 m_o[e]	0.76 m_o	0.75 m_o^2	-404 m_o^2
4,6	41	0.76	-0.71	R2	34	26	0.99 m_o	0.28 m_o	0.28 m_o^2	-10 m_o^2
4,7	57	0.54	0.12	R3	47	9	0.99 m_o	0.28 m_o	0.28 m_o^2	1 m_o^2
4,8	74	0.28	0.76	R4	57	5	0.99 m_o	0.76 m_o	0.75 m_o^2	6 m_o^2
4,9	90	0.00	1.00	R5	62	4	0.99 m_o	0.99 m_o	0.98 m_o^2	8 m_o^2
4,10	74	0.28	0.76	R5	62	4	0.99 m_o	0.91 m_o	0.90 m_o^2	6 m_o^2
4,11	57	0.54	0.12	R4	57	5	0.99 m_o	0.54 m_o	0.54 m_o^2	1 m_o^2
5,6	57	0.54	0.12	R1	18	182	0.76 m_o	0.28 m_o	0.21 m_o^2	10 m_o^2
5,7	74	0.28	0.76	R2	34	26	0.76 m_o	0.28 m_o	0.21 m_o^2	8 m_o^2
5,8	90	0.00	1.00	R3	47	9	0.76 m_o	0.76 m_o	0.57 m_o^2	11 m_o^2
5,9	74	0.28	0.76	R4	57	5	0.76 m_o	0.99 m_o	0.75 m_o^2	6 m_o^2
5,10	57	0.54	0.12	R5	62	4	0.76 m_o	0.91 m_o	0.69 m_o^2	1 m_o^2
5,11	41	0.76	-0.71	R5	62	4	0.76 m_o	0.54 m_o	0.41 m_o^2	-2 m_o^2
6,7	90	0.00	1.00	R1	18	182	0.28 m_o	0.28 m_o	0.08 m_o^2	29 m_o^2
6,8	74	0.28	0.76	R2	34	26	0.28 m_o	0.76 m_o	0.21 m_o^2	8 m_o^2
6,9	57	0.54	0.12	R3	47	9	0.28 m_o	0.99 m_o	0.28 m_o^2	1 m_o^2
6,10	41	0.76	-0.71	R4	57	5	0.28 m_o	0.91 m_o	0.26 m_o^2	-2 m_o^2
6,11	25	0.91	-1.48	R5	62	4	0.28 m_o	0.54 m_o	0.15 m_o^2	-2 m_o^2
7,8	57	0.54	0.12	R1	18	182	0.28 m_o	0.76 m_o	0.21 m_o^2	10 m_o^2
7,9	41	0.76	-0.71	R2	34	26	0.28 m_o	0.99 m_o	0.28 m_o^2	-10 m_o^2
7,10	25	0.91	-1.48	R3	47	9	0.28 m_o	0.91 m_o	0.26 m_o^2	-7 m_o^2
7,11	8	0.99	-1.94	R4	57	5	0.28 m_o	0.54 m_o	0.15 m_o^2	-3 m_o^2
8,9	25	0.91	-1.48	R1	18	182	0.76 m_o	0.99 m_o	0.75 m_o^2	-404 m_o^2
8,10	8	0.99	-1.94	R2	34	26	0.76 m_o	0.91 m_o	0.69 m_o^2	-69 m_o^2
8,11	8	0.99	-1.94	R3	47	9	0.76 m_o	0.54 m_o	0.41 m_o^2	-15 m_o^2
9,10	8	0.99	-1.94	R1	18	182	0.99 m_o	0.91 m_o	0.90 m_o^2	-637 m_o^2
9,11	25	0.91	-1.48	R2	34	26	0.99 m_o	0.54 m_o	0.54 m_o^2	-41 m_o^2
10,11	41	0.76	-0.71	R1	18	182	0.91 m_o	0.54 m_o	0.49 m_o^2	-128 m_o^2
Total										-2491 m_o^2

[a] Angle between center of dipole moment $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [b] Orientation factor of $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [c] Center-to-center distance between $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [d] X-components of the transition dipole moments of m-th and n-th complementary dimer units, [e] $|\boldsymbol{m}_m|$.

Table S8-1. Orientation factors calculated from equation (2) and the excitonic coupling energy in 12 mer estimated from equation (1).

12 mer	θ [a]	cosθ	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}{}^3$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
1,2	75	0.26	0.80	R1	18	179	0.00 m_o[e]	0.50 m_o	0.00 m_o^2	0 m_o^2
1,3	60	0.50	0.25	R2	34	25	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
1,4	45	0.71	-0.50	R3	49	9	0.00 m_o	1.00 m_o	0.00 m_o^2	0 m_o^2
1,5	30	0.87	-1.25	R4	59	5	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
1,6	15	0.97	-1.80	R5	66	3	0.00 m_o	0.50 m_o	0.00 m_o^2	0 m_o^2
1,7	0	1.00	-2.00	R6	69	3	0.00 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
1,8	15	0.97	-1.80	R5	66	3	0.00 m_o	0.50 m_o	0.00 m_o^2	0 m_o^2
1,9	30	0.87	-1.25	R4	59	5	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
1,10	45	0.71	-0.50	R3	49	9	0.00 m_o	1.00 m_o	0.00 m_o^2	0 m_o^2
1,11	60	0.50	0.25	R2	34	25	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
1,12	75	0.26	0.80	R1	18	179	0.00 m_o	0.50 m_o	0.00 m_o^2	0 m_o^2
2,3	45	0.71	-0.50	R1	18	179	0.50 m_o	0.87 m_o	0.43 m_o^2	-77 m_o^2
2,4	30	0.87	-1.25	R2	34	25	0.50 m_o	1.00 m_o	0.50 m_o^2	-31 m_o^2
2,5	15	0.97	-1.80	R3	49	9	0.50 m_o	0.87 m_o	0.43 m_o^2	-14 m_o^2
2,6	0	1.00	-2.00	R4	59	5	0.50 m_o	0.50 m_o	0.25 m_o^2	-5 m_o^2
2,7	15	0.97	-1.80	R5	66	3	0.00 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
2,8	30	0.87	-1.25	R6	69	3	0.50 m_o	0.50 m_o	0.25 m_o^2	-2 m_o^2
2,9	45	0.71	-0.50	R5	66	3	0.50 m_o	0.87 m_o	0.43 m_o^2	-1 m_o^2
2,10	60	0.50	0.25	R4	59	5	0.50 m_o	1.00 m_o	0.50 m_o^2	1 m_o^2
2,11	75	0.26	0.80	R3	49	9	0.50 m_o	0.87 m_o	0.43 m_o^2	6 m_o^2
2,12	90	0.00	1.00	R2	34	25	0.50 m_o	0.50 m_o	0.25 m_o^2	12 m_o^2
3,4	15	0.97	-1.80	R1	18	179	0.87 m_o	1.00 m_o	0.87 m_o^2	-557 m_o^2
3,5	0	1.00	-2.00	R2	34	25	0.87 m_o	0.87 m_o	0.75 m_o^2	-74 m_o^2
3,6	15	0.97	-1.80	R3	49	9	0.87 m_o	0.50 m_o	0.43 m_o^2	-14 m_o^2
3,7	30	0.87	-1.25	R4	59	5	0.87 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
3,8	45	0.71	-0.50	R5	66	3	0.87 m_o	0.50 m_o	0.43 m_o^2	-1 m_o^2
3,9	60	0.50	0.25	R6	69	3	0.87 m_o	0.87 m_o	0.75 m_o^2	1 m_o^2
3,10	75	0.26	0.80	R5	66	3	0.87 m_o	1.00 m_o	0.87 m_o^2	5 m_o^2
3,11	90	0.00	1.00	R4	59	5	0.87 m_o	0.87 m_o	0.75 m_o^2	7 m_o^2
3,12	75	0.26	0.80	R3	49	9	0.87 m_o	0.50 m_o	0.43 m_o^2	6 m_o^2
4,5	15	0.97	-1.80	R1	18	179	1.00 m_o	0.87 m_o	0.87 m_o^2	-557 m_o^2
4,6	30	0.87	-1.25	R2	34	25	1.00 m_o	0.50 m_o	0.50 m_o^2	-31 m_o^2
4,7	45	0.71	-0.50	R3	49	9	1.00 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
4,8	60	0.50	0.25	R4	59	5	1.00 m_o	0.50 m_o	0.50 m_o^2	1 m_o^2
4,9	75	0.26	0.80	R5	66	3	1.00 m_o	0.87 m_o	0.87 m_o^2	5 m_o^2
4,10	90	0.00	1.00	R6	69	3	1.00 m_o	1.00 m_o	1.00 m_o^2	6 m_o^2
4,11	75	0.26	0.80	R5	66	3	1.00 m_o	0.87 m_o	0.87 m_o^2	5 m_o^2
4,12	60	0.50	0.25	R4	59	5	1.00 m_o	0.50 m_o	0.50 m_o^2	1 m_o^2

Table S8-2 (continued). Orientation factors calculated from equation (2) and the excitonic coupling energy in 12 mer estimated from equation (1).

12 mer	θ [a]	cosθ	$\kappa_{mx,nx}$ [b]	$R_{mx,nx}$ [c]		$1/R_{mx,nx}^3$	dipole moment [d]			E
m, n					Å	× 10^6	m_{mx}	m_{nx}	$m_{mx} \times m_{nx}$	× 10^6
5,6	45	0.71	-0.50	R1	18	179	0.87 m_o[e]	0.50 m_o	0.43 m_o^2	-77 m_o^2
5,7	60	0.50	0.25	R2	34	25	0.87 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
5,8	75	0.26	0.80	R3	49	9	0.87 m_o	0.50 m_o	0.43 m_o^2	6 m_o^2
5,9	90	0.00	1.00	R4	59	5	0.87 m_o	0.87 m_o	0.75 m_o^2	7 m_o^2
5,10	75	0.26	0.80	R5	66	3	0.87 m_o	1.00 m_o	0.87 m_o^2	5 m_o^2
5,11	60	0.50	0.25	R6	69	3	0.87 m_o	0.87 m_o	0.75 m_o^2	1 m_o^2
5,12	45	0.71	-0.50	R5	66	3	0.87 m_o	0.50 m_o	0.43 m_o^2	-1 m_o^2
6,7	75	0.26	0.80	R1	18	179	0.50 m_o	0.00 m_o	0.00 m_o^2	0 m_o^2
6,8	90	0.00	1.00	R2	34	25	0.50 m_o	0.50 m_o	0.25 m_o^2	12 m_o^2
6,9	75	0.26	0.80	R3	49	9	0.50 m_o	0.87 m_o	0.43 m_o^2	6 m_o^2
6,10	60	0.50	0.25	R4	59	5	0.50 m_o	1.00 m_o	0.50 m_o^2	1 m_o^2
6,11	45	0.71	-0.50	R5	66	3	0.50 m_o	0.87 m_o	0.43 m_o^2	-1 m_o^2
6,12	30	0.87	-1.25	R6	69	3	0.50 m_o	0.50 m_o	0.25 m_o^2	-2 m_o^2
7,8	75	0.26	0.80	R1	18	179	0.00 m_o	0.50 m_o	0.00 m_o^2	0 m_o^2
7,9	60	0.50	0.25	R2	34	25	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
7,10	45	0.71	-0.50	R3	49	9	0.00 m_o	1.00 m_o	0.00 m_o^2	0 m_o^2
7,11	30	0.87	-1.25	R4	59	5	0.00 m_o	0.87 m_o	0.00 m_o^2	0 m_o^2
7,12	15	0.97	-1.80	R5	66	3	0.00 m_o	0.50 m_o	0.00 m_o^2	0 m_o^2
8,9	45	0.71	-0.50	R1	18	179	0.50 m_o	0.87 m_o	0.43 m_o^2	-77 m_o^2
8,10	30	0.87	-1.25	R2	34	25	0.50 m_o	1.00 m_o	0.50 m_o^2	-31 m_o^2
8,11	15	0.97	-1.80	R3	49	9	0.50 m_o	0.87 m_o	0.43 m_o^2	-14 m_o^2
8,12	0	1.00	-2.00	R4	59	5	0.50 m_o	0.50 m_o	0.25 m_o^2	-5 m_o^2
9,10	15	0.97	-1.80	R1	18	179	0.87 m_o	1.00 m_o	0.87 m_o^2	-557 m_o^2
9,11	0	1.00	-2.00	R2	34	25	0.87 m_o	0.87 m_o	0.75 m_o^2	-74 m_o^2
9,12	15	0.97	-1.80	R3	49	9	0.87 m_o	0.50 m_o	0.43 m_o^2	-14 m_o^2
10,11	15	0.97	-1.80	R1	18	179	1.00 m_o	0.87 m_o	0.87 m_o^2	-557 m_o^2
10,12	30	0.87	-1.25	R2	34	25	1.00 m_o	0.50 m_o	0.50 m_o^2	-31 m_o^2
11,12	45	0.71	-0.50	R1	18	179	0.87 m_o	0.50 m_o	0.43 m_o^2	-77 m_o^2
Total										-2788 m_o^2

[a] Angle between center of dipole moment $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [b] Orientation factor of $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [c] Center-to-center distance between $\boldsymbol{m}_{mx}$ and $\boldsymbol{m}_{nx}$, [d] X-components of the transition dipole moments of m-th and n-th complementary dimer units, [e] $|\boldsymbol{m}_m|$.

Experimental

General.

All solvents and reagents were of reagent quality, purchased commercially, and used without further purification, except as noted otherwise. Chloroform contains 0.5% ethanol as a stabilizer. Tetrahydrofuran (THF) and diethyl ether was distilled from purple sodium benzophenone ketyl before use. Benzylidene-bis(tricyclohexylphosphine)dichlororuthenium (Grubbs Catalyst, 1st generation) and [1,3-bis(diphenylphosphino)propane]dichloronickel(II) ($NiCl_2(PPh_3)_2$) were obtained commercially from Aldrich and WAKO, respectively. ^1H and ^{13}C NMR spectra were recorded on a JEOL ECP-600 (600 MHz) spectrometer. The chemical shifts are reported in parts per million (ppm) using tetramethylsilane (TMS) or the residual proton in the NMR solvent as an internal reference. UV-vis and steady-state fluorescence spectra were recorded on a Shimadzu UV-3100PC spectrophotometer and on a HITACHI F-4500 fluorescence spectrophotometer, respectively. Fluorescence quantum yields were estimated by comparison of integrated emission spectra with that of ZnTPP (Φ = 0.033 in chloroform and 0.038 in pyridine) as a standard.[34 in the main text]

The local minimized structures.

The molecular models in Figure S3 were obtained by geometry optimization using the semiempirical MO calculation (AM130 method in WinMOPAC Ver. 3.9 (Fujitsu Co. Ltd.)[1]). As the initial parameter for the calculation, the torsional angle between the porphyrin and the thiophenylene planes were set by 0°. The substituents at *meso*-positions of porphyrins were replaced by hydrogen atoms for simplicity.

3,4-Dioctylthiophene (**S1**).[2]

To a suspension of magnesium turning (3.0 g, 123.4 mmol) in dry ether (40 mL) under Ar, 1,2-dibromoethane (0.5 mL) was added for activation of the magnesium. The mixture was stirred for 10 min. Then, 1-bromooctane (3.9 mL) was added to the mixture in two portions. After confirming heat evolution, additional 1-bromooctane (15.5 mL, total 113.0 mmol) was added. The mixture was stirred for 120 min. The prepared Grignard reagent (18 mL, ca 2.8 M) was added dropwise to a solution of Ni(dppp)Cl_2 (344.4 mg, 0.62 mmol) and 3,4-dibromothiophene (3.5 g, 14.47 mmol) in dry ether (6.0 mL) over a period of 30 min at 0°C. The mixture was stirred at rt for 15 h. The reaction was quenched with a saturated NH_4Cl aqueous solution (30 mL). The organic layer was extracted with diethyl ether, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/diethyl ether (9/1)) to give a mixture of 3-octylthiophene and the title compound **S1**. The mixture was purified by fractional distillation (200-250°C, 200 Pa) to afford 1.9 g (40.1%) of the title compound. ^{1}H NMR ($CDCl_3$, 600 MHz) $\delta = 6.90$ (2H, d, $J = 3.6$ Hz, thiophene-$H_{a, b}$), 2.50 (4H, t, $J = 7.8$ Hz, -H_1), 1.62-1.61 (4H, m, -H_2), 1.40-1.26 (20H, m, -$H_{3\text{-}7}$), 0.88 (6H, t, $J = 7.0$ Hz, -H_8) ^{13}C NMR ($CDCl_3$, 150 MHz) $\delta = 142.1$ (C or CH, Thiophene), 119.9 (C or CH, Thiophene), 31.9 (CH_2, -$C_{1\text{-}7}$), 29.7 (CH_2, -$C_{1\text{-}7}$), 29.6 (CH_2, -$C_{1\text{-}7}$), 29.5 (CH_2, -$C_{1\text{-}7}$), 29.3 (CH_2, -$C_{1\text{-}7}$), 28.8 (CH_2, -$C_{1\text{-}7}$), 22.7 (CH_2, -$C_{1\text{-}7}$), 14.1 (2C, -C_8).

3,4-Dioctyl-thiophene-1-carbaldehyde (**S2**).

A solution of 3,4-dioctylthiophene (**S1**) (1.0 g, 3.24 mmol) in THF (15.4 mL) was added to a mixture of *N,N,N',N'*-tetramethyl ethylene diamine (TMEDA, 0.26 mL, 3.24 mmol) and *n*-BuLi (1.58 M, *n*-hexane solution, 4.5 mL, 7.13 mmol) at -65°C under Ar. The mixture was stirred for 30 min at -65°C and then stirred for 2 h at -30°C. DMF (2.0 mL, 25.9 mmol) was added to the mixture and the mixture was allowed to warm to -10ºC over 30 min. The mixture was stirred for 2 h at -10ºC. A solution of 3M-HCl (3 mL) was added to the mixture. The organic layer was extracted with diethyl ether and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (*n*-hexane/petroleum ether/diethyl ether (50/10/1)), to obtain the title compound **S2** (855.1 mg, 78.4%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 9.97 (1H, d, *J* = 1.1 Hz, -CHO), 7.30 (1H, s, thiophene-H_d), 2.85 (2H, td, *J* = 8.0, 1.1 Hz, -H_1), 2.50 (2H, td, *J* = 8.0, 1.1 Hz, -H_9), 1.59 (1H, td, *J* = 15.9, 7.8 Hz, -H_2), 1.53 (1H, td, *J* = 15.9, 7.8 Hz, -H_{10}), 1.38-1.23 (20H, m, -$H_{3\text{-}7,\ 11\text{-}15}$), 0.86 (3H, t, *J* = 3.5 Hz, -$H_{8\text{ or }16}$), 0.84 (3H, t, *J* = 3.5 Hz, -$H_{8\text{ or }16}$) ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 182.5 (CH, CHO), 151.4 (C, Thiophene-C_a), 144.3 (C, Thiophene-C_b), 138.1 (C, Thiophene-C_c), 130.1 (CH, Thiophene-C_d), 31.8 (CH_2, -$C_{2\text{ or }10}$), 31.8 (CH_2, -$C_{2\text{ or }10}$), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 28.2 (CH_2, -C_1), 26.9 (CH_2, -C_9), 22.6 (CH_3, -C_8), 14.0 (CH_3, -C_{16}).

5-(5,5-Dimethyl-[1,3]dioxan-2-yl)-3,4-dioctyl-thiophene (**S3**).

To 200 mL of a three-necked flask attached with a Dean-Stark trap condenser, 3,4-dioctyl-thiophene-1-carbaldehyde **S2** (761 mg, 2.26 mmol), *p*-TsOH (7.6 mg, 0.13 mmol), neopentylglycohol (708.9 mg, 6.78 mmol), and benzene (90 mL) were added under N_2. The mixture was refluxed by stirring for 3 h. The mixture was neutralized with saturated $NaHCO_3$ aqueous solution. The organic layer was extracted with benzene, dried over anhydrous Na_2SO_4, and evaporated to dryness. The residue was purified by Al_2O_3 (activity 2) column chromatography (*n*-hexane/diethyl ether (50/1)) to afford the title compound **S3** (443.1 mg, 51.0%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 6.86 (1H, s, thiophene-H_d), 5.62 (1H, s, acetal-CH), 3.75 (2H, d, *J* = 10.8 Hz, acetal-CH_2), 3.62 (2H, d, *J* = 10.8 Hz, acetal-CH_2), 2.54 (4H, t, *J* = 8.0 Hz, -H_1), 2.45 (4H, t, *J* = 7.5 Hz, -H_9), 1.59 (2H, t, *J* = 6.7 Hz, -$H_{2\ or\ 10}$), 1.47 (2H, t, *J* = 6.7 Hz, -$H_{2\ or\ 10}$), 1.37 (3H, s, acetal-CH_3), 1.37-1.28 (20H, m, -$H_{3-7,\ 11-15}$), 0.90-0.86 (6H, m, -$H_{8,\ 16}$), 0.78 (3H, s, acetal-CH_3) ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 142.1 (C, Thiophene-C_a), 139.6 (C, Thiophene-$C_{b\ or\ c}$), 134.8 (C, Thiophene-$C_{b\ or\ c}$), 119.8 (C, Thiophene-C_d), 97.7 (CH, acetal), 77.7 (CH_2, acetal), 31.8 (CH_2, -$H_{2,\ 9}$), 31.9 (CH_3 or CH_2), 30.7 (CH_3 or CH_2), 30.1 (CH_3 or CH_2), 29.8 (CH_3 or CH_2), 29.5 (CH_3 or CH_2), 29.5 (CH_3 or CH_2), 29.3 (CH_3 or CH_2), 29.3 (CH_3 or CH_2), 29.2 (CH_3 or CH_2), 28.7 (CH_3 or CH_2), 27.1 (CH_3 or CH_2), 23.0 (CH_3 or CH_2), 22.7 (CH_3 or CH_2), 22.7 (CH_3 or CH_2), 21.8 (CH_3 or CH_2), 14.1 (CH_3 or CH_2).

5-(5’,5’-Dimethyl-[1,3]dioxan-2’-yl)-thiophene-2-carbaldehyde (**3a**).

5-(5,5-Dimethyl-1,3-dioxan-2-yl)-thiophene-2-carbaldehyde **3a** was synthesized from 2-(5,5-dimethyl-1,3-dioxan-2-yl)-thiophene by referring to the procedure described in the literature[3]. A solution of 5,5-dimethyl-2-thiophen-2-yl-[1,3]dioxane (3.88 g, 29.7 mmol) in THF (139 mL) was added to a mixture of TMEDA (4.5 mL, 29.7 mmol) and *n*-BuLi (27.8 mL, 44.5 mmol) at -78°C under N_2. The mixture was stirred for 2 h. DMF (9.3 mL) was added to the mixture. The mixture was warmed to rt over 4 h and stirred for 4 h at rt. Water (158 mL) was added to the mixture. The organic layer was extracted with ethyl acetate, washed with brine (160 mL × 3), dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate (8/2)) to afford the title compound **3a** (3.88 g, 58%). ^{1}H NMR ($CDCl_3$, 270 MHz) δ = 9.90 (1H, s, CHO), 7.67 (1H, d, *J* = 3.8 Hz, thiophene-H_2), 7.22 (1H, d, *J* = 3.8 Hz, thiophene-H_3), 5.63 (1H, s, acetal-CH), 3.75 (2H, d, *J* = 10.7 Hz, acetal-CH_2), 3.64 (2H, d, *J* = 10.7 Hz, acetal-CH_2), 1.22 (3H, s, acetal-CH_3), 0.81 (3H, s, acetal-CH_3) ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 192.7 (CHO), 151.34 (C, Thiophene-C_d), 143.40 (C, Thiophene-C_a), 135.72 (C, Thiophene-C_b), 125.83 (C, Thiophene-C_c), 97.44 (CH, acetal), 77.40 (CH_2, acetal), 30.17 (C, acetal), 22.81 (CH_3, acetal), 21.68 (CH_3, acetal).

5-(5,5-Dimethyl-[1,3]dioxan-2-yl)-3,4-dioctyl-thiophene-2-carbaldehyde (3b).

5-(5,5-Dimethyl-[1,3]dioxan-2-yl)-3,4-dioctyl-thiophene **S3** (650 mg, 1.54 mmol) was dissolved in THF (15 mL). TMEDA (120 μL, 1.54 mmol) and *n*-BuLi (2.9 mL, 4.61 mmol) was added to the mixture at -30°C under Ar. The mixture was stirred for 30 min at -30°C and stirred for 2 h at -20°C. DMF (1.3 mL, 16.9 mmol) was added to the mixture. The mixture was warmed to -5°C over 30 min. After stirring the mixture, water (10 mL) was added to the mixture. The organic layer was extracted with ethyl acetate and washed with brine (30 mL × 3). The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by silica gel column chromatography (*n*-hexane/ethyl acetate/Et_3N (95/5/3)) to afford the title compound **3b** (559.3 mg, 80.6%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 9.97 (1H, s, CHO), 5.60 (1H, s, acetal-CH), 3.74 (2H, dd, J = 10.2, 1.1 Hz, acetal-CH_2), 3.61 (2H, dd, J = 10.2, 1.1 Hz, acetal-CH_2), 2.81 (2H, td, J = 8.1 Hz, -H_1), 2.54 (2H, t, J = 8.1 Hz, -H_9), 1.53-1.52 (2H, m, -H_2), 1.47-1.46 (2H, m, -H_{10}), 1.28-1.25 (20H, m, -$H_{3\text{-}7,\ 11\text{-}15}$), 1.26 (3H, s, acetal-$CH_3$), 0.87 (3H, t, J = 10.5 Hz, -$H_{8 \text{ or } 16}$), 0.85 (3H, t, J = 10.5 Hz, -$H_{8 \text{ or } 16}$), 0.78 (3H, s, acetal-CH_3) ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 182.8(CH, CHO), 151.6 (CH, Thiophene-C_a), 145.3 (C, Thiophene-C_b), 141.6 (C, Thiophene-C_c), 137.0 (C, Thiophene-C_d), 97.0 (CH, acetal-CH), 77.7 (CH_2, acetal-CH_2), 32.2 (CH_2, -C_2), 30.2 (CH_2, -C_{10}), 31.8 (CH_2), 31.8 (CH_2), 30.7 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 27.0 (CH_2), 26.7 (CH_2), 22.9 (CH_2), 22.7 (CH_2), 22.6 (CH_3, acetal-CH_3), 21.7 (CH_3, acetal-CH_3), 14.1 (CH_3, -$C_{8 \text{ or } 16}$), 14.1 (CH_3, -$C_{8 \text{ or } 16}$).

5,15-Bis-(3’-allyloxypropyl)-10-[5’’-(5’’’,5’’’-dimethyl-[1,3]dioxan-2’’’-yl)-thiophen-2’’-yl]-20-(1’’’’-methylimidazol-2’’’’-yl)-porphyrin (**5a**).

meso-(3-Allyloxypropyl)dipyrromethane **2** (488.7 mg, 2.0 mmol), 5-(5’,5’-dimethyl-[1,3]dioxan-2’-yl)-thiophen-2-carbaldehyde **3a** (339.5 mg, 1.5 mmol), and 1-methyl-2-imidazolecarbaldehyde **4** (110.1 mg, 1.0 mmol) were dissolved in chloroform (400 mL, dried over molecular sieve 3A). After bubbling with an N_2 stream for 5 min, trifluoroacetic acid (0.19 mL, 2.5 mmol) was added slowly over 30 sec. The mixture was stirred for 4 h at rt under darkness. A solution of *p*-chloranil (737.6 mg, 3.0 mmol) in chloroform (100 mL) was added to the mixture, followed by addition of triethylamine (0.35 mL, 2.5 mmol). After stirring for 5 h, the mixture was concentrated under reduced pressure. The residue was suspended in toluene by sonication. The precipitates were filtrated and the filtrate was evaporated. The residue was purified by silica gel column chromatography (chloroform/ethyl acetate (6/4 to 0/1)) to give a mixture of **5a** and dyad **12**. The fractions were combined and purified again by silica gel column chromatography (chloroform/acetone (6/4 to 0/1)). Further purification by GPC under atmospheric pressure (Biobeads SX-3) afforded **5a** (172.7 mg, 5.5%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 9.48 (4H, d, J = 4.6 Hz, pyrrole-H_β), 9.46 (4H, d, J = 4.6 Hz, pyrrole-H_β), 9.14 (2H, d, J = 4.6 Hz, pyrrole-H_β), 8.76 (2H, d, J = 4.6 Hz, pyrrole-H_β), 7.79 (4H, d, J = 3.3 Hz, thiophene-H_3), 7.68 (4H, s, imidazole-H_2), 7.53 (1H, d, J = 3.3 Hz, thiophene-H_2), 7.43 (1H, s, imidazole-H_1), 6.11-6.03 (2H, m, Allyl-CH=), 5.96 (1H, s, acetal-CH), 5.41 (2H, d, J = 17.3 Hz, Allyl-=CH_{trans}), 5.25 (2H, d, J = 10.4 Hz, Allyl-=CH_{cis}), 5.04 (4H, t, J = 7.4 Hz, Allyl-CH_2CH$_2$CH$_2$-), 4.05 (4H, d, J = 4.8 Hz, OCH_2), 3.91 (3H, d, J = 10.9 Hz, acetal-CH_2), 3.79 (3H, d, J = 10.9 Hz, acetal-CH_2), 3.61 (4H, t, J = 5.4 Hz, Allyl-CH$_2$CH$_2$CH_2-), 3.33 (3H, s, imidazole-N-CH_3), 2.75 (4H, t, J = 5.4 Hz, Allyl-CH$_2$CH_2CH$_2$-), 1.41 (3H, s, acetal-CH_3), 0.88 (3H, s, acetal-CH_3), -2.71 (2H, s, inner-NH) (Figure S5) ^{13}C NMR ($CDCl_3$, 150 MHz) δ =

148.6 (C, imidazole-C_3), 144.6 (br. C, pyrrole-C_α), 143.5 (C, Thiophene-C_d), 143.5 (C, Thiophene-C_a), 134.8 (CH, Allyl), 131.6 (br, CH, pyrrole-C_β), 130.0 (br, CH, pyrrole-C_β), 128.0 (br, CH, pyrrole-C_β), 128.0 (br, CH, pyrrole-C_β), 128.8 (C, Thiophene-C_b or C_c), 128.0 (C, Thiophene-C_b or C_c), 125.0 (CH, imidazole-C_1), 123.8 (CH, imidazole-C_2), 121.1 (C, *meso*-C_{15}), 119.5 (C, *meso*-$C_{10,\ 20}$), 116.6 (CH, acetal), 111.0 (C, *meso*-C_5), 104.9 (*C*H_2, Allyl), 77.1 (*C*H_2, acetal), 71.7 (O*C*H_2, Allyl), 68.9 (CH_2, Allyl), 37.5 (CH_2, Allyl), 34.3 (CH_3, imidazole-CH_3), 31.1 (CH_2, Allyl), 30.1 (C, acetal), 22.9 (CH_3, acetal), 21.7 (CH_3, acetal) (Figure S6) MS (MALDI-TOF, dithranol): Found *m/z* 782.0 $[M+H]^+$, calculated for $C_{46}H_{50}N_6O_4S$; 782.36.

5,15-Bis-(3'-allyloxy-propyl)-10-[5''-formylthiophen-2''-yl]-20-(1'''-methylimidazol-2-yl)-porphyrin (6a)

Protected porphyrin **5a** (162.5 mg, 0.21 mmol) was dissolved in a mixture of trifluoroacetic acid (8.1 mL), acetic acid (62 mL) and a 5% H_2SO_4 aqueous solution (4.0 mL). The mixture was stirred at rt for 6 h under darkness. The mixture was neutralized with saturated $NaHCO_3$ aqueous solution and the organic layer was extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by reprecipitation from chloroform and *n*-hexane to afford **6a** (122.2 mg, 84.3%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 10.23 (1H, s, CHO), 9.49 (4H, d, *J* = 4.7 Hz, pyrrole-$H_{\beta 4\ \mathrm{or}\ 1}$), 9.01 (2H, d, *J* = 4.7 Hz, pyrrole-$H_{\beta 4\ \mathrm{or}\ 1}$), 8.79 (2H, d, J = 4.7 Hz, pyrrole-$H_{\beta 3}$), 8.11 (1H, d, *J* = 3.6 Hz, Thiophene-H_2), 7.95 (1H, d, *J* = 3.6 Hz, Thiophene-H_1), 7.70 (1H, d, *J* = 1.4 Hz, imidazole-H_2), 7.46 (1H, d, *J* = 1.4 Hz, imidazole-H_1), 6.08-6.05 (2H, m, Allyl-C*H*=), 5.41 (2H, dd, *J* = 17.3, 1.7 Hz, Allyl-=CH_{trans}), 5.26 (2H, dd, *J* = 10.4, 1.4 Hz, Allyl-=CH_{cis}), 5.03 (4H, t, *J* = 7.4 Hz, Allyl-C$H_2$$CH_2CH_2$-), 4.05 (4H, t, *J* = 5.8 Hz, Allyl-OCH_2), 3.61 (4H, t, *J* = 5.8 Hz, Allyl-CH_2CH_2CH_2-), 3.37 (3H, s, imidazole-N-CH_3), 2.74 (4H, tt, J = 7.4, 5.8 Hz, Allyl-CH_2C$H_2$$CH_2$-), -2.77 (2H, s, inner-N*H*) (Figure S7) ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 183.6 (CHO), 153.8 (C, imidazole-C_3), 148.5 (C, Thiophene-C_d), 145.3 (CH, Thiophene-C_a), 135.0 (CH, Allyl-*C*H_2=), 134.9 (C, Thiophene-C_c), 134.7 (CH, Thiophene-C_b), 131.0 (br. CH, pyrrole-$C_{\beta 2}$), 130.9 (br. CH, pyrrole-$C_{\beta 3}$), 129.1 (br. CH, pyrrole-$C_{\beta 1}$), 128.3 (br. CH, pyrrole-$C_{\beta 4}$), 128.4 (CH, imidazole-C_2), 121.5(CH, imidazole-C_1), 119.9 (C, *meso*-$C_{10,\ 20}$) 116.8 (CH_2, Allyl-=*C*H), 109.0 (C, *meso*-$C_{5\ or\ 15}$), 105.9 (C, *meso*-$C_{5\ or\ 15}$), 71.9 (OCH_2, Allyl-O*C*H_2), 69.4 (CH_2, Allyl-CH_2CH_2*C*H_2-), 37.8 (CH_2, Allyl-CH_2*C*H_2CH_2-), 34.4 (CH_3, imidazole-CH_3), 31.2 (CH_2, Allyl-*C*$H_2CH_2CH_2$-) (Figure S8, H-H COSY; Figure S9, HMQC; Figure S10) MS (MALDI-TOF): Found m/z = 696.9 $[M+H]^+$, calculated for $C_{41}H_{40}N_6O_3S$; 696.3.

5,15-Bis-(3'-allyloxypropyl)-10-[3'',4''-dioctyl-5''-formylthiophen-2''-yl]-20-(1'''-methylimidazol-2'''-yl)-porphyrin (**6b**).

meso-(3-Allyoxypropyl)dipyrromethane **2** (391 mg, 1.6 mmol), monoprotected thiophene-2-carbaldehyde **3b** (360 mg, 0.8 mmol), 1-methyl-2-imidazole-carbaldehyde **4** (88 mg, 0.8 mmol) were dissolved in chloroform (80 mL, dried over molecular sieve 3A). After bubbling with an N_2 stream for 5 min, trifluoroacetic acid (123 μL, 1.6 mmol) was added slowly over 30 sec. The mixture was stirred at rt for 5 h under darkness. A solution of *p*-chloranil (591 mg, 2.4 mmol) in chloroform (80 mL) was added to the mixture, followed by addition of triethylamine (223 μL, 1.6 mmol). After stirring for 4 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (chloroform/ethyl acetate (1/0 to 6/4)) to give a mixture of **5b**, **6b**, and **12**. Further purification of the mixture was carried out with GPC under atmospheric pressure (Biobeads SX-3) to give a mixture of **5b** and **6b** (37.1 mg, 5.1%). Protected porphyrin **5b** and deprotected porphyrin **6b** (30.5 mg, 30.3 μmol) were dissolved in a mixture of 10% trifluoroacetic acid in THF (8.1 mL), 5% H_2SO_4 (70 mL) aqueous solution and THF (35 mL). The mixture was stirred at 0°C for 6 h under darkness. The mixture was neutralized with saturated $NaHCO_3$ aqueous solution. The organic layer was extracted with chloroform. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by silica gel column chromatography (chloroform/ethyl acetate/Et_3N (10/0/0.3 to 6/4/0.3)) to afford the title compound **6b** (24.2 mg, 79%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 10.40 (0.5 H, s, CHO), 10.39 (0.5 H, s, CHO), 9.54 (2H, dd, *J* = 4.7, 2.4 Hz, pyrrole-$H_{\beta1 \text{ or } 4}$), 9.51 (2H, dd, *J* =4.7, 2.4 Hz, pyrrole-$H_{\beta1 \text{ or } 4}$), 8.90 (2H, dd, *J* = 4.7, 2.4 Hz, pyrrole-$H_{\beta2 \text{ or } 3}$), 8.81 (2H, dd, *J* = 4.7, 2.2 Hz, pyrrole-$H_{\beta2 \text{ or } 3}$), 7.69 (0.5H, d, *J* = 1.4 Hz, imidazole-H_2), 7.68 (0.5H, d, *J* = 1.4 Hz, imidazole-H_2), 7.48 (0.5H, d, *J* = 1.4 Hz, imidazole-H_1), 7.48 (0.5H, d, *J* = 1.4 Hz, imidazole-H_1), 6.12-6.05 (2H, m, Allyl-C*H*=), 5.42 (1H, dt, *J* = 17.3, 1.5 Hz, Allyl-=CH_{trans}), 5.27 (2H, dd, *J* = 10.4, 0.5 Hz, Allyl-=CH_{cis}), 5.10 (4H, dd, *J* = 12.1, 7.7 Hz, Allyl-CH_2CH_2CH_2-), 4.12-4.05 (4H, m, Allyl-OCH_2), 3.66 (4H, td, *J* = 10.4, 5.5 Hz, Allyl-CH_2CH_2CH_2-), 3.40 (1.5H, s, imidazole-N-CH_3), 3.38(1.5H, s, imidazole-N-CH_3), 3.27-3.24 (2H, m, octyl-$H_{1 \text{ anti}}$), 2.80-2.77 (4H, m, Allyl-CH_2CH_2CH_2-), 2.52-0.46 (1H, m, octyl-$H_{1 \text{ syn}}$), 2.41 (1H, t, *J* = 8.0 Hz, octyl-$H_{9 \text{ syn}}$), 1.99 (2H, tt, *J* = 15.0, 7.4 Hz, octyl-$H_{2 \text{ anti}}$), 1.66 (2H, td, *J* = 15.0, 7.4 Hz, octyl-$H_{3 \text{ anti}}$), 1.52 (2H, td, *J* = 15.4, 7.4 Hz, octyl-$H_{4 \text{ anti}}$),1.43-1.39 (6H, m, octyl-$H_{5,\ 6,\ 7 \text{ anti}}$), 1.21-1.20 (1H, m, octyl-$H_{2 \text{ syn}}$), 1.14-1.10 (1H, m, octyl-$H_{10 \text{ syn}}$), 0.95 (3H, td, *J* = 7.0, 3.0 Hz, octyl-$H_{8 \text{ anti}}$), 0.77 (2H, td, *J* = 13.7, 7.0 Hz, octyl-$H_{7,\ 15 \text{ syn}}$), 0.70-0.57 (8H, m, octyl-$H_{3,\ 4,\ 5,\ 6,\ 11,\ 12,\ 13,\ 14 \text{ syn}}$), 0.47 (3H, td, *J* = 7.0, 3.0 Hz, octyl-$H_{8,16 \text{ syn}}$), -2.68 (1H, s, inner-N*H*), -2.69 (1H, s, inner-N*H*) (Figure S11) ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 182.9 (CH, CHO), 151.0 (C, imidazole-C_1), 150.8 (C, Thiophene-C_a), 148.7 (C, Thiophene-C_b), 148.6 (C, Thiophene-C_b), 147.6 (C, Thiophene-C_c), 149.0-144.0 (br. C, pyrrole-C_α), 138.3 (C, Thiophene-C_d), 135.0 (CH, Allyl-*C*H=), 131.2 (br. CH, pyrrole-$C_{\beta2 \text{ or } 3}$), 130.9 (br. CH, pyrrole-$C_{\beta2 \text{ or } 3}$), 129.1 (br. CH, pyrrole-$C_{\beta 1 \text{ or } 4}$), 128.6 (br. CH, pyrrole-$C_{\beta 1 \text{ or } 4}$), 128.4 (CH, imidazole-$C_2$), 121.5 (CH, imidazole-$C_1$), 119.9 (C, *meso*-$C_{10,\ 20}$), 116.9 (C, Allyl-=*C*H), 109.0 (C, *meso*-C_{15}), 109.0 (C, *meso*-C_{15}), 105.8 (C, *meso*-C_5), 105.7 (C, *meso*-C_5), 72.0 (CH_2, Allyl-O*C*H_2), 69.1 (CH_2, Allyl-CH_2CH_2*C*H_2-), 69.0 (CH_2, Allyl-CH_2CH_2*C*H_2-), 37.8 (CH_2, Allyl-CH_2*C*H_2CH_2-), 37.8 (CH_2, Allyl-CH_2*C*H_2CH_2-), 34.5 (CH_3, imidazole-N-*C*H_3), 34.5 (CH_3, imidazole-N-*C*H_3), 33.0 (CH_2, octyl-$C_{2\ \text{anti}}$), 32.9 (CH_2, octyl-$C_{2\ \text{anti}}$), 31.9 (CH_2, octyl-$C_{7\ \text{anti}}$), 31.3 (CH_2, octyl-$C_{7,\ 15\ \text{syn}}$), 31.3 (CH_2, Allyl-*C*$H_2CH_2CH_2$-), 30.2 (CH_2, octyl-$C_{2 \text{ or } 10\ \text{syn}}$), 30.2 ($CH_2$, octyl-$C_{2 \text{ or } 10\ \text{syn}}$), 30.0 ($CH_2$, octyl-$C_{3\ \text{anti}}$), 29.5 ($CH_2$, octyl-$C_{4\ \text{anti}}$), 29.3 ($CH_2$, octyl-$C_{5\ \text{anti}}$), 29.2 ($CH_2$, octyl-$C_{3 \text{ or } 11\ \text{syn}}$), 29.2 ($CH_2$, octyl-$C_{3 \text{ or } 11\ \text{syn}}$), 28.7 ($CH_2$ × 2, octyl-$C_{4 \text{ or } 5 \text{ or } 12 \text{ or } 13\ \text{syn}}$), 28.6 ($CH_2$ × 2, octyl-$C_{4 \text{ or } 5 \text{ or } 12 \text{ or } 13\ \text{syn}}$), 27.9 ($CH_2$, octyl-$C_{1\ \text{anti}}$), 27.7 ($CH_2$, octyl-$C_{1 \text{ or } 9\ \text{syn}}$), 27.6 ($CH_2$, octyl-$C_{1 \text{ or } 9\ \text{syn}}$), 22.7 ($CH_2$, octyl-$C_{6 \text{ or } 14\ \text{anti}}$), 22.2 ($CH_2$, octyl-$C_{6 \text{ or } 14\ \text{syn}}$), 14.2 ($CH_2$, octyl-$C_{8\ \text{anti}}$), 13.7 ($CH_2$, octyl-$C_{8,\ 16\ \text{syn}}$) (Figure S12, H-H COSY ; Figure S13, HMQC ; Figure S14) MS (MALDI-TOF, dithranol): Found *m*/*z* 921.1 $[M+H]^+$, calculated for $C_{46}H_{50}N_6O_4S$; 920.54.

2,5-Bis(15-*N*-methylimidazolylporphynyl)-3,4-dioctyl-thiophene (8b).

Porphyrin-aldehyde **6b** (20.0 mg, 21.7 μmol) and *meso*-(3-allyoxypropyl)dipyrromethane **2** (37.1 mg, 151.9 μmol) were dissolved in chloroform (6.2 mL). After bubbling with an N_2 stream for 5 min, a 10 v/v% trifluoroacetic acid solution in chloroform (70.2 μL, 91.1 μmol) was added. The mixture was stirred for 3 h at rt under darkness. A solution of 1-methyl-2-imidazolcarbaldehyde **4** (11.9 mg, 108.5 μmol) in chloroform (5.6 mL) and 10 v/v% trifluoroacetic acid in chloroform (83.5 μL, 108.5 μmol) were added to the mixture. The mixture was stirred for 3.5 h. A solution of *p*-chloranil (56.0 mg, 277.9 μmol) in chloroform (6.2 mL) was added, followed by addition of 10 v/v% triethylamine in chloroform (278.6 μL, 199.9 μmol). After stirring for 2 h, the mixture was evaporated to dryness. The residue was purified by GPC (Biobeads SX-3), silica gel column chromatography (chloroform/acetone (10/3 to 3/10)), and GPC (Biobeads SX-3) to afford the title compound **8b** (2.1 mg, 6.5%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 9.73 (2H × 2, t, J = 4.9 Hz, pyrrole-H_β), 9.59-9.57 (2H × 4, m, , pyrrole-H_β), 8.85-8.83 (2H × 2, m, pyrrole-H_β), 7.71 (2H, t, J = 1.6 Hz, imidazole-H_1), 7.51-7.50 (2H, m, imidazole-H_2), 6.19-6.11 (4H, m, Allyl-CH=), 5.48 (4H, dq, J = 16.8, 1.8 Hz, Allyl-=CH_{trans}), 5.33 (4H, dq, J = 10.2, 1.9 Hz, Allyl-=CH_{cis}), 5.21 (8H, dd, J = 12.5, 4.5 Hz, Allyl-C$H_2$$CH_2CH_2$-), 4.19-4.11 (8H, m, Allyl-OCH_2), 3.76-3.73 (8H, m, Allyl-CH_2CH_2CH_2-), 3.43 (3H, s, imidazole-N-CH_3), 3.42 (1.5H, s, imidazole-N-CH_3), 3.42 (1.5H, s, imidazole-N-CH_3), 2.91-2.78 (12H, m, Allyl-CH_2C$H_2$$CH_2$-, octhyl-$H_1$), 1.25 (4H, d, J = 7.4 Hz, octhyl-H_2), 0.97-0.80 (20H, m, octhyl-$H_{3,4,5,6,7}$), 0.58-0.54 (6H, m, octhyl-H_8), -2.51 (2H, s, inner-NH), -2.52 (2H, s, inner-NH) (Figure S15) MS (MALDI-TOF, dithranol): Found m/z 1477.4 $[M+H]^+$, calculated for $C_{92}H_{108}N_{12}O_4S$; 1477.8 (av.).

2,5-Bis(15-*N*-methylimidazolylporphynyl)-thiophene (**8a**).

According to the similar procedure for **8b**, **8a** was obtained (5.5 mg, 10.0%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 9.75 (2H, d, J = 4.7 Hz, pyrrole-H_β), 9.70 (2H, d, J = 4.7 Hz, pyrrole-H_β), 9.59 (4H, d, J = 4.7 Hz, pyrrole-H_β), 8.84 (4H, d, J = 4.7 Hz, pyrrole-H_β), 8.33 (2H, s thiophene-H), 7.72 (2H, d, J = 1.4 Hz, imidazole-H_1), 7.51 (2H, d, J = 1.4 Hz, imidazole-H_2), 6.14 (4H, ddt, J = 17.0, 10.3, 5.6 Hz, Allyl-CH=), 5.48 (4H, dd, J = 17.0, 1.6 Hz, Allyl-=CH_{trans}), 5.32 (4H, dd, J = 10.3, 1.6 Hz, Allyl-=CH_{cis}), 5.20 (7H, t, J = 7.6 Hz, Allyl-C$H_2$$CH_2CH_2$-), 4.14 (8H, t, J = 5.6 Hz, Allyl-OCH_2), 3.73 (8H, t, J = 5.6 Hz, Allyl-CH_2CH_2CH_2-), 3.44 (6H, s, imidazole-N-CH_3), 2.88 (8H, tt, J = 7.6, 5.6 Hz, Allyl-CH_2C$H_2$$CH_2$-), -2.54 (4H, s, inner-NH) (Figure S16, H-H COSY; Figure S17) MS (MALDI-TOF, dithranol): Found m/z 1252.18 $[M+H]^+$, calculated for $C_{76}H_{76}N_{12}O_4S$; 1252.58. UV-vis (λ (abs)/nm, in chloroform): 416.5 (0.80), 432 (1.00), 519 (0.08), 558.5 (0.06), 594 (0.03), 654 (0.04).

[1] J. J. P. Stewart in *MOPAC 2002*, *Vol.* Fujitsu Ltd., Tokyo, Japan, **2001**.

[2] G. A. Diaz-Quijada, N. Weinberg, S. Holdcroft and B. M. Pinto, *J. Phys. Chem. A* **2002**, *106*, 1266-1276.

[3] A. J. Carpenter and D. J. Chadwick, *Tetrahedron* **1985**, *41*, 3803-3812.

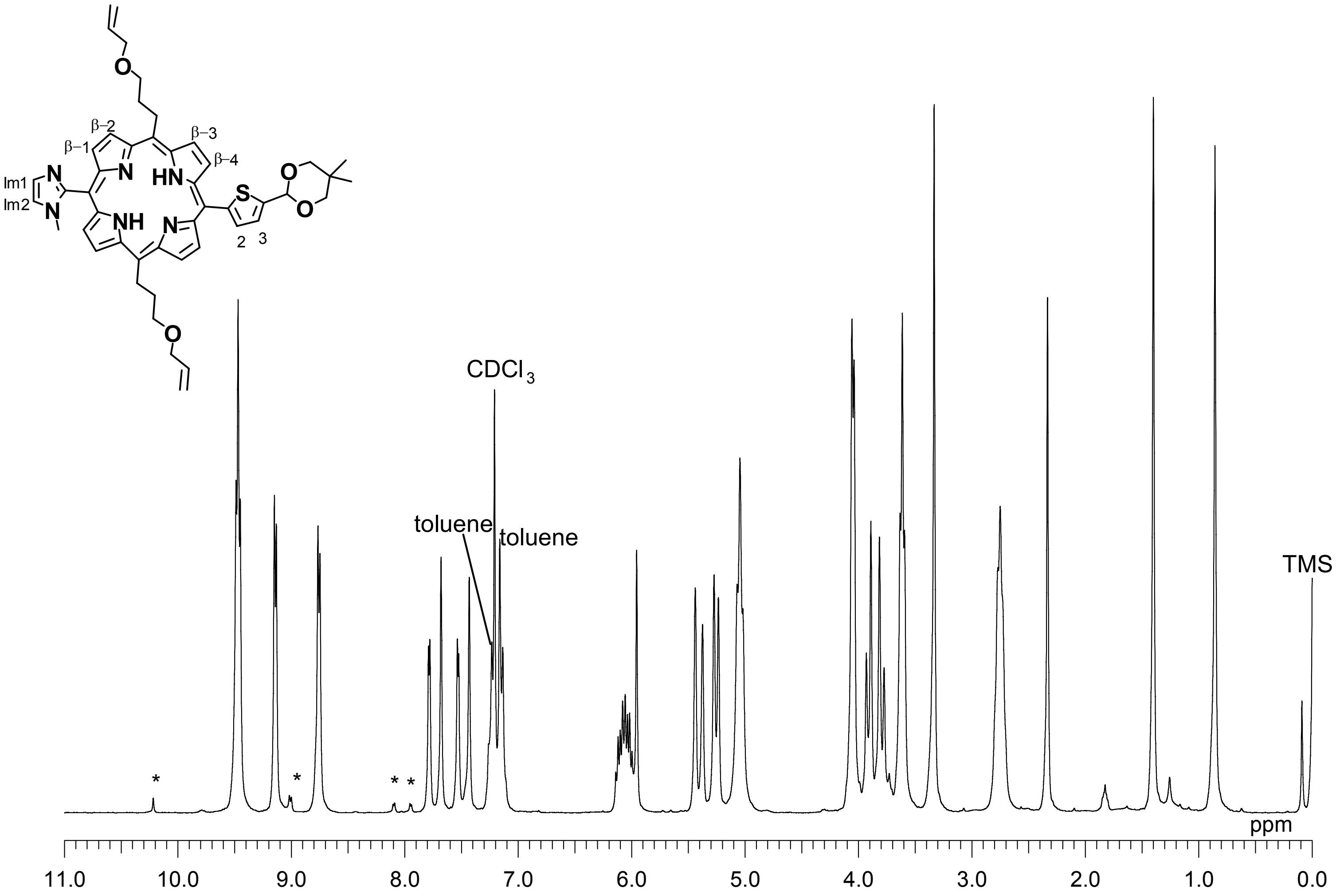


Figure S5. ^{1}H NMR (600 MHz) spectra of **5a** in CDCl$_3$ at 25°C.

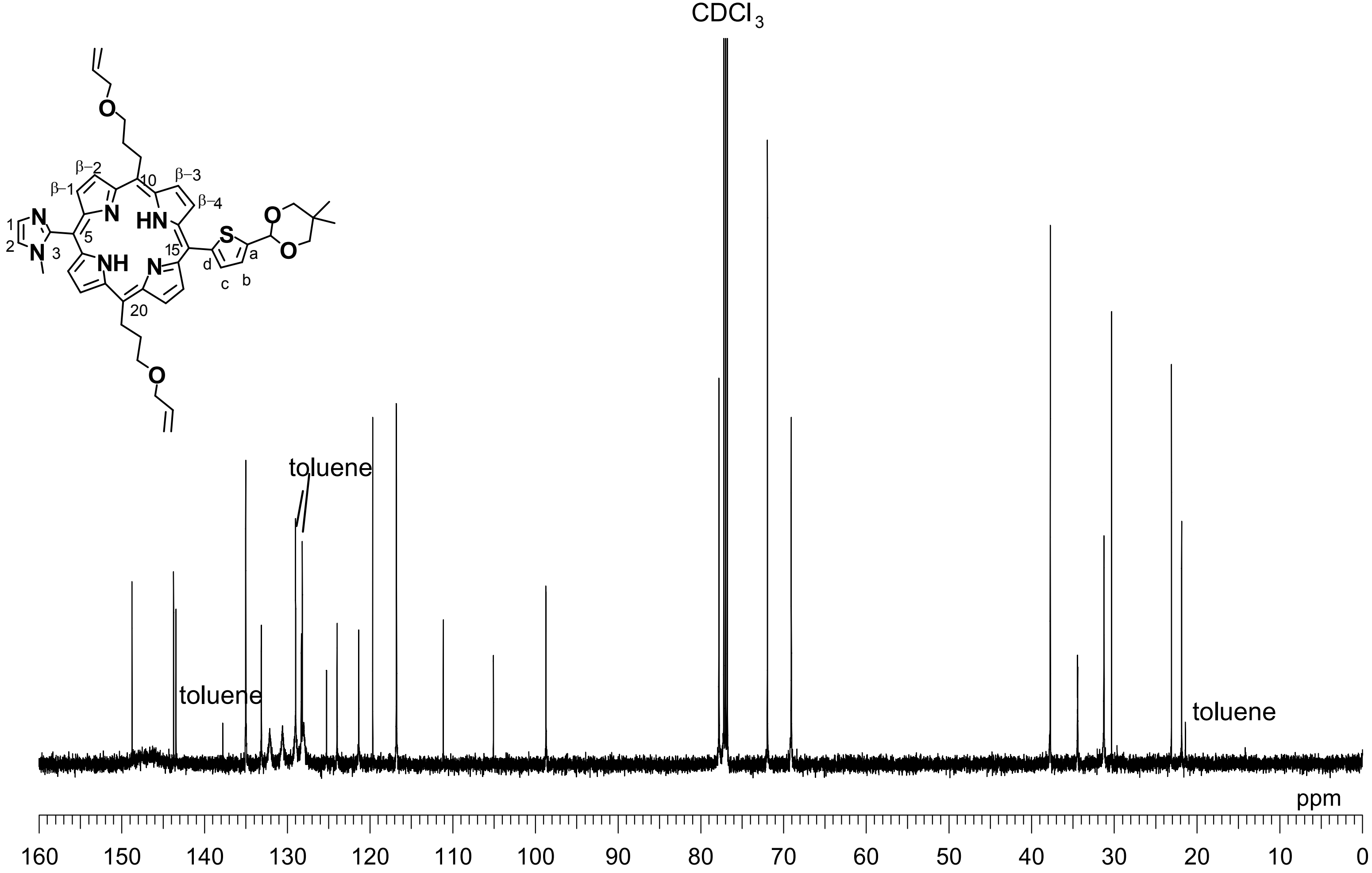


Figure S6. ^{13}C NMR (150 MHz) spectra of **5a** in $CDCl_3$ at 25°C.

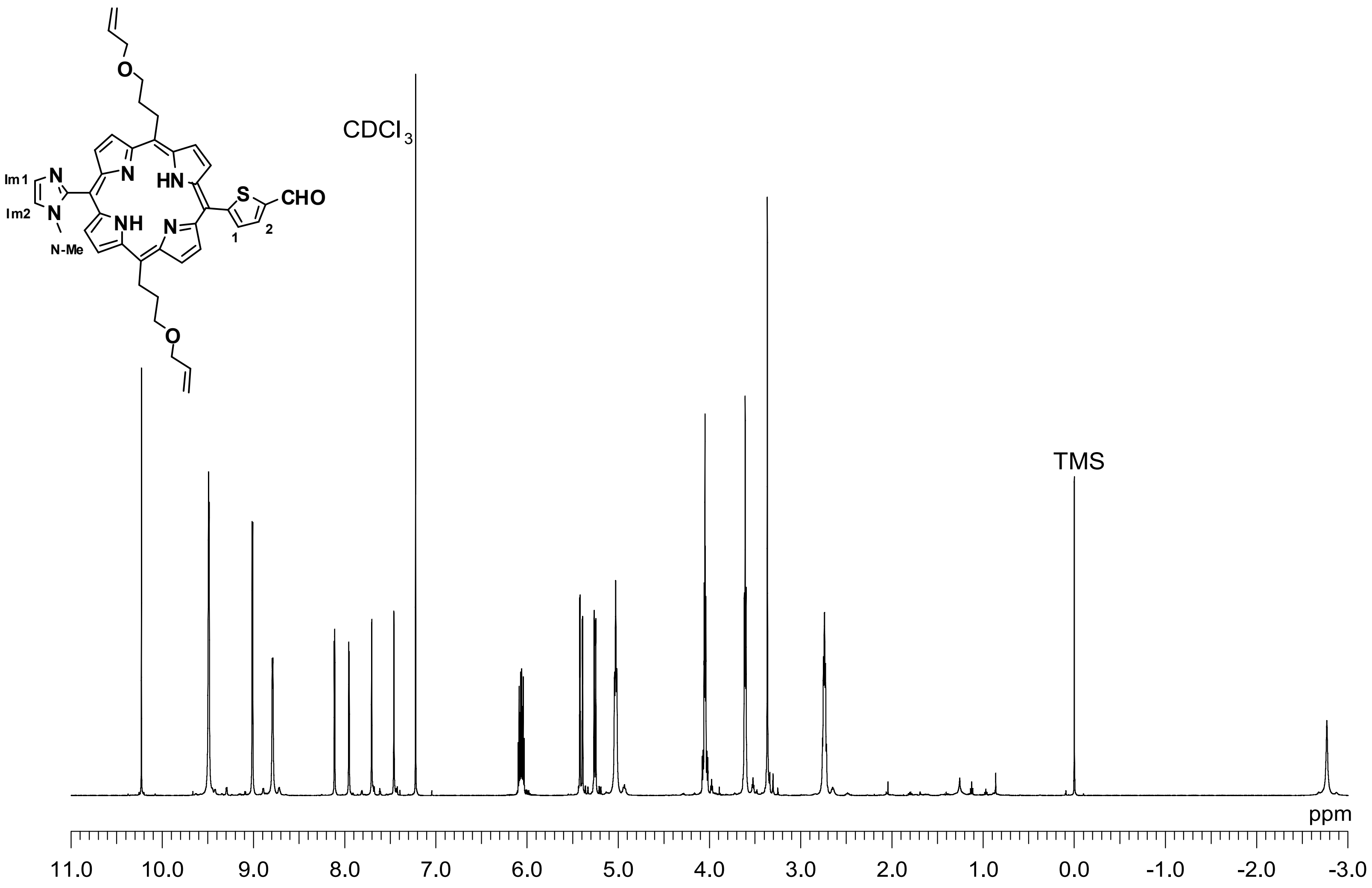


Figure S7. ^{1}H NMR (600 MHz) spectrum of **6a** in $CDCl_3$ at 25°C.

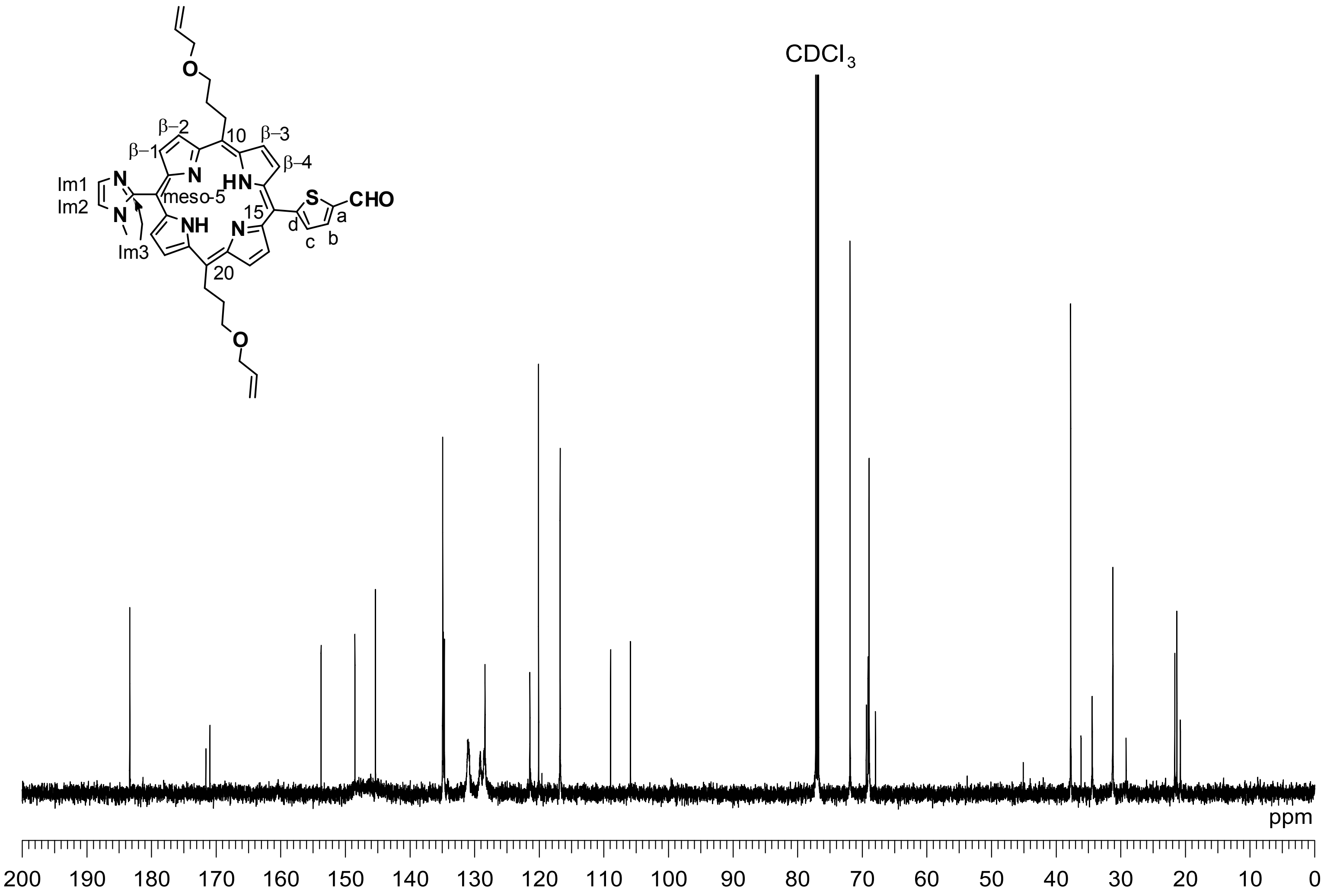


Figure S8. ^{13}C NMR (150 MHz) spectrum of **6a** in CDCl$_3$ at 25°C.

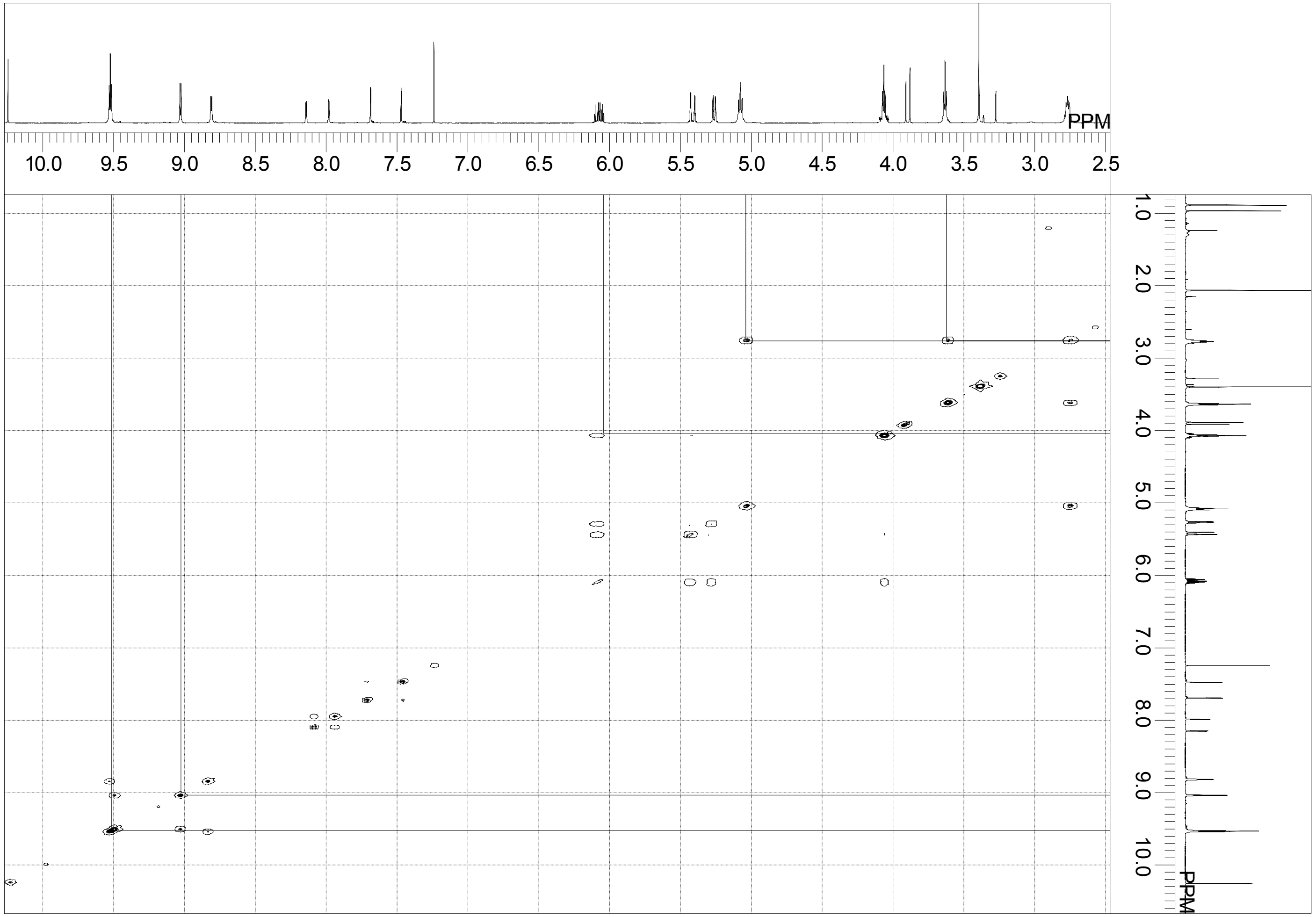


Figure S9. H-H COSY spectrum of **6a** in $CDCl_3$ at 25°C.

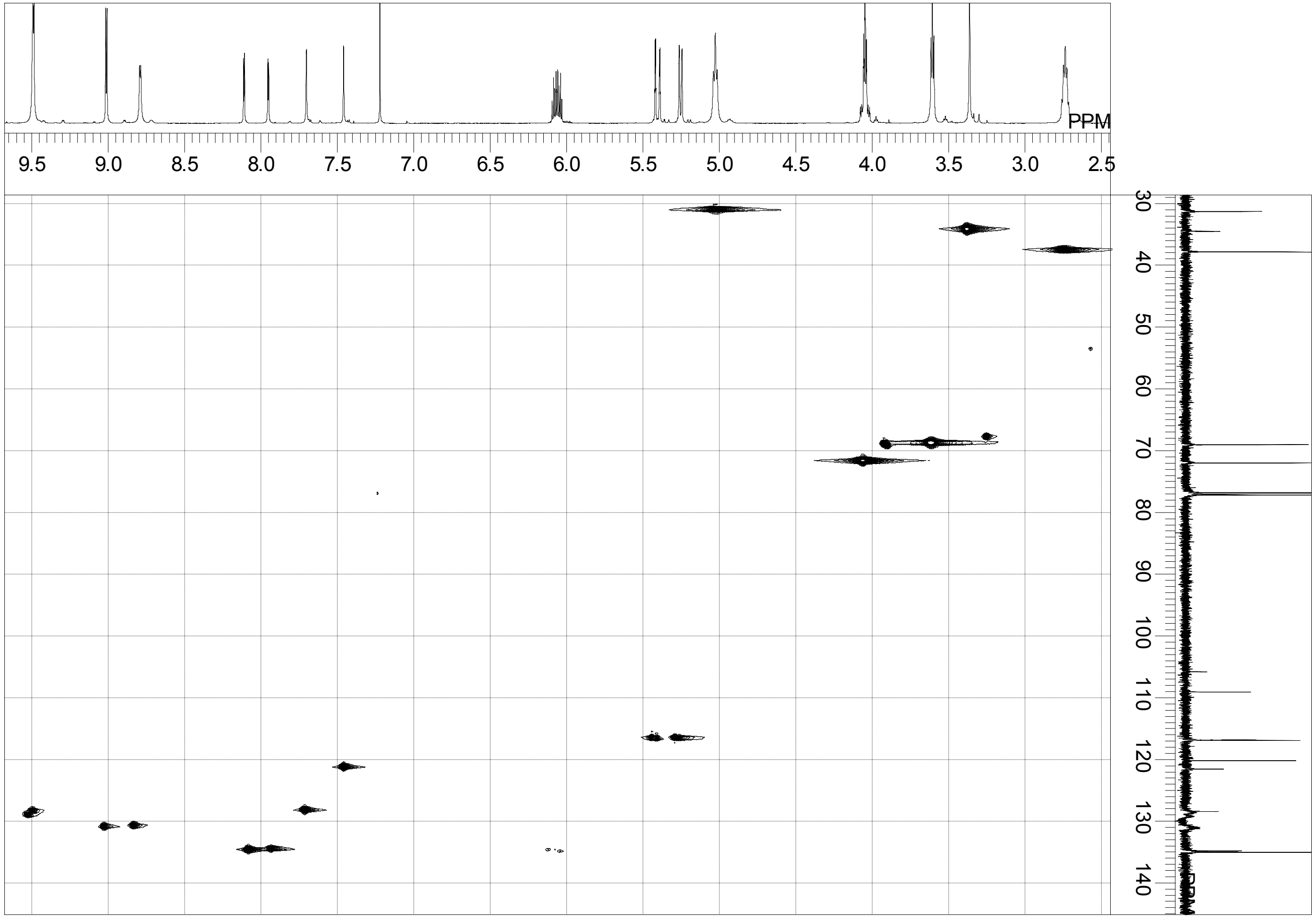


Figure S10. HMQC spectrum of **6a** in $CDCl_3$ at 25°C.

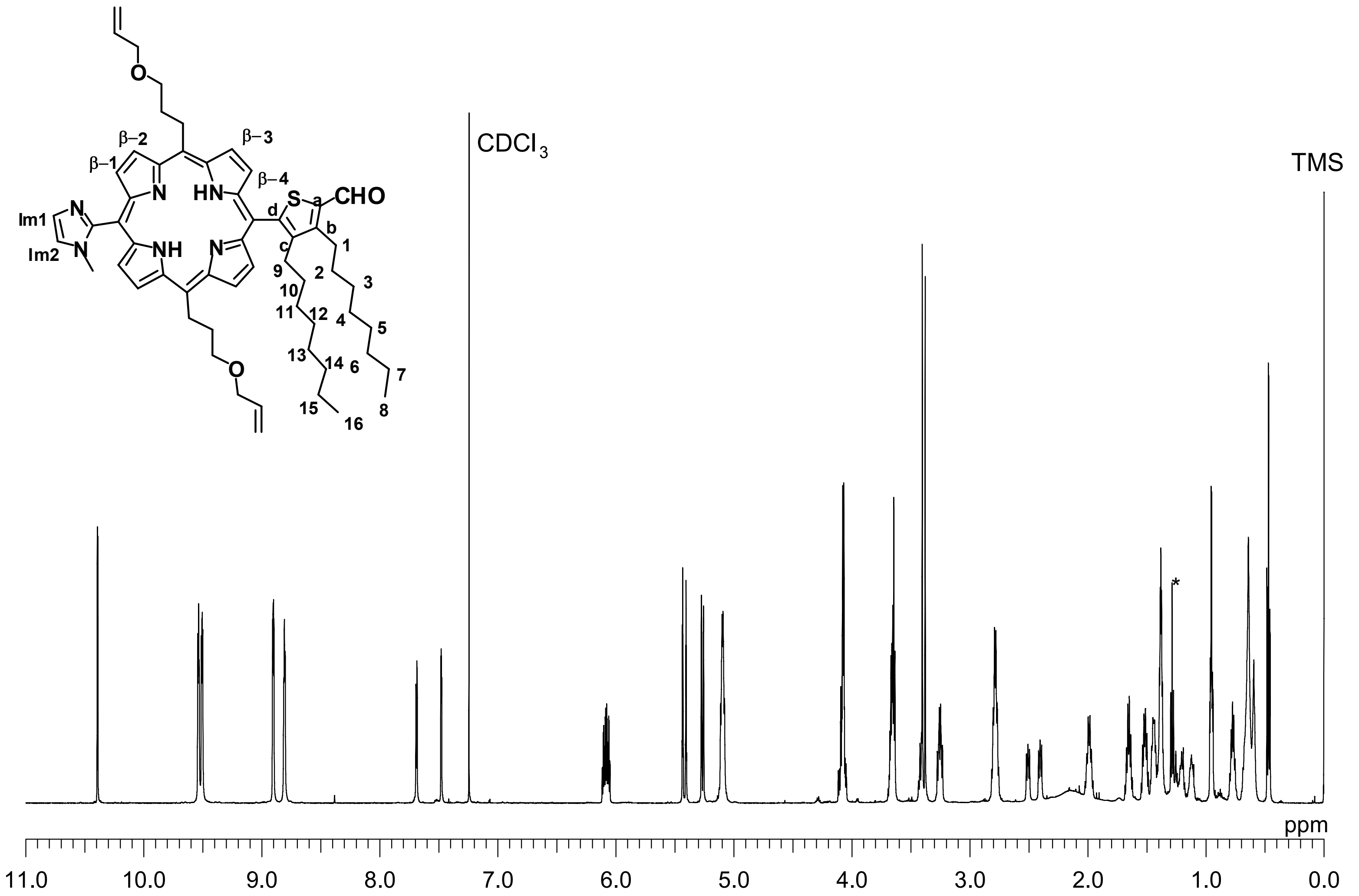


Figure S11. ^{1}H NMR (600 MHz) spectra of **6b** in CDCl$_3$ at 25°C. "*" denotes impurity.

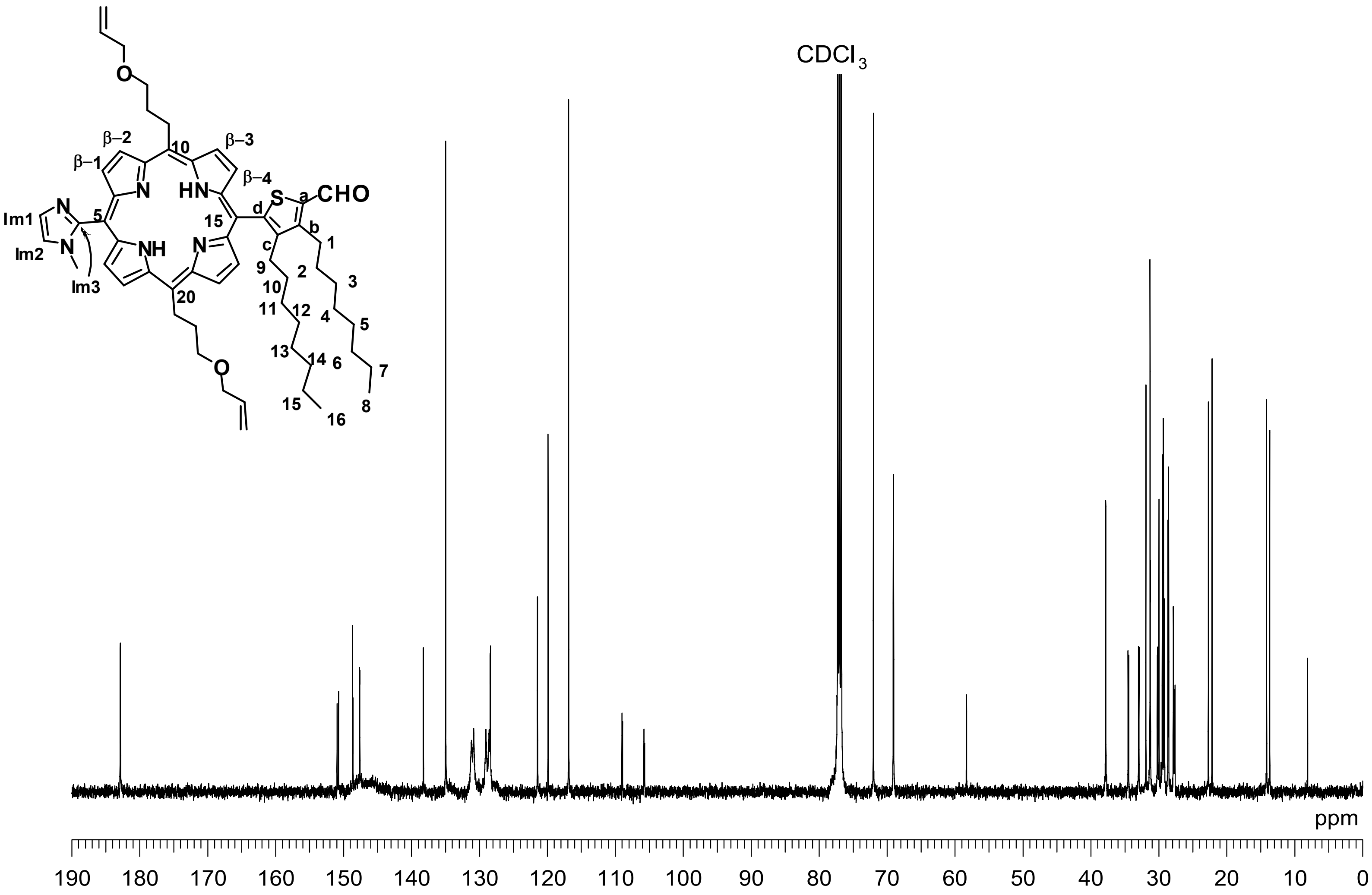


Figure S12. ^{13}C NMR (150 MHz) spectra of **6b** in $CDCl_3$ at 25°C.

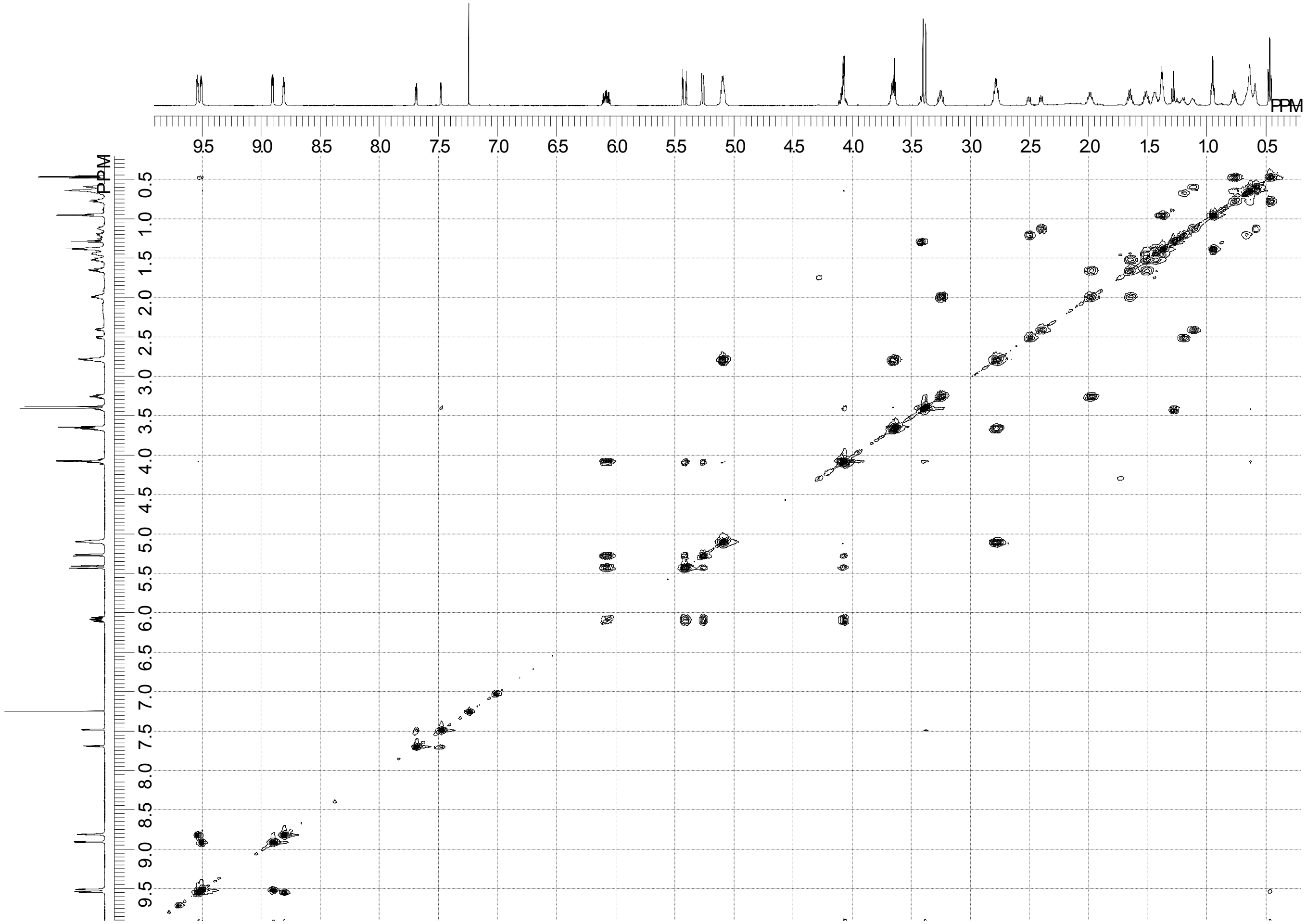


Figure S13. H-H COSY spectrum of **6b** in $CDCl_3$ at 25°C.

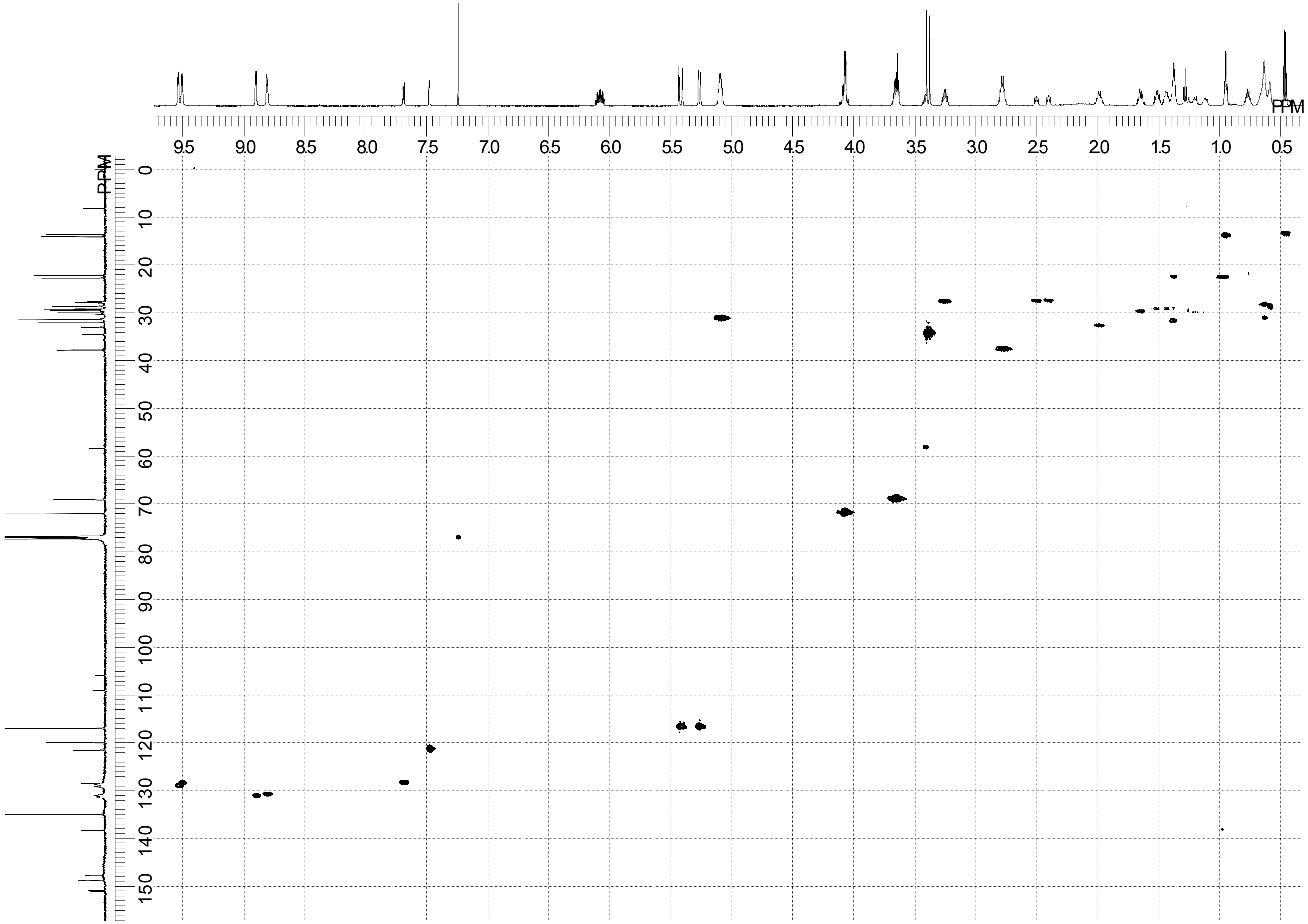


Figure S14. HMQC spectrum of **6b** in $CDCl_3$ at 25°C.

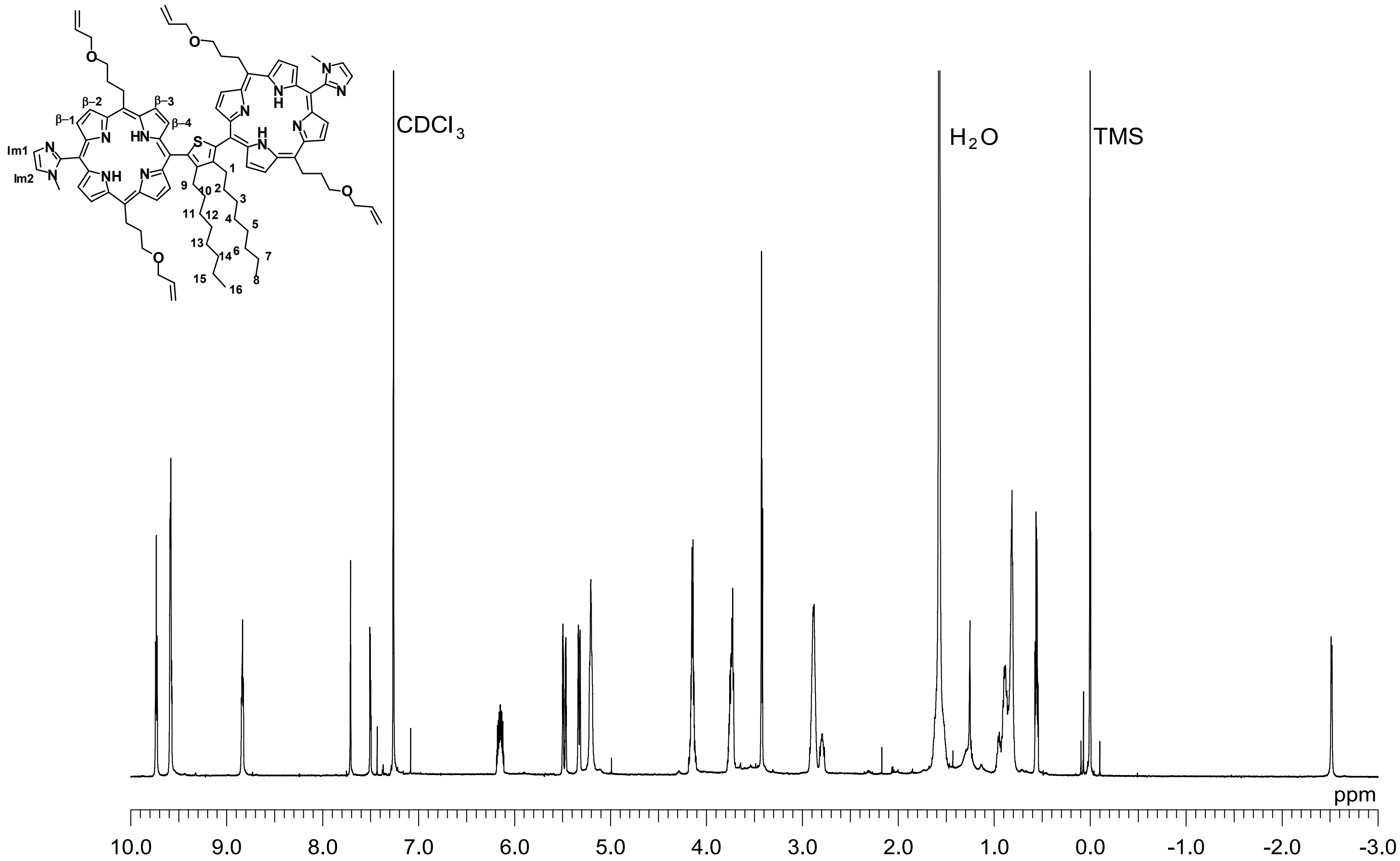


Figure S15. ^{1}H NMR (600 MHz) spectrum of **8b** in CDCl$_3$ at 25°C.

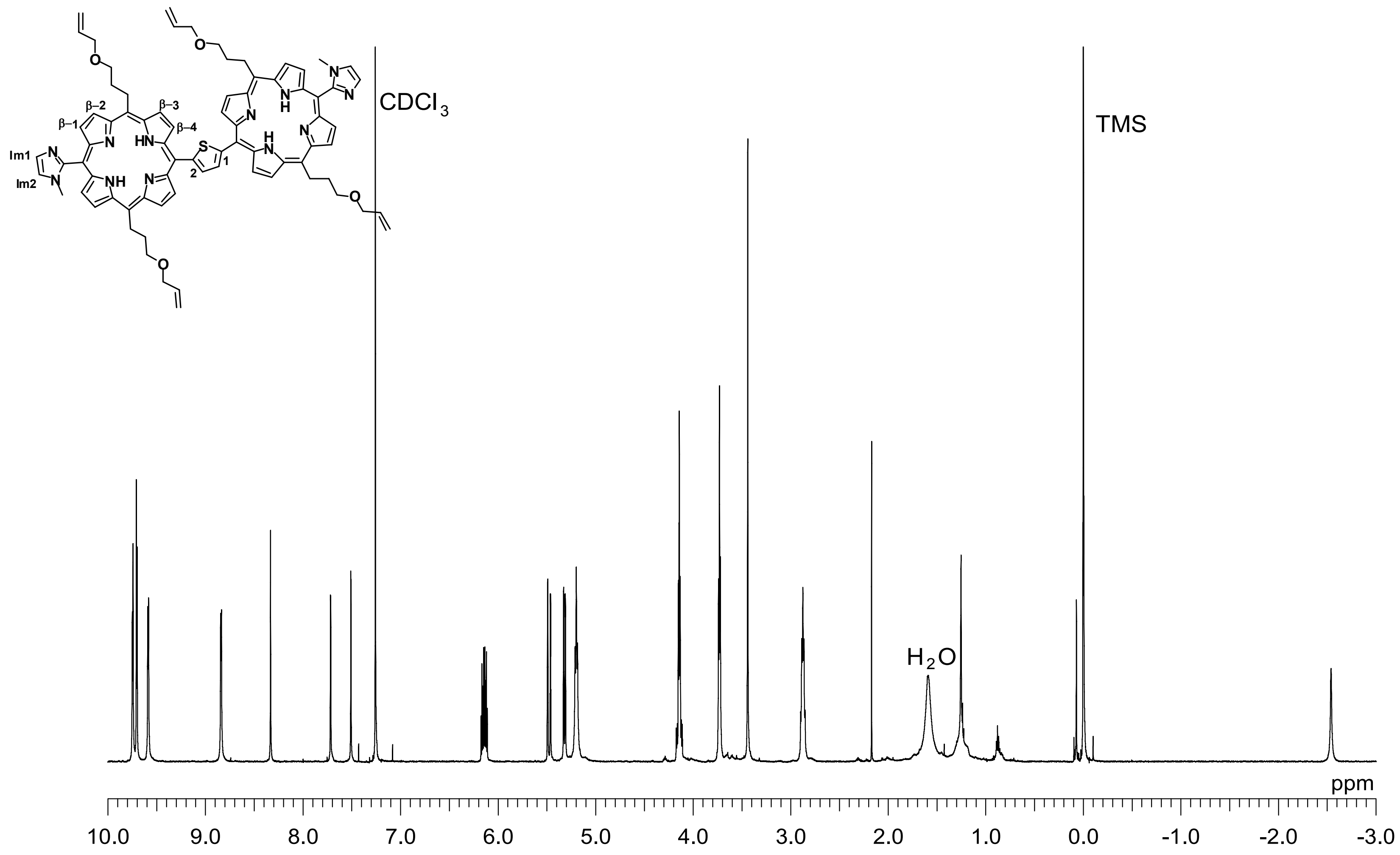


Figure S16. ^{1}H NMR (600 MHz) spectrum of **8a** in $CDCl_3$ at 25°C.

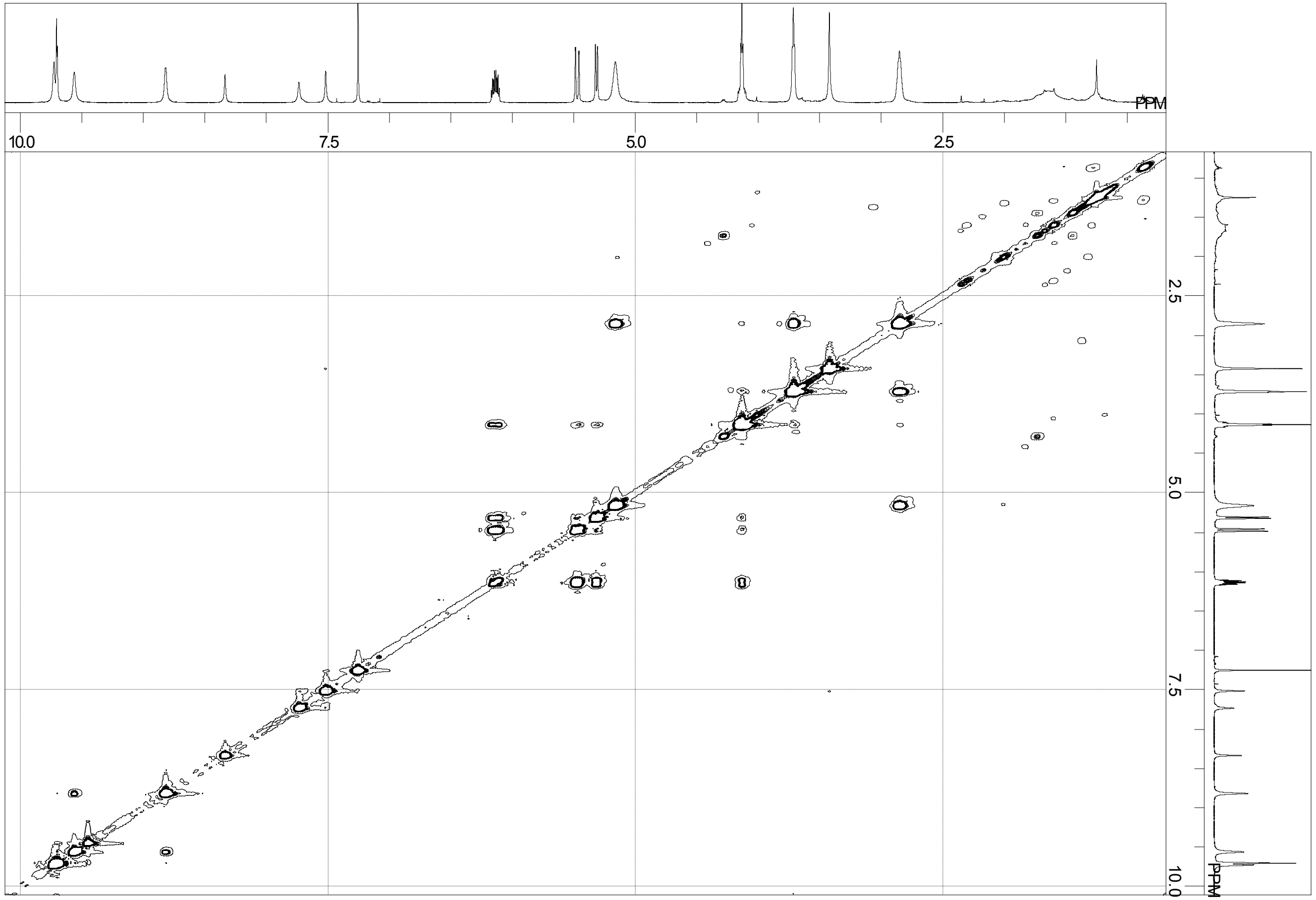


Figure S17. HH-COSY spectrum of **8a** in $CDCl_3$ at 25°C.

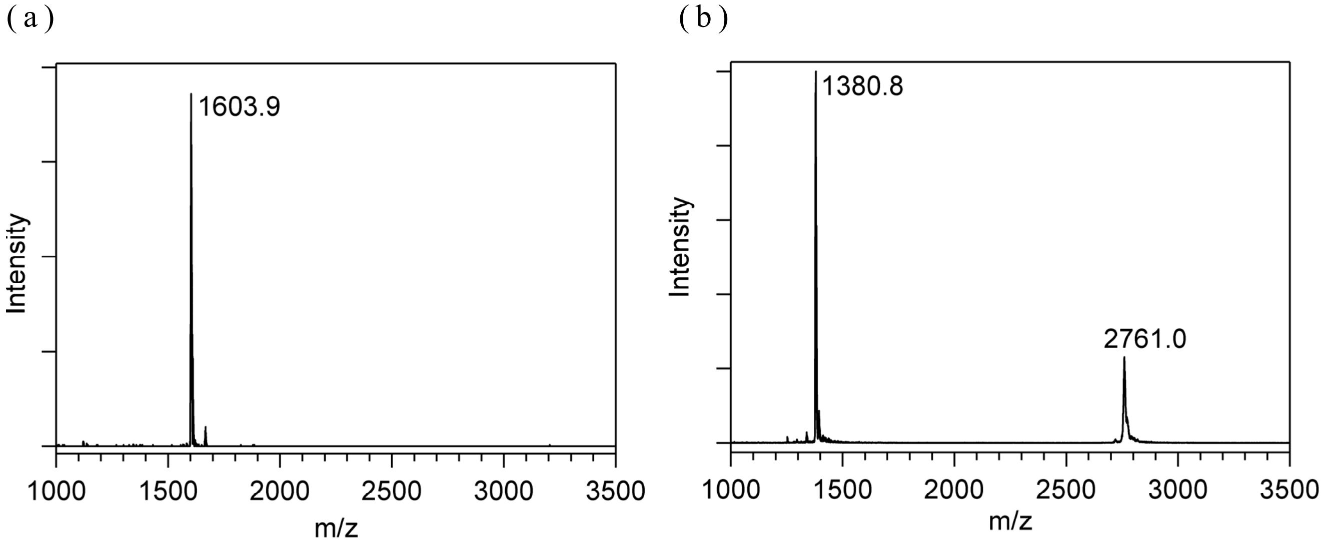


Figure S18. Mass spectrum of (a) **1b** and (b) **1a**.