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Electronic supplementary information

Phenothiazine cyclic hexamers: synthesis, properties, and complexation behavior with C_{60}

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Table of Contents

1. General Information

Commercially available reagents and solvents were used as received. Compounds **5b**[1] and **6b**[1] were prepared according to the literature procedures. Oil bath was used as the heat source. Column chromatography and plug filtrations were carried out with SiO_2. Thin-layer chromatography (TLC) was conducted on aluminum sheets coated with SiO_2 60 F_{254}. Melting points (M.p.) were measured with a hot-stage apparatus (Yanako MP-S3) and are uncorrected. Recycling gel-permeation chromatography (JAI LC-9210 NEXT) was performed with $CHCl_3$. ^1H and ^{13}C NMR spectra were measured on a spectrometer (JEOL JNM-ECA600, JNM-ECZ500, or JNM-ECS400) at 600, 500, or 400 MHz for ^1H and 150 or 125 MHz for ^{13}C, respectively. Chemical shifts are given as δ values. ^1H NMR shifts in deuterated solvents were relative to the residual solvent signals: $CDCl_3$ (δ 7.26), CD_2Cl_2 (δ 5.32), toluene-d_8 (δ 2.08), and THF-d_8 (δ 3.58). ^{13}C NMR shifts in deuterated solvents were relative to the residual solvent signals: $CDCl_3$ (δ 77.16) and CD_2Cl_2 (δ 53.82). The coupling constants (J) are given in Hz. The apparent resonance multiplicity is described as s (singlet), d (doublet), t (triplet), sept (septet), and m (multiplet). UV–vis spectra were measured on a SHIMADZU UV-2550. The absorption maxima (λ_{max}) are reported in nm with the molar absorptivity in brackets. Fluorescence spectra in CH_2Cl_2 were measured on a HITACHI F-4500 fluorescence spectrophotometer. Fluorescence lifetimes were measured by the time-correlated single-photon counting method using a nanosecond laser system based on an LED pulse (HORIBA). The absolute fluorescence quantum yields were measured by an integrating sphere system (Hamamatsu Photonics K.K.). The spectra were measured in a cuvette of 1 cm at 298 K. Cyclic voltammetry and differential pulse voltammetry were performed by using a cell equipped with a platinum as a working electrode, a platinum wire as a counter electrode, and Ag/Ag^+ as a referential electrode. All electrochemical measurements were performed in *o*-DCB solution (*ca*. 1.0×10^{-3} mol L^{-1}) containing 0.05 mol L^{-1} *n*-Bu_4NPF_6 at ambient temperature. MALDI-TOF-MS spectra were measured with a SHIMADZU AXIMA Performance mass spectrometer with dithranol as a matrix in a positive mode. ESI-TOF-MS spectra were measured on Bruker Compact^{TM} ESI-QTOF in a positive mode.

2. Supporting Figures and Tables

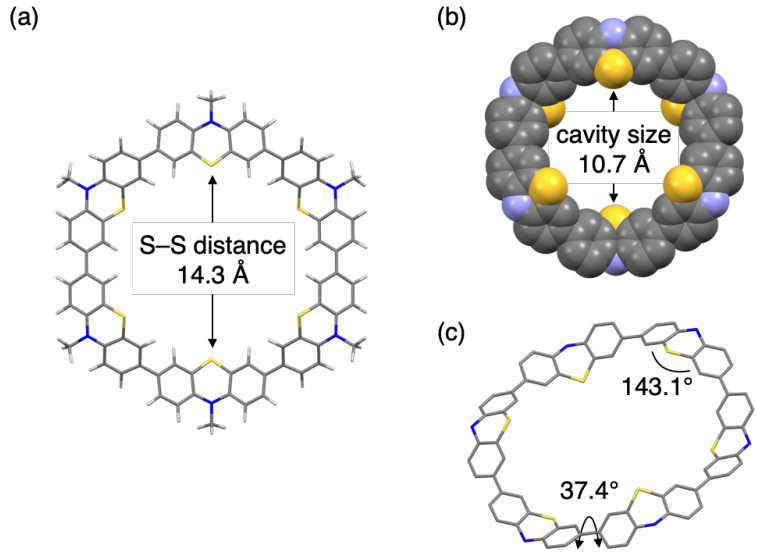


Figure S1. Calculated structures of **1a'** at B3LYP-D3/6-31G(d,p) level of theory.

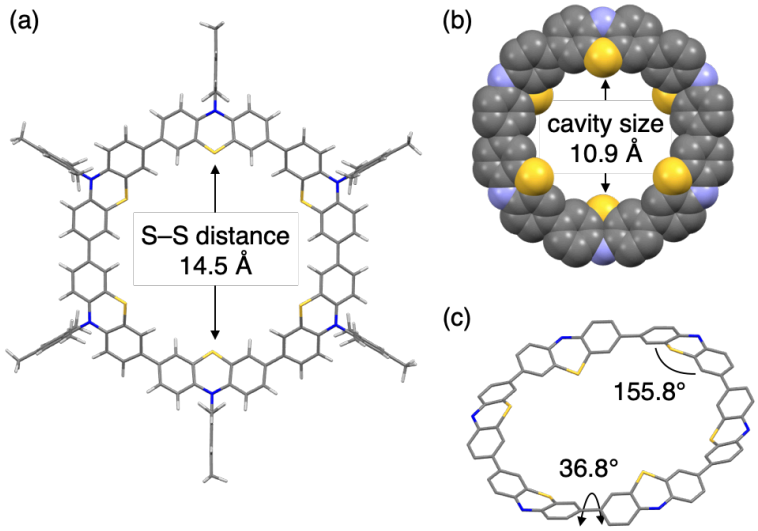


Figure S2. Calculated structures of **1b** at B3LYP-D3/6-31G(d,p) level of theory.

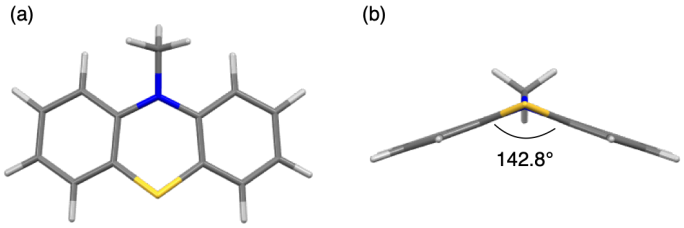


Figure S3. Calculated structures of *N*-methylphenothiazine at B3LYP-D3/6-31G(d,p) level of theory.

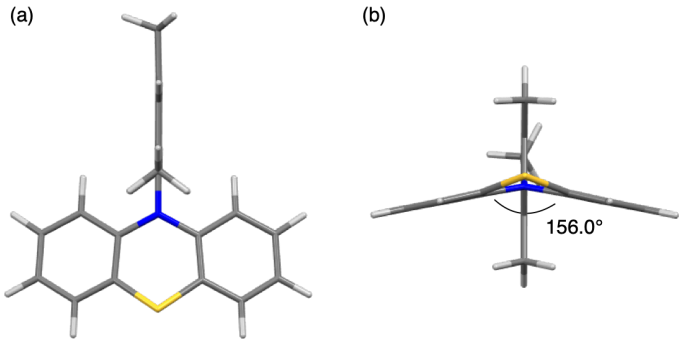


Figure S4. Calculated structures of *N*-mesitylphenothiazine at B3LYP-D3/6-31G(d,p) level of theory.

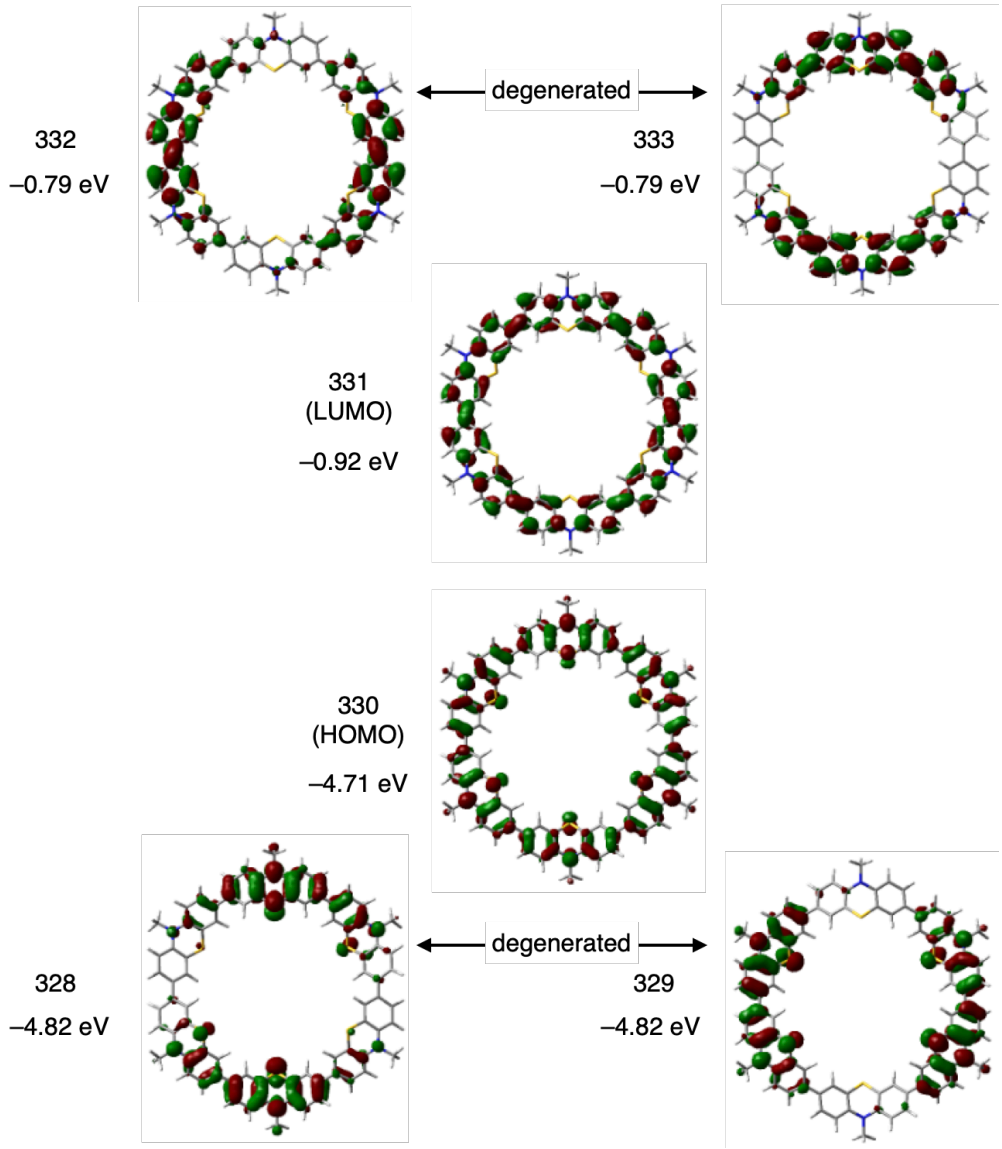


Figure S5. Frontier molecular orbitals and the energy levels of **1a'** calculated at B3LYP-D3/6-31G(d,p) level of theory (isosurface value = 0.02).

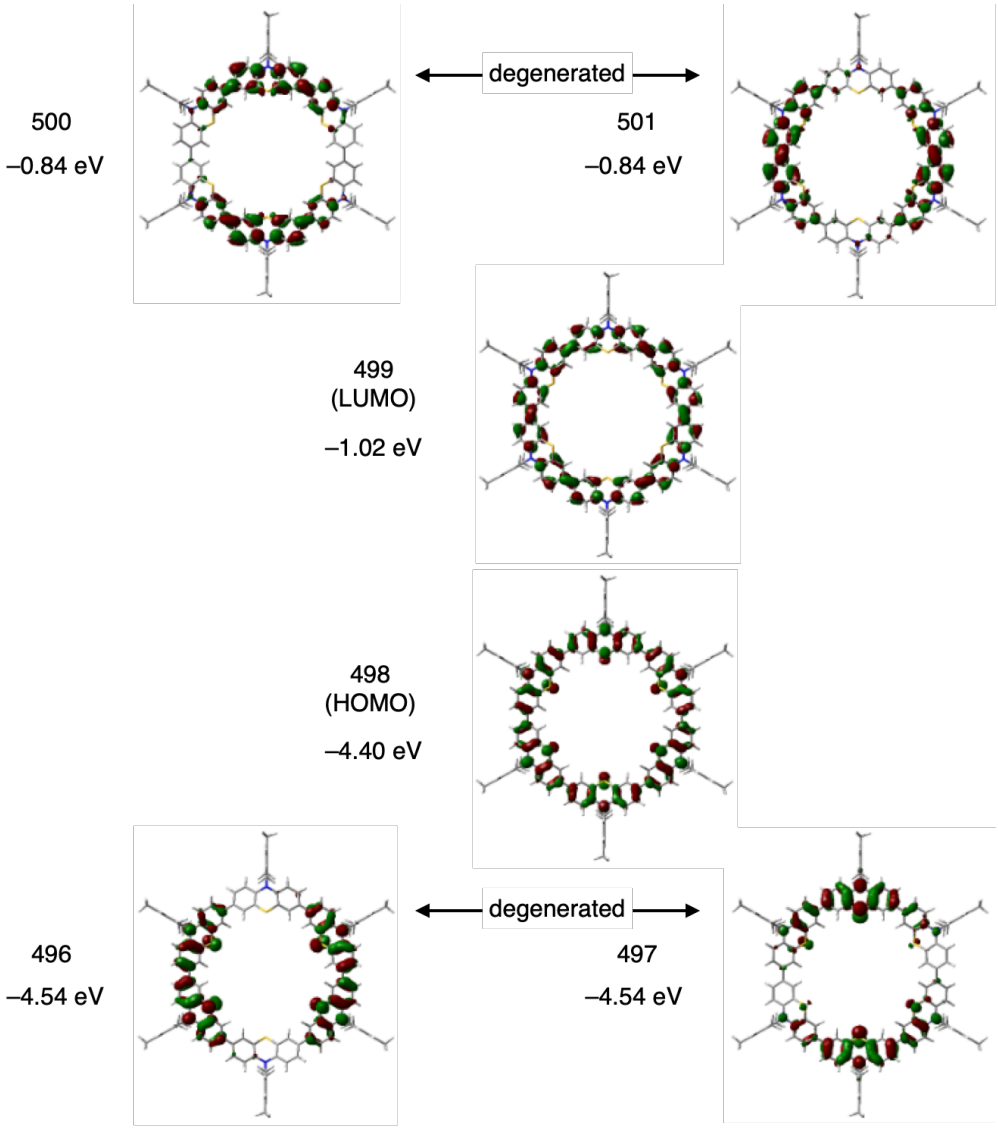


Figure S6. Frontier molecular orbitals and the energy levels of **1b** calculated at B3LYP-D3/6-31G(d,p) level of theory (isosurface value = 0.02).

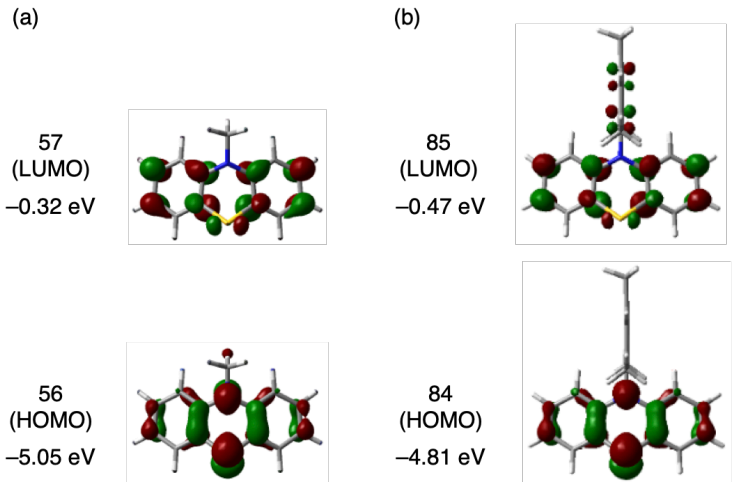


Figure S7. Frontier molecular orbitals and the energy levels of (a) *N*-methylphenothiazine and (b) *N*-mesitylphenothiazine calculated at B3LYP-D3/6-31G(d,p) level of theory (isosurface value = 0.05).

Table S1. Calculated Lowest Excitation Energies of **1a'** and **1b**[a]

	λ_{max}^{calcd} (nm)	f[b]	Configuration
1a'	392.12	0.0000	H (330) -> L (331) (62%)
	377.23	0.6771	H−1 (329) -> L (331) (48%), H (330) -> L+1 (332) (36%)
	377.19	0.6768	H−2 (328) -> L (331) (48%), H (330) -> L+2 (333) (36%)
1b	444.19	0.0000	H (498) -> L (499) (70%)
	421.17	0.8898	H−1 (497)-> L (499) (51%), H (498)-> L+1 (500) (36%)
	421.00	0.8878	H−2 (496)-> L (499) (51%), H (498)-> L+2 (501) (36%)

[a]TD-DFT (TD-B3LYP-D3/6-31+G(d,p)) calculations were carried out with use of optimized structures at B3LYP-D3/6-31G(d,p). [b]f = oscillator strength; H = HOMO; L = LUMO. The numbers in the parentheses correspond to the numbers of orbitals in Figure S5 for **1a'** and Figure S6 for **1b**.

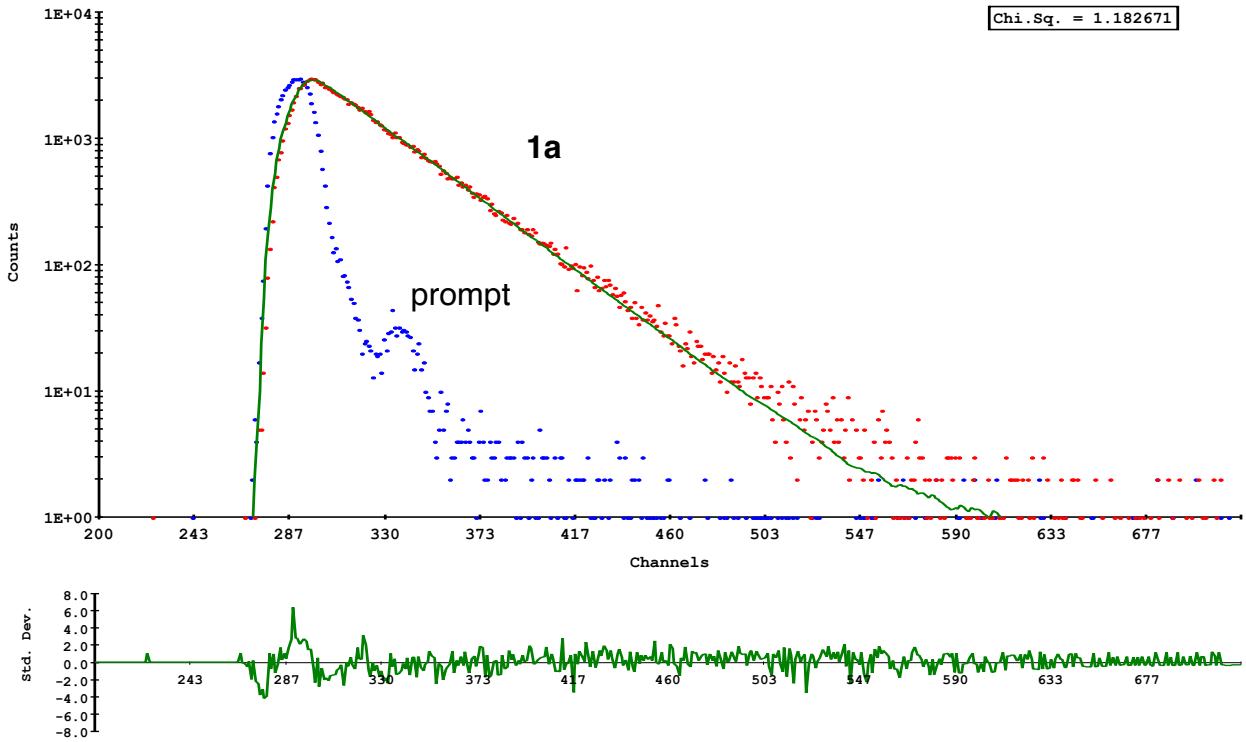


Figure S8. Fluorescence decay curve (top) and residual (bottom) of **1a** in CH_2Cl_2 after bubbling with Ar.

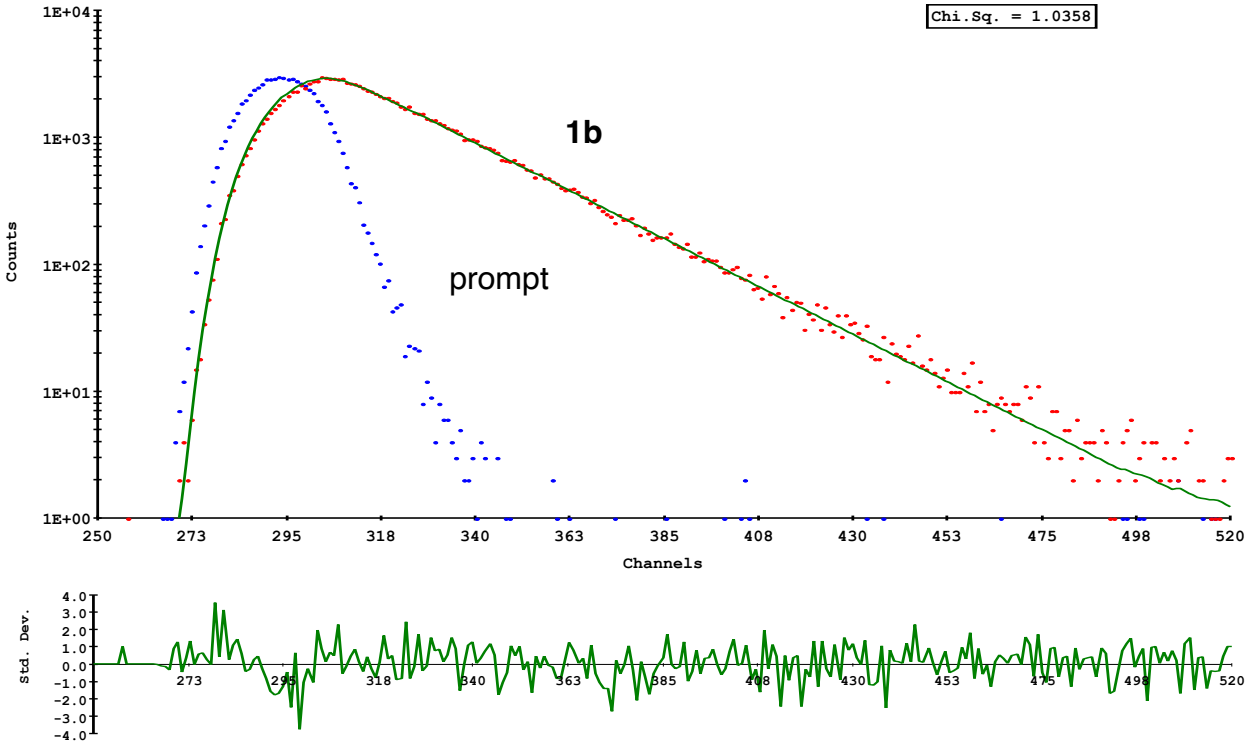


Figure S9. Fluorescence decay curve (top) and residual (bottom) of **1b** in CH_2Cl_2 after bubbling with Ar.

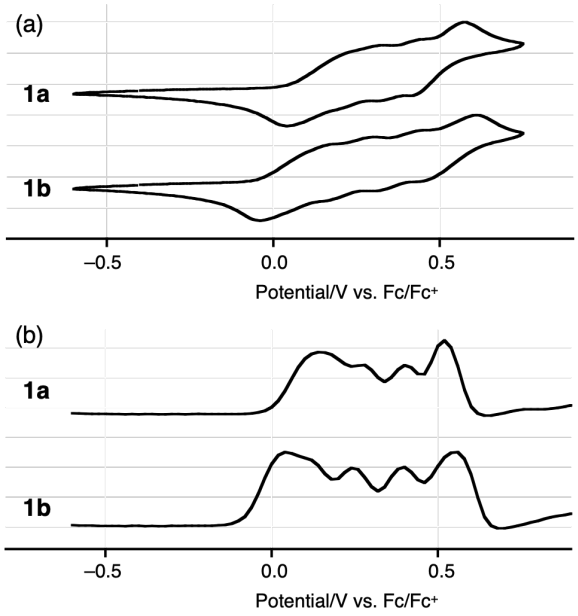


Figure S10. (a) Cyclic voltammograms of **1a** and **1b** measured at scan rate of 100 mV s^{-1} and (b) differential pulse voltammograms of **1a** and **1b** measured at pulse width of 100 ms in a period of 200 ms in *o*-DCB (0.05 mol L^{-1} nBu$_4$NPF$_6$) at 298 K.

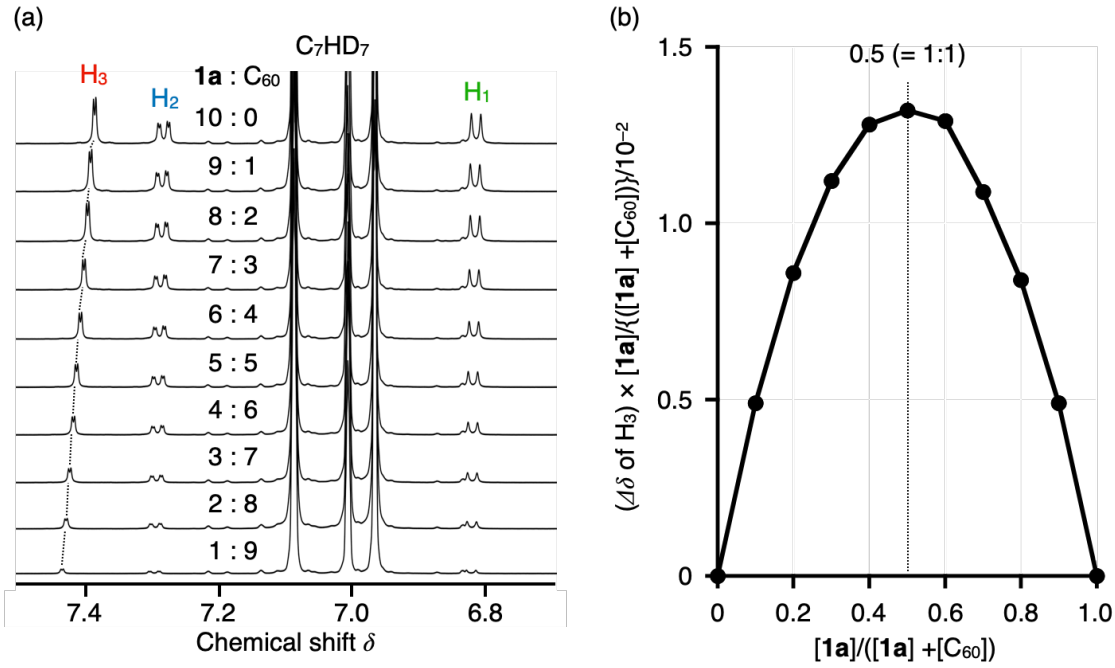


Figure S11. (a) ^{1}H NMR spectra of the mixture of **1a** and C_{60} in various ratios and (b) Job's plot of complexation of **1a** and C_{60} at the total concentration of 1.0 mM in toluene-d_8 at 298 K. [**1a**] = 0 to 1.0×10^{-3} mol L^{-1} and [C_{60}] = 0 to 1.0×10^{-3} mol L^{-1}.

Table S2. Observed ^{1}H NMR Chemical Shifts of H_1, H_2, and H_3 Signals of **1a** at Various Molar Fractions of **1a** and C_{60} in Toluene-d_8 at 298 K

[**1a**] /10^{-3} mol L^{-1}	[C_{60}] /10^{-3} mol L^{-1}	[**1a**]/([**1a**]+[C_{60}])	δ of H_1	δ of H_2	δ of H_3
1.0	0	1.0	6.816 (δ_0)	7.286 (δ_0)	7.390 (δ_0)
0.90	0.10	0.90	6.817	7.288	7.395
0.80	0.20	0.80	6.818	7.289	7.400
0.70	0.30	0.70	6.819	7.290	7.405
0.60	0.40	0.60	6.820	7.292	7.411
0.50	0.50	0.50	6.820	7.294	7.416
0.40	0.60	0.40	6.281	7.295	7.422
0.30	0.70	0.30	6.822	7.297	7.427
0.20	0.80	0.20	6.823	7.298	7.433
0.10	0.90	0.10	6.824	7.300	7.439

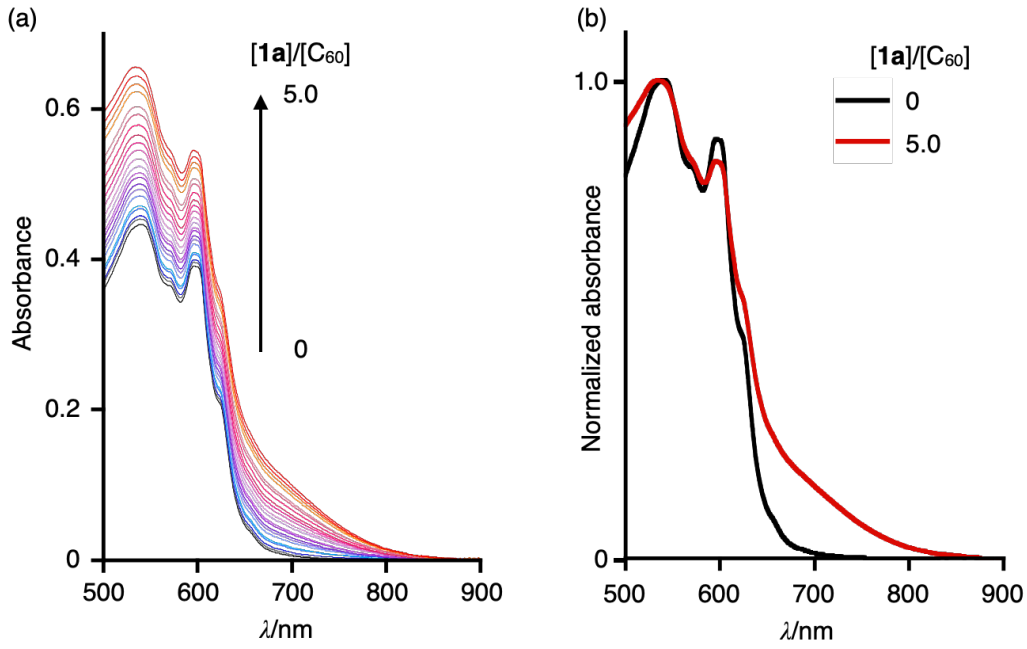


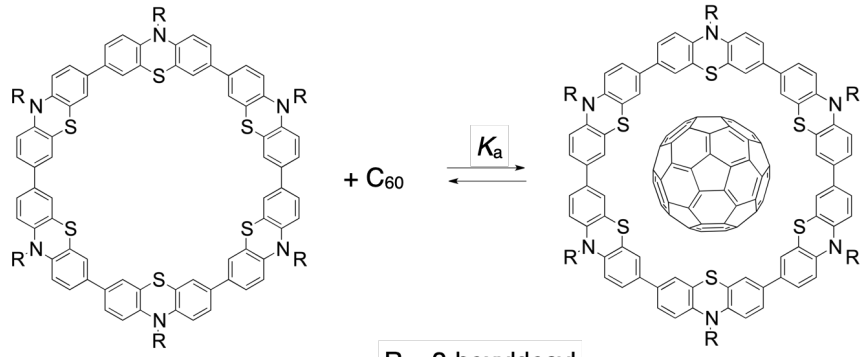
Figure S12. (a) UV–vis spectral change of C_{60} upon addition of **1a** in toluene at 298 K. [C_{60}] = 0.50×10^{-3} mol L^{-1} and [**1a**] = 0 to 2.5×10^{-3} mol L^{-1}. The absorption of **1a** was not observed in the region above 500 nm as shown in Fig. 3a. (b) Normalized UV–vis spectra of C_{60} (0.50×10^{-3} mol L^{-1}) (black line) and the mixture of C_{60} (0.50×10^{-3} mol L^{-1}) and **1a** (2.5×10^{-3} mol L^{-1}, 5.0 eq. to C_{60}) (red line) are also shown.

Table S3. Changes in Absorbances at 540, 600, and 611 nm at Various Molar Ratios of **1a** and C_{60} in Toluene at 298 K in the UV–vis Spectra

$[C_{60}]^a$	[**1a**]	[**1a**]/ $[C_{60}]$	A^b			$\Delta A = A - A_0{}^c$		
$/10^{-3}$ mol L^{-1}	$/10^{-3}$ mol L^{-1}		540 nm	600 nm	611 nm	540 nm	600 nm	611 nm
0.50	0	0	0.446	0.390	0.280	0	0	0
0.50	0.050	0.10	0.453	0.395	0.285	0.007	0.005	0.005
0.50	0.099	0.20	0.457	0.398	0.290	0.011	0.008	0.010
0.50	0.148	0.30	0.467	0.405	0.297	0.021	0.015	0.017
0.50	0.244	0.49	0.471	0.408	0.301	0.025	0.018	0.021
0.50	0.338	0.68	0.484	0.419	0.311	0.038	0.029	0.031
0.50	0.431	0.86	0.493	0.425	0.318	0.047	0.035	0.038
0.50	0.521	1.0	0.500	0.430	0.323	0.054	0.040	0.043
0.50	0.610	1.2	0.509	0.437	0.330	0.063	0.047	0.050
0.50	0.698	1.4	0.515	0.441	0.335	0.069	0.051	0.055
0.50	0.783	1.6	0.523	0.447	0.343	0.077	0.057	0.063
0.50	0.909	1.8	0.533	0.454	0.350	0.087	0.064	0.070
0.50	1.03	2.1	0.545	0.462	0.359	0.099	0.072	0.079
0.50	1.15	2.3	0.554	0.470	0.367	0.108	0.080	0.087
0.50	1.30	2.6	0.564	0.477	0.375	0.118	0.087	0.095
0.50	1.45	2.9	0.578	0.487	0.385	0.132	0.097	0.105
0.50	1.60	3.2	0.591	0.498	0.396	0.145	0.108	0.116
0.50	1.74	3.5	0.602	0.505	0.404	0.156	0.115	0.124
0.50	1.94	3.9	0.621	0.520	0.419	0.175	0.130	0.139
0.50	2.13	4.3	0.631	0.527	0.427	0.185	0.137	0.147
0.50	2.31	4.6	0.642	0.534	0.435	0.196	0.144	0.155
0.50	2.50	5.0	0.653	0.542	0.444	0.207	0.152	0.164

[a] Concentration of C_{60} was fixed at 0.50×10^{-3} mol L^{-1}.

[b] A: observed absorbance. [c] A_0: absorbance of $[C_{60}]$ without **1a** ([**1a**] = 0 mol L^{-1}).



1a **1a⊃C60**

$$\Delta A = \frac{l\Delta\varepsilon}{2K_a}\,[1 + K_a[\mathbf{1a}]_0 + K_a[C_{60}]_0 - \{(1 + K_a[\mathbf{1a}]_0 + K_a[C_{60}]_0)^2 - 4K_a^2[\mathbf{1a}]_0[C_{60}]_0\}^{1/2}]$$

ΔA = difference between absorbance of mixture of **1a** and C_{60} (A) and that of only C_{60} (A_0)

l = optical path length (= 1 cm)

$\Delta\varepsilon$ = difference between molar absorption coefficient of **1a**⊃C_{60} and that of C_{60}

K_a = binding constant of **1a** and C_{60}

$[\mathbf{1a}]_0$ = initial concentration of **1a** (= (0–2.5) × 10^{-3} mol L^{-1})

$[C_{60}]_0$ = initial concentration of C_{60} (= 0.5 × 10^{-3} mol L^{-1})

Figure S13. Complexation of **1a** with C_{60}.

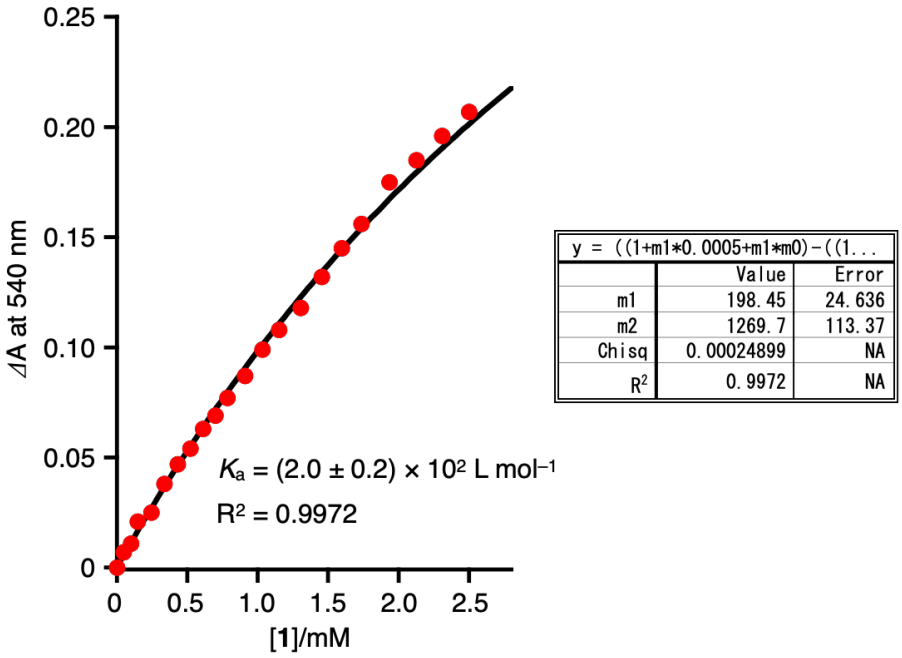
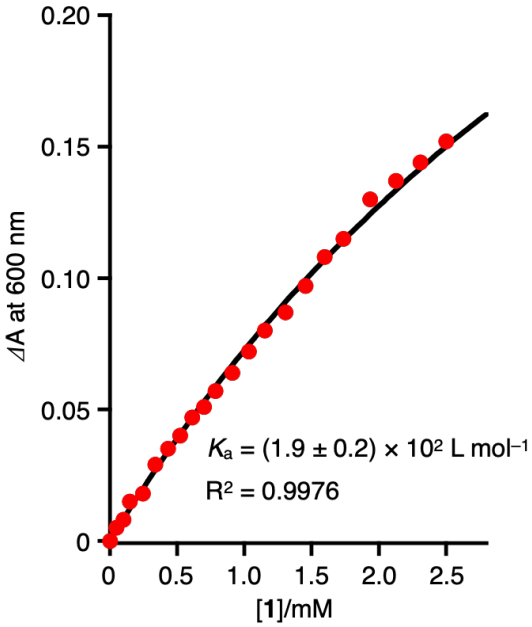
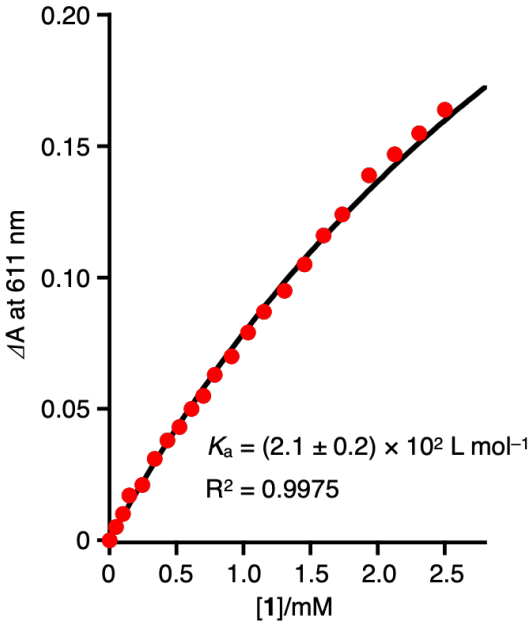


Figure S14. Non-linear curve-fitting plot of absorbance changes at 540 nm upon addition of **1a** to C_{60} to a 1:1 isotherm in toluene at 298 K. $[C_{60}]$ = 0.50 × 10^{-3} mol L^{-1} and $[\mathbf{1a}]$ = 0 to 2.5 × 10^{-3} mol L^{-1}.



y = ((1+m1*0.0005+m1*m0)-((1...		
	Value	Error
m1	185.31	21.86
m2	989.92	85.374
Chisq	0.00011561	NA
R^2	0.99761	NA

Figure S15. Non-linear curve-fitting plot of absorbance changes at 600 nm upon addition of **1a** to C_{60} to a 1:1 isotherm in toluene at 298 K. $[C_{60}] = 0.50 \times 10^{-3}$ mol L^{-1} and [**1a**] = 0 to 2.5×10^{-3} mol L^{-1}.



y = ((1+m1*0.0005+m1*m0)-((1...		
	Value	Error
m1	213.19	24.059
m2	962.05	76.719
Chisq	0.00014008	NA
R^2	0.99748	NA

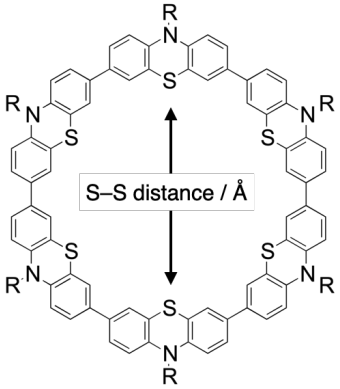
Figure S16. Non-linear curve-fitting plot of absorbance changes at 611 nm upon addition of **1a** to C_{60} to a 1:1 isotherm in toluene at 298 K. $[C_{60}] = 0.50 \times 10^{-3}$ mol L^{-1} and [**1a**] = 0 to 2.5×10^{-3} mol L^{-1}.

Table S4. Calculated Thermochemical Energies and Charges for Complexation between **1a'** and C_{60} at B3LYP-D3/6-31G(d,p) Level of Theory (gas phase, 1 atm, 298.15 K)

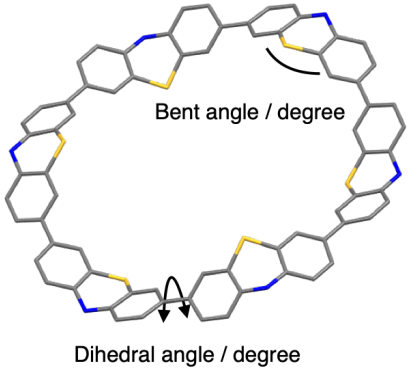
1a' + C_{60} → **1a'**⊃C_{60}

	ΔE [kJ mol^{-1}]	ΔH_{298} [kJ mol^{-1}]	ΔS_{298} [J mol^{-1} K^{-1}]	ΔG_{298} [kJ mol^{-1}]	Charge (natural)	
					on **1a'**	on C_{60}
uncorrected	−149.60	−142.69	−195.75	−84.33	−0.0085	0.0086
BSSE corrected	−109.39	−102.84	−180.27	−49.10		

Table S5. Comparison of Structural Parameters between Calculated **1a'** and **1a'**⊃C_{60} at B3LYP-D3/6-31G(d,p) Level of Theory



1a' R = Me



	S–S distances [Å]	Dihedral angles [degree]	Bent angles [degree]	Mean plane deviation [Å]
1a'[a]	14.3, 14.3, 14.3	37.3, 37.3, 37.4	143.1, 143.1, 143.1	0.459[b]
		37.4, 37.4, 37.4	143.1, 143.1, 143.1	
1a'⊃C_{60}[a]	13.8, 13.8, 13.8	33.0, 33.0, 33.1	135.0, 135.0, 135.0	0.528[c]
		33.1, 33.1, 33.1	135.0, 135.0, 135.0	

[a] Nearly S_6-symmetric on phenothiazine cyclic hexamer skeleton. [b] Calculated from the core 84 atoms in phenothiazine cyclic hexamer skeleton of **1a'**. [c] Calculated from the core 84 atoms in phenothiazine cyclic hexamer skeleton of **1a'**⊃C_{60}.

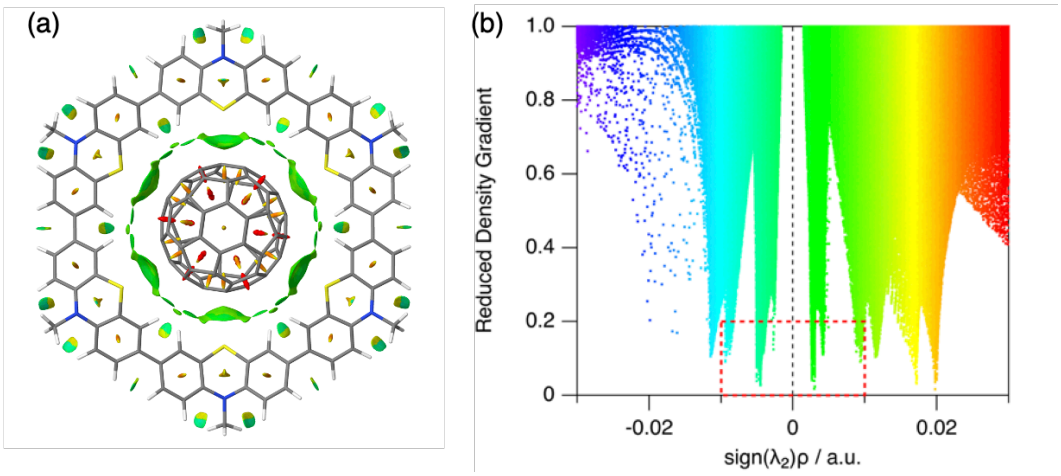


Figure S17. (a) NCI plots (isosurface value: 0.5) of **1a'**⊃C_{60}. Green isosurface shows regions having noncovalent (van der Waals) interactions. Blue and red isosurfaces show regions having attractive and repulsive interactions, respectively. (b) Reduced density gradient (RDG) plots for SCF density for **1a'**⊃C_{60}. Spikes at ρ below 0.01 a.u. (indicated by red dashed rectangle lines) are due to van der Waals interactions.

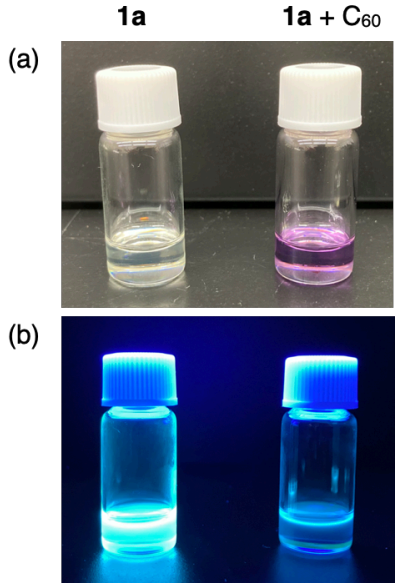


Figure S18. Photographic images of **1a** (0.50×10^{-4} mol L^{-1}) (left) and a mixture of **1a** (0.50×10^{-4} mol L^{-1}) and C_{60} (0.50×10^{-3} mol L^{-1}) (right) in toluene under (a) room right and (b) black light (λ = 365 nm).

3. Synthesis of Compounds

Preparation of N-(2-hexyldecyl)phenothiazine

To a mixture of 10*H*-phenothiazine (5.87 g, 29.5 mmol) and NaOH (7.39 g, 185 mmol) in DMSO (45 mL) was added dropwise 1-bromo-2-hexyldecane (10.8 g, 35.3 mmol) in DMSO (30 mL). The mixture was stirred at room temperature for 17 h. After addition of water (120 mL), the aqueous phase was extracted with toluene (90 mL × 3). The organic phase was washed with water (90 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane) to give *N*-(2-hexyldecyl)phenothiazine (8.61 g, 20.3 mmol, 69%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16–7.11 (4H, m), 6.90 (2H, t, J = 7.5 Hz), 6.8 (2H, d, J = 8.0 Hz), 3.71 (2H, d, J = 6.6 Hz), 1.97 (1H, sept, J = 6.6 Hz), 1.44–1.16 (24H, m), 0.90–0.82 (6H, m). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 145.9, 127.6, 127.1, 126.0, 122.4, 116.0, 34.5, 32.0. 31.84, 31.77, 31.76. 30.1, 29.8, 29.6, 29.4, 26.4, 26.3, 22.83, 22.77, 14.3, 14.2. ESI-TOF-MS (positive): *m/z* calcd. for $C_{28}H_{41}NS^+$ 423.2954; found 423.2960 [M^+].

Preparation of 5a

To a solution of *N*-(2-hexyldecyl)phenothiazine (8.36 g, 19.7 mmol) in CH_2Cl_2 (50 mL) was added dropwise Br_2 (2.2 mL, 43 mmol) at room temperature under argon atmosphere. The mixture was stirred at room temperature for 2 h. After addition of saturated aqueous $NaHSO_3$ (50 mL), the aqueous phase was extracted with CH_2Cl_2 (15 mL × 3). The organic phase was washed with water (30 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane) to give **5a** (11.2 g, 19.3 mmol, 98%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.22 (4H, m), 6.69 (2H, d, J = 9.4 Hz), 3.62 (2H, d, J = 6.6 Hz), 1.89 (1H, sept, J = 6.6 Hz), 1.40–1.14 (24H, m), 0.92–0.82 (6H, m). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 144.7, 130.2, 129.9, 127.4, 117.3, 114.9, 51.8, 34.6, 32.0, 31.8, 31.7, 31.6, 30.1, 29.7, 29.5, 29.4, 26.3, 22.83, 22.76, 14.3, 14.2. ESI-TOF-MS (positive): *m/z* calcd. for $C_{28}H_{39}Br_2NS^+$ 581.1146; found 581.1144 [M^+].

Preparation of 6a

To a solution of **5a** (2.51 g, 4.32 mmol) in THF (50 mL) was added dropwise a *n*-BuLi hexane solution (1.6 M, 6.0 mL, 9.6 mmol) at −78 °C under argon atmosphere. After the solution was stirred at −78 °C for 1 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.0 mL, 9.9 mmol) was added dropwise to the mixture. Then, the mixture was warmed to room temperature and stirred for 21 h. The reaction was quenched by addition of water (50 mL), and the aqueous phase was extracted with CH_2Cl_2 (30 mL × 3). The combined organic phase was washed with water (30 mL × 3), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 = 1:1) to give **6a** (1.61 g, 2.38 mmol, 55%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (2H, d, J = 7.9 Hz), 7.54 (2H, s), 6.82 (2H, d, J = 7.9 Hz), 3.73 (2H, d, J = 6.5 Hz), 1.94 (1H, sept, J = 6.5 Hz), 1.32 (24H, s), 1.40–1.14 (24H, m), 0.90–0.81 (6H, m). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 148.0, 134.02, 133.97, 125.2, 122.6, 115.4, 83.7, 51.6, 34.7, 32.0, 31.8, 31.69, 31.67, 30.0, 29.7, 29.5, 29.4, 26.34, 26.32, 24.9, 22.8, 22.7, 14.3, 14.2. ESI-TOF-MS (positive): *m/z* calcd. for $C_{40}H_{63}B_2NO_4S^+$ 675.4672; found 675.4666 [M^+].

Preparation of 7a

A mixture of **5a** (1.76 g, 3.03 mmol), **6a** (676 mg, 1.00 mmol), and K_2CO_3 (706 mg, 5.11 mmol) in 1,2-dimethoxyethane (80 mL) and H_2O (40 mL) was bubbled with argon for 1 h. $Pd(PPh_3)_4$ (81 mg, 0.070 mmol) was added to the mixture, and the resulting mixture was refluxed for 2 h under argon atmosphere. After addition of water (150 mL), the aqueous phase was extracted with CH_2Cl_2 (50 mL × 3). The combined organic phase was washed with water (50 mL × 3), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 = 30:1) to give **7a** (548 mg, 0.385 mmol, 39%) as yellow solids. ^{1}H NMR (400 MHz, THF-d_8): δ 7.43–7.36 (8H, m), 7.30–7.25 (4H, m), 7.01 (4H, d, J = 9.0 Hz), 6.88 (2H, d, J = 8.7 Hz), 3.84 (2H, d, J = 6.9 Hz), 3.79 (4H, d, J = 7.1 Hz), 2.10–1.92 (3H, m), 1.53–1.18 (72H, m), 0.90–0.80 (18H, m). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 145.3, 145.0, 144.7, 134.9, 134.5, 130.2, 130.0, 128.1, 126.2, 125.8, 125.7, 125.55, 125.51, 125.49, 117.6, 116.7, 116.5, 114.6, 51.9, 35.0, 34.9, 32.3, 32.2, 32.1, 31.94, 31.90, 30.4, 30.0, 29.90, 29.88, 29.8, 29.7, 26.7, 26.6, 23.15, 23.07, 14.4, 14.3. ESI-TOF-MS (positive): *m/z* calcd. for $C_{84}H_{117}Br_2N_3S_3^+$ 1423.6764; found 1423.6764 [M^+].

Preparation of 1a

A mixture of **7a** (300 mg, 0.211 mmol), 1,5-cyclooctadiene (77 mg, 0.63 mmol), and 2,2'-bipyridine (106 mg, 0.679 mmol) in THF (100 mL) was bubbled with argon for 1 h. $Ni(cod)_2$ (189 mg, 0.687 mmol) was added to the mixture, and the resulting mixture was refluxed for 2 h under argon atmosphere. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 = 5:1) and recycling GPC ($CHCl_3$, 9.0 mL/min) to give **1a** (51 mg, 20 μmol, 19%) as yellow solids. ^1H NMR (600 MHz, toluene-d_8): δ 7.39 (12H, d, J = 2.1 Hz), 7.29 (12H, dd, J = 8.5 & 2.1 Hz), 6.82 (12H, d, J = 8.5 Hz), 3.68 (12H, d, J = 6.6 Hz), 2.21–2.15 (6H, m), 1.55–1.19 (144H, m), 0.94–0.87 (36H, m). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 145.0, 134.7, 126.2, 125.7, 125.4, 116.4, 51.9, 35.0, 32.3, 32.1, 31.99, 31.95, 30.4, 30.1, 29.9, 29.7, 26.6, 23.1, 23.0, 14.29, 14.26. MALDI-TOF-MS (Dithranol, positive): m/z 2528.8 [M^+]. ESI-TOF-MS (positive): m/z calcd. for $C_{168}H_{234}N_6S_6^{2+}$ 1264.3420; found 1264.3384 [M^{2+}].

Preparation of 7b

A mixture of **5b**[1] (1.25 g, 2.63 mmol), **6b**[1] (501 mg, 0.880 mmol), and K_2CO_3 (606 mg, 4.38 mmol) in 1,2-dimethoxyethane (70 mL) and H_2O (14 mL) was bubbled with argon for 30 min. Then, $Pd(PPh_3)_4$ (72 mg, 0.062 mmol) was added to the mixture, and the resulting mixture was refluxed for 2 h under argon atmosphere. The reaction was quenched by addition of water (50 mL), and the aqueous phase was extracted with CH_2Cl_2 (40 mL × 3). The combined organic phase was washed with water (40 mL × 2), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/CH_2Cl_2 = 30:1) to give **7b** (437 mg, 0.395 mmol, 45%) as yellow solids. M.p. 231–233 °C. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.09 (6H, s), 7.02–6.99 (6H, m), 6.89–6.82 (6H, m), 5.87 (4H, d, J = 8.4 Hz), 5.73 (2H, d, J = 8.4 Hz), 2.37 (3H, s), 2.36 (6H, s), 2.16 (6H, s), 2.14 (12H, s). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 140.9, 140.4, 140.2, 139.1, 138.9, 138.2, 138.1, 134.9, 134.6, 134.2, 133.8, 130.8, 130.7, 130.2, 128.7, 125.4, 125.2, 124.01, 123.99, 120.9, 119.0, 118.5, 115.7, 114.9, 114.7, 114.0, 21.26, 21.25, 17.92, 17.88. UV-Vis (CH_2Cl_2): λ_{max} (ε) 272 (69500), 346 (21300), 418 nm (21100). ESI-TOF-MS (positive): m/z calcd. for $C_{63}H_{51}Br_2N_3S_3^+$ 1105.1594; found 1105.1605 [M^+].

Preparation of 1b

A mixture of **7b** (425 mg, 0.384 mmol), 1,5-cyclooctadiene (113 mg, 1.04 mmol), and 2,2'-bipyridyl (156 mg, 0.999 mmol) in THF (100 mL) was bubbled with argon for 1 h. $Ni(cod)_2$ (266 mg, 0.967 mmol) was added to the mixture, and the resulting mixture was refluxed for 3 h under argon atmosphere. After the solvent was removed by under reduced pressure, the residue was purified by column chromatography (SiO_2, hexane/$CHCl_3$ = 3:1) and washed with toluene and CH_2Cl_2. The filtrate was further purified by recycling GPC ($CHCl_3$, 9.0 mL/min) to give **1b** (41 mg, 0.022 mmol, 11%) as yellow solids. M.p. > 300 °C. ^{1}H NMR (400 MHz, THF-d_8): δ 7.28 (12H, d, J = 2.3 Hz), 7.11 (12H, s), 6.93 (12H, dd, J = 8.7 & 2.3 Hz), 5.91 (12H, d, J = 8.7 Hz), 2.36 (18H, s), 2.16 (36H, s). ^{13}C{^{1}H} NMR: Not available due to low solubility. UV-Vis (CH_2Cl_2): λ_{max} (ε) 287 (165000), 413 nm (58400). MALDI-TOF-MS (Dithranol, positive): *m/z* 1891.4 [M^+]. ESI-TOF-MS (positive): *m/z* calcd. for $C_{126}H_{102}N_6S_6^{2+}$ 945.8255; found 945.8227 [M^{2+}].

4. X-ray Crystallographic Analysis

All measurements were performed on a Rigaku XtaLAB P100 diffractometer with Mo-Kα (0.71075 Å) radiation. Using Olex2[2], the X-ray crystal structures were solved by direct methods (SHELXT[3]) and refined by full-matrix least-squares analysis (2018/3[4]), using an isotropic extinction correction. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. CCDC-2314515 (**1b**) contains the supplementary crystallographic data for this paper.

X-ray crystallographic data for 1b

1b: Crystal data at 130 K for $C_{126}H_{102}N_6S_6$, M_r = 1892.49, cubic, space group *I*a-3 (No. 206), D_{calcd} = 0.696 g cm^{-3}, Z = 8, $a = b = c$ = 33.0600(2) Å, V = 36133.4 (7) Å^3, Mo-$K\alpha$ radiation, λ = 0.71073 Å, μ = 0.107 mm^{-1}. A clear dark yellow block crystal (linear dimensions *ca*. 0.15 × 0.13 × 0.09 mm^3) was obtained from $CHCl_3$/ethyl acetate at room temperature. Numbers of measured and unique reflections were 266714 and 5514, respectively (R_{int} = 0.0776). Final $R(F)$ = 0.0574, $wR(F^2)$ = 0.1837 for 211 parameters and 4297 reflections with $I > 2\sigma(I)$ (corresponding R values are 0.0679 and 0.1938, respectively, for all data).

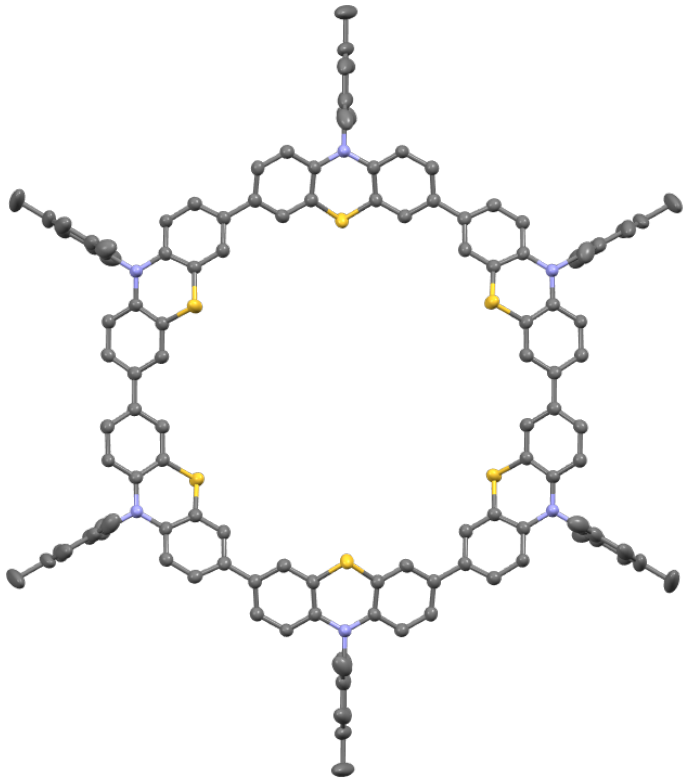


Figure S19. ORTEP drawing of **1b** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity.

5. Theoretical Calculations

DFT calculations were carried out by Gaussian16 program.[5] The optimized structures were obtained by the DFT calculations at the B3LYP-D3/6-31G(d,p) level of theory. Frequency calculations were carried out to ensure that the structures obtained were a minimum, giving no imaginary wavenumber. The molecular orbitals and energies were calculated at the B3LYP-D3/6-31G(d,p) by using the optimized structures, and the given energies were zero-point corrected. The calculations were also carried out with basis set superposition error (BSSE) correction by CP methods. TD-DFT calculations were employed at the B3LYP-D3/6-31+G(d,p) by using the optimized structures. The calculations for the NCI analysis were carried out with NCIPLOT 4.0 program.[6–8] The input file (.wfx format) for the optimized structure of **1a'**⊃C_{60} at the B3LYP-D3/6-31G(d,p) level was prepared by the Gaussian program. The output file (.dat format) was used to generate reduced density gradient (RDG) vs. sign(λ_2)ρ plot (Figure S17b). The 3D RDG isosurface (Figure S17a) was visualized by using other output files (grad.cube, dens.cube, and .vmd formats) with Jmol program.[9]

Table S6. Cartesian Coordinates of **1a'** at the B3LYP-D3/6-31G(d,p) Level

Electronic energy = –5721.676781 hartree

Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-6.657876	-1.867959	1.724476
2	6	0	-7.850356	-0.805149	0.932054
3	6	0	-7.123473	-3.396195	0.932208
4	6	0	-9.143596	-1.300543	0.668767
5	6	0	-8.485649	-3.645755	0.668996
6	7	0	-9.449375	-2.651216	0.949347
7	6	0	-7.521984	0.516921	0.652499
8	6	0	-6.155204	-4.354418	0.652813
9	6	0	-8.473443	1.413671	0.138157
10	6	0	-6.501244	-5.615289	0.138627
11	6	0	-9.761001	0.920261	-0.110350
12	6	0	-7.857583	-5.863645	-0.109994
13	6	0	-10.087708	-0.412931	0.132535
14	6	0	-8.830089	-4.895035	0.132748
15	16	0	-4.947334	4.832188	-1.725899
16	6	0	-4.622786	6.396200	-0.933157

17	6	0	-6.503191	4.471090	-0.933178
18	6	0	-5.698446	7.268370	-0.669483
19	6	0	-7.400408	5.525906	-0.669497
20	7	0	-7.021102	6.857876	-0.949998
21	6	0	-3.313639	6.772666	-0.653764
22	6	0	-6.848852	3.153423	-0.653779
23	6	0	-3.012686	8.044915	-0.139058
24	6	0	-8.113649	2.822670	-0.139139
25	6	0	-4.083716	8.913112	0.109966
26	6	0	-9.006886	3.873028	0.109748
27	6	0	-5.401676	8.529565	-0.132825
28	6	0	-8.654394	5.199591	-0.133003
29	16	0	1.710952	6.699747	1.724429
30	6	0	3.227817	7.201210	0.932206
31	6	0	0.620356	7.867027	0.932005
32	6	0	3.445280	8.568865	0.668971
33	6	0	1.085267	9.171522	0.668831
34	7	0	2.428347	9.508974	0.949472
35	6	0	4.208592	6.255785	0.652843
36	6	0	-0.693624	7.507605	0.652506
37	6	0	5.460915	6.631417	0.138559
38	6	0	-1.612505	8.437686	0.138201
39	6	0	5.677254	7.993186	-0.110179
40	6	0	-1.149501	9.736526	-0.110272
41	6	0	4.686039	8.942657	0.132602
42	6	0	0.175594	10.094484	0.132570
43	16	0	6.657876	1.867959	-1.724476
44	6	0	7.850356	0.805149	-0.932054
45	6	0	7.123473	3.396195	-0.932208
46	6	0	9.143596	1.300543	-0.668767
47	6	0	8.485649	3.645755	-0.668996
48	7	0	9.449375	2.651216	-0.949347
49	6	0	7.521984	-0.516921	-0.652499
50	6	0	6.155204	4.354418	-0.652813
51	6	0	8.473443	-1.413671	-0.138157
52	6	0	6.501244	5.615289	-0.138627
53	6	0	9.761001	-0.920261	0.110350
54	6	0	7.857583	5.863645	0.109994

55	6	0	10.087708	0.412931	-0.132535
56	6	0	8.830089	4.895035	-0.132748
57	16	0	4.947334	-4.832188	1.725899
58	6	0	4.622786	-6.396200	0.933157
59	6	0	6.503191	-4.471090	0.933178
60	6	0	5.698446	-7.268370	0.669483
61	6	0	7.400408	-5.525906	0.669497
62	7	0	7.021102	-6.857876	0.949998
63	6	0	3.313639	-6.772666	0.653764
64	6	0	6.848852	-3.153423	0.653779
65	6	0	3.012686	-8.044915	0.139058
66	6	0	8.113649	-2.822670	0.139139
67	6	0	4.083716	-8.913112	-0.109966
68	6	0	9.006886	-3.873028	-0.109748
69	6	0	5.401676	-8.529565	0.132825
70	6	0	8.654394	-5.199591	0.133003
71	16	0	-1.710952	-6.699747	-1.724429
72	6	0	-3.227817	-7.201210	-0.932206
73	6	0	-0.620356	-7.867027	-0.932005
74	6	0	-3.445280	-8.568865	-0.668971
75	6	0	-1.085267	-9.171522	-0.668831
76	7	0	-2.428347	-9.508974	-0.949472
77	6	0	-4.208592	-6.255785	-0.652843
78	6	0	0.693624	-7.507605	-0.652506
79	6	0	-5.460915	-6.631417	-0.138559
80	6	0	1.612505	-8.437686	-0.138201
81	6	0	-5.677254	-7.993186	0.110179
82	6	0	1.149501	-9.736526	0.110272
83	6	0	-4.686039	-8.942657	-0.132602
84	6	0	-0.175594	-10.094484	-0.132570
85	1	0	-6.518820	0.865427	0.877353
86	1	0	-5.117203	-4.130051	0.877651
87	1	0	-10.510595	1.575072	-0.543785
88	1	0	-8.157096	-6.812789	-0.543508
89	1	0	-11.082430	-0.762051	-0.118324
90	1	0	-9.861186	-5.114271	-0.118309
91	1	0	-2.510258	6.078182	-0.878861
92	1	0	-6.135671	2.366684	-0.878877

93	1	0	-3.891419	9.889520	0.543791
94	1	0	-9.978519	3.657808	0.543487
95	1	0	-6.201260	9.216381	0.118506
96	1	0	-9.359812	5.982892	0.118197
97	1	0	4.008765	5.212795	0.877704
98	1	0	-1.018391	6.496509	0.877376
99	1	0	6.619069	8.314912	-0.543756
100	1	0	-1.821806	10.470489	-0.543725
101	1	0	4.880942	9.978613	-0.118472
102	1	0	0.501225	11.097151	-0.118342
103	1	0	6.518820	-0.865427	-0.877353
104	1	0	5.117203	4.130051	-0.877651
105	1	0	10.510595	-1.575072	0.543785
106	1	0	8.157096	6.812789	0.543508
107	1	0	11.082430	0.762051	0.118324
108	1	0	9.861186	5.114271	0.118309
109	1	0	2.510258	-6.078182	0.878861
110	1	0	6.135671	-2.366684	0.878877
111	1	0	3.891419	-9.889520	-0.543791
112	1	0	9.978519	-3.657808	-0.543487
113	1	0	6.201260	-9.216381	-0.118506
114	1	0	9.359812	-5.982892	-0.118197
115	1	0	-4.008765	-5.212795	-0.877704
116	1	0	1.018391	-6.496509	-0.877376
117	1	0	-6.619069	-8.314912	0.543756
118	1	0	1.821806	-10.470489	0.543725
119	1	0	-4.880942	-9.978613	0.118472
120	1	0	-0.501225	-11.097151	0.118342
121	6	0	-10.848042	-3.043387	1.009382
122	1	0	-11.311276	-3.173468	0.019451
123	1	0	-10.930588	-3.984358	1.557107
124	1	0	-11.407783	-2.282250	1.556777
125	6	0	-8.060318	7.872832	-1.008858
126	1	0	-8.403939	8.208493	-0.018523
127	1	0	-7.681723	8.738442	-1.556194
128	1	0	-8.916815	7.473792	-1.556079
129	6	0	2.787766	10.916440	1.009418
130	1	0	3.726695	11.020857	1.557025

131	1	0	2.906842	11.382545	0.019449
132	1	0	2.013870	11.458267	1.556940
133	6	0	10.848042	3.043387	-1.009382
134	1	0	11.311276	3.173468	-0.019451
135	1	0	10.930588	3.984358	-1.557107
136	1	0	11.407783	2.282250	-1.556777
137	6	0	8.060318	-7.872832	1.008858
138	1	0	8.403939	-8.208493	0.018523
139	1	0	7.681723	-8.738442	1.556194
140	1	0	8.916815	-7.473792	1.556079
141	6	0	-2.787766	-10.916440	-1.009418
142	1	0	-3.726695	-11.020857	-1.557025
143	1	0	-2.906842	-11.382545	-0.019449
144	1	0	-2.013870	-11.458267	-1.556940

Table S7. Cartesian Coordinates of **1b** at the B3LYP-D3/6-31G(d,p) Level

Electronic energy = –7579.221976 hartree

Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-6.855332	-1.928553	1.399514
2	6	0	-8.036867	-0.849286	0.618749
3	6	0	-7.303448	-3.463641	0.616447
4	6	0	-9.309434	-1.327299	0.243948
5	6	0	-8.639279	-3.717016	0.242444
6	7	0	-9.624181	-2.704447	0.288395
7	6	0	-7.719069	0.500033	0.500518
8	6	0	-6.330101	-4.450441	0.496010
9	6	0	-8.660477	1.446621	0.064749
10	6	0	-6.642016	-5.748131	0.059130
11	6	0	-9.941753	0.976054	-0.250133
12	6	0	-7.981384	-6.012642	-0.254401
13	6	0	-10.257976	-0.378023	-0.172242
14	6	0	-8.955848	-5.020865	-0.174468
15	16	0	-5.090568	4.968549	-1.384193

16	6	0	-4.748886	6.532918	-0.605405
17	6	0	-6.646093	4.589914	-0.604832
18	6	0	-5.799973	7.396127	-0.233169
19	6	0	-7.533915	5.620216	-0.232520
20	7	0	-7.149697	6.979533	-0.278331
21	6	0	-3.421741	6.933244	-0.486671
22	6	0	-7.014644	3.253660	-0.485562
23	6	0	-3.073661	8.222797	-0.053039
24	6	0	-8.295317	2.875097	-0.051160
25	6	0	-4.122535	9.097087	0.259486
26	6	0	-9.194182	3.902933	0.261574
27	6	0	-5.453023	8.693071	0.181108
28	6	0	-8.822013	5.242663	0.182622
29	16	0	1.763255	6.899515	1.398449
30	6	0	3.287231	7.384256	0.615478
31	6	0	0.655893	8.054297	0.616979
32	6	0	3.508346	8.725671	0.241024
33	6	0	1.103128	9.337856	0.241671
34	7	0	2.472249	9.685829	0.286345
35	6	0	4.297259	6.434972	0.495492
36	6	0	-0.685365	7.703982	0.498749
37	6	0	5.587094	6.777973	0.058638
38	6	0	-1.654316	8.622098	0.062440
39	6	0	5.819271	8.123254	-0.255185
40	6	0	-1.214694	9.914127	-0.253211
41	6	0	4.804257	9.073519	-0.175686
42	6	0	0.131342	10.262968	-0.175295
43	16	0	6.855332	1.928553	-1.399514
44	6	0	8.036867	0.849286	-0.618749
45	6	0	7.303448	3.463641	-0.616447
46	6	0	9.309434	1.327299	-0.243948
47	6	0	8.639279	3.717016	-0.242444
48	7	0	9.624181	2.704447	-0.288395
49	6	0	7.719069	-0.500033	-0.500518
50	6	0	6.330101	4.450441	-0.496010
51	6	0	8.660477	-1.446621	-0.064749
52	6	0	6.642016	5.748131	-0.059130
53	6	0	9.941753	-0.976054	0.250133

54	6	0	7.981384	6.012642	0.254401
55	6	0	10.257976	0.378023	0.172242
56	6	0	8.955848	5.020865	0.174468
57	16	0	5.090568	-4.968549	1.384193
58	6	0	4.748886	-6.532918	0.605405
59	6	0	6.646093	-4.589914	0.604832
60	6	0	5.799973	-7.396127	0.233169
61	6	0	7.533915	-5.620216	0.232520
62	7	0	7.149697	-6.979533	0.278331
63	6	0	3.421741	-6.933244	0.486671
64	6	0	7.014644	-3.253660	0.485562
65	6	0	3.073661	-8.222797	0.053039
66	6	0	8.295317	-2.875097	0.051160
67	6	0	4.122535	-9.097087	-0.259486
68	6	0	9.194182	-3.902933	-0.261574
69	6	0	5.453023	-8.693071	-0.181108
70	6	0	8.822013	-5.242663	-0.182622
71	16	0	-1.763255	-6.899515	-1.398449
72	6	0	-3.287231	-7.384256	-0.615478
73	6	0	-0.655893	-8.054297	-0.616979
74	6	0	-3.508346	-8.725671	-0.241024
75	6	0	-1.103128	-9.337856	-0.241671
76	7	0	-2.472249	-9.685829	-0.286345
77	6	0	-4.297259	-6.434972	-0.495492
78	6	0	0.685365	-7.703982	-0.498749
79	6	0	-5.587094	-6.777973	-0.058638
80	6	0	1.654316	-8.622098	-0.062440
81	6	0	-5.819271	-8.123254	0.255185
82	6	0	1.214694	-9.914127	0.253211
83	6	0	-4.804257	-9.073519	0.175686
84	6	0	-0.131342	-10.262968	0.175295
85	1	0	-6.728524	0.827948	0.800706
86	1	0	-5.313232	-4.215545	0.795401
87	1	0	-10.698315	1.669937	-0.603085
88	1	0	-8.266848	-6.998552	-0.607865
89	1	0	-11.253974	-0.705285	-0.443234
90	1	0	-9.977005	-5.259331	-0.444432
91	1	0	-2.641866	6.239243	-0.784991

92	1	0	-6.302418	2.490472	-0.784062
93	1	0	-3.900744	10.100004	0.610775
94	1	0	-10.191345	3.657419	0.613455
95	1	0	-6.235024	9.392150	0.449927
96	1	0	-9.539382	6.007882	0.451603
97	1	0	4.086928	5.412815	0.795135
98	1	0	-0.989361	6.705975	0.799397
99	1	0	6.798055	8.432325	-0.608601
100	1	0	-1.926542	10.653518	-0.606760
101	1	0	5.018036	10.100053	-0.445925
102	1	0	0.434546	11.266401	-0.446832
103	1	0	6.728524	-0.827948	-0.800706
104	1	0	5.313232	4.215545	-0.795401
105	1	0	10.698315	-1.669937	0.603085
106	1	0	8.266848	6.998552	0.607865
107	1	0	11.253974	0.705285	0.443234
108	1	0	9.977005	5.259331	0.444432
109	1	0	2.641866	-6.239243	0.784991
110	1	0	6.302418	-2.490472	0.784062
111	1	0	3.900744	-10.100004	-0.610775
112	1	0	10.191345	-3.657419	-0.613455
113	1	0	6.235024	-9.392150	-0.449927
114	1	0	9.539382	-6.007882	-0.451603
115	1	0	-4.086928	-5.412815	-0.795135
116	1	0	0.989361	-6.705975	-0.799397
117	1	0	-6.798055	-8.432325	0.608601
118	1	0	1.926542	-10.653518	0.606760
119	1	0	-5.018036	-10.100053	0.445925
120	1	0	-0.434546	-11.266401	0.446832
121	6	0	-11.002018	-3.090591	0.121067
122	6	0	-11.770530	-3.299261	1.276069
123	6	0	-11.547636	-3.244312	-1.165579
124	6	0	-13.109516	-3.670406	1.123199
125	6	0	-12.891046	-3.616870	-1.270467
126	6	0	-13.685737	-3.836634	-0.140087
127	1	0	-13.716001	-3.831840	2.011252
128	1	0	-13.327086	-3.736463	-2.259506
129	6	0	-8.173877	7.979357	-0.114571

130	6	0	-8.746255	8.528765	-1.271593
131	6	0	-8.581163	8.378223	1.170639
132	6	0	-9.743793	9.496569	-1.122226
133	6	0	-9.581852	9.349250	1.272011
134	6	0	-10.172067	9.920892	0.139543
135	1	0	-10.197100	9.927384	-2.011850
136	1	0	-9.908849	9.665126	2.259905
137	6	0	2.824984	11.072541	0.118596
138	6	0	3.014316	11.846413	1.273368
139	6	0	2.966046	11.621183	-1.168198
140	6	0	3.352931	13.193934	1.120088
141	6	0	3.305930	12.973215	-1.273501
142	6	0	3.505789	13.773484	-0.143378
143	1	0	3.499131	13.804553	2.007949
144	1	0	3.415361	13.411600	-2.262678
145	6	0	11.002018	3.090591	-0.121067
146	6	0	11.770530	3.299261	-1.276069
147	6	0	11.547636	3.244312	1.165579
148	6	0	13.109516	3.670406	-1.123199
149	6	0	12.891046	3.616870	1.270467
150	6	0	13.685737	3.836634	0.140087
151	1	0	13.716001	3.831840	-2.011252
152	1	0	13.327086	3.736463	2.259506
153	6	0	8.173877	-7.979357	0.114571
154	6	0	8.746255	-8.528765	1.271593
155	6	0	8.581163	-8.378223	-1.170639
156	6	0	9.743793	-9.496569	1.122226
157	6	0	9.581852	-9.349250	-1.272011
158	6	0	10.172067	-9.920892	-0.139543
159	1	0	10.197100	-9.927384	2.011850
160	1	0	9.908849	-9.665126	-2.259905
161	6	0	-2.824984	-11.072541	-0.118596
162	6	0	-3.014316	-11.846413	-1.273368
163	6	0	-2.966046	-11.621183	1.168198
164	6	0	-3.352931	-13.193934	-1.120088
165	6	0	-3.305930	-12.973215	1.273501
166	6	0	-3.505789	-13.773484	0.143378
167	1	0	-3.499131	-13.804553	-2.007949

168	1	0	-3.415361	-13.411600	2.262678
169	6	0	-11.151004	-3.117908	2.638757
170	1	0	-10.294988	-3.787443	2.772650
171	1	0	-10.773530	-2.097819	2.765401
172	1	0	-11.875454	-3.319554	3.431668
173	6	0	-10.703040	-3.008099	-2.393669
174	1	0	-9.839623	-3.680878	-2.414806
175	1	0	-11.283804	-3.167651	-3.305385
176	1	0	-10.309049	-1.986851	-2.412055
177	6	0	-15.124795	-4.272400	-0.281838
178	1	0	-15.201429	-5.366218	-0.316686
179	1	0	-15.732116	-3.930565	0.561510
180	1	0	-15.572164	-3.885663	-1.202342
181	6	0	-8.286757	8.070409	-2.632630
182	1	0	-7.214640	8.249184	-2.765324
183	1	0	-8.442361	6.993683	-2.757271
184	1	0	-8.825531	8.592102	-3.427457
185	6	0	-7.955175	7.768390	2.400924
186	1	0	-6.874515	7.942364	2.422026
187	1	0	-8.387806	8.190731	3.311108
188	1	0	-8.101614	6.683658	2.422738
189	6	0	-11.226451	10.993308	0.277632
190	1	0	-10.769276	11.989844	0.315436
191	1	0	-11.919651	10.985374	-0.568723
192	1	0	-11.808487	10.867674	1.195515
193	6	0	2.847240	11.223312	2.636254
194	1	0	1.836351	10.821780	2.762701
195	1	0	3.536859	10.383495	2.770769
196	1	0	3.031319	11.952684	3.428925
197	6	0	2.750922	10.770623	-2.396045
198	1	0	2.896483	11.354801	-3.307921
199	1	0	3.444616	9.923900	-2.416703
200	1	0	1.739615	10.351776	-2.414559
201	6	0	3.906542	15.222653	-0.285445
202	1	0	3.547952	15.822136	0.556561
203	1	0	4.998236	15.326012	-0.317756
204	1	0	3.511155	15.659654	-1.207248
205	6	0	11.151004	3.117908	-2.638757

206	1	0	10.294988	3.787443	-2.772650
207	1	0	10.773530	2.097819	-2.765401
208	1	0	11.875454	3.319554	-3.431668
209	6	0	10.703040	3.008099	2.393669
210	1	0	9.839623	3.680878	2.414806
211	1	0	11.283804	3.167651	3.305385
212	1	0	10.309049	1.986851	2.412055
213	6	0	15.124795	4.272400	0.281838
214	1	0	15.201429	5.366218	0.316686
215	1	0	15.732116	3.930565	-0.561510
216	1	0	15.572164	3.885663	1.202342
217	6	0	8.286757	-8.070409	2.632630
218	1	0	7.214640	-8.249184	2.765324
219	1	0	8.442361	-6.993683	2.757271
220	1	0	8.825531	-8.592102	3.427457
221	6	0	7.955175	-7.768390	-2.400924
222	1	0	6.874515	-7.942364	-2.422026
223	1	0	8.387806	-8.190731	-3.311108
224	1	0	8.101614	-6.683658	-2.422738
225	6	0	11.226451	-10.993308	-0.277632
226	1	0	10.769276	-11.989844	-0.315436
227	1	0	11.919651	-10.985374	0.568723
228	1	0	11.808487	-10.867674	-1.195515
229	6	0	-2.847240	-11.223312	-2.636254
230	1	0	-1.836351	-10.821780	-2.762701
231	1	0	-3.536859	-10.383495	-2.770769
232	1	0	-3.031319	-11.952684	-3.428925
233	6	0	-2.750922	-10.770623	2.396045
234	1	0	-2.896483	-11.354801	3.307921
235	1	0	-3.444616	-9.923900	2.416703
236	1	0	-1.739615	-10.351776	2.414559
237	6	0	-3.906542	-15.222653	0.285445
238	1	0	-3.547952	-15.822136	-0.556561
239	1	0	-4.998236	-15.326012	0.317756
240	1	0	-3.511155	-15.659654	1.207248

Table S8. Cartesian Coordinates of *N*-Methylphenothiazine at the B3LYP-D3/6-31G(d,p) Level
Electronic energy = –954.781502 hartree
Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.000000	-1.814744	0.772295
2	6	0	1.348823	-0.830099	0.146662
3	6	0	-1.348823	-0.830099	0.146662
4	6	0	1.218187	0.573364	0.121151
5	6	0	-1.218187	0.573364	0.121151
6	7	0	0.000000	1.168891	0.524283
7	6	0	2.538753	-1.440479	-0.247515
8	6	0	-2.538753	-1.440479	-0.247515
9	6	0	3.635014	-0.667602	-0.634861
10	6	0	-3.635015	-0.667602	-0.634861
11	6	0	3.517306	0.719895	-0.659009
12	6	0	-3.517306	0.719895	-0.659009
13	6	0	2.316024	1.336274	-0.303540
14	6	0	-2.316024	1.336274	-0.303540
15	1	0	2.606623	-2.524055	-0.234042
16	1	0	-2.606623	-2.524055	-0.234042
17	1	0	4.565043	-1.148954	-0.919667
18	1	0	-4.565043	-1.148954	-0.919667
19	1	0	4.356305	1.334790	-0.970493
20	1	0	-4.356305	1.334790	-0.970494
21	1	0	2.238120	2.415387	-0.362688
22	1	0	-2.238120	2.415387	-0.362688
23	6	0	0.000000	2.587880	0.840508
24	1	0	0.884065	2.818622	1.438420
25	1	0	0.000000	3.238568	-0.047472
26	1	0	-0.884065	2.818622	1.438420

Table S9. Cartesian Coordinates of *N*-Mesityphenothiazine at the B3LYP-D3/6-31G(d,p) Level
Electronic energy = –1264.371706 hartree
Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.195429	0.004090	0.763938
2	6	0	-2.250066	-1.359373	0.116838
3	6	0	-2.246174	1.366194	0.119642
4	6	0	-0.859387	-1.241814	-0.085469
5	6	0	-0.855765	1.245247	-0.082684
6	7	0	-0.195888	0.000636	0.045972
7	6	0	-2.894835	-2.582177	-0.073671
8	6	0	-2.887566	2.591163	-0.068349
9	6	0	-2.172083	-3.728123	-0.406448
10	6	0	-2.161650	3.735877	-0.398463
11	6	0	-0.791925	-3.632739	-0.561721
12	6	0	-0.781707	3.637087	-0.553500
13	6	0	-0.144515	-2.406108	-0.415067
14	6	0	-0.137683	2.408383	-0.409345
15	1	0	-3.970577	-2.634707	0.066464
16	1	0	-3.963191	2.646305	0.071677
17	1	0	-2.683187	-4.676882	-0.533291
18	1	0	-2.670154	4.686281	-0.523415
19	1	0	-0.204576	-4.511974	-0.808471
20	1	0	-0.191904	4.515280	-0.798115
21	1	0	0.928892	-2.350954	-0.544710
22	1	0	0.935608	2.350570	-0.538695
23	6	0	1.244753	-0.001645	0.068713
24	6	0	1.881297	-0.010613	1.318926
25	6	0	1.977813	-0.000755	-1.131137
26	6	0	3.278770	-0.017329	1.351788
27	6	0	3.373494	-0.007363	-1.050359
28	6	0	4.040868	-0.012971	0.179354
29	1	0	3.782943	-0.027554	2.315226
30	1	0	3.952830	-0.009813	-1.970698
31	6	0	1.271631	0.002683	-2.464805

32	1	0	0.630470	0.883849	-2.569969
33	1	0	1.989670	0.001285	-3.288498
34	1	0	0.624831	-0.874140	-2.571753
35	6	0	1.061141	-0.017581	2.584184
36	1	0	0.408336	0.860174	2.633072
37	1	0	0.408682	-0.896114	2.623869
38	1	0	1.701623	-0.022153	3.469603
39	6	0	5.549669	0.015355	0.238383
40	1	0	5.921689	1.047216	0.257868
41	1	0	5.925148	-0.482664	1.137218
42	1	0	5.994464	-0.474278	-0.633066

Table S10. Cartesian Coordinates of C_{60} at the B3LYP-D3/6-31G(d,p) Level

Electronic energy = –2285.910695 hartree

Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.176049	-0.382121	3.327454
2	6	0	-0.726838	1.000407	3.327454
3	6	0	0.726838	1.000407	3.327454
4	6	0	-0.000000	-1.236571	3.327454
5	6	0	1.176049	-0.382121	3.327454
6	6	0	-2.304556	-0.748796	2.594105
7	6	0	-2.304556	-1.985367	1.829862
8	6	0	-3.031395	-1.749203	0.593292
9	6	0	-3.031395	0.251611	1.829862
10	6	0	-3.480605	-0.366674	0.593292
11	6	0	-1.424294	1.960373	2.594105
12	6	0	-2.600343	1.578251	1.829862
13	6	0	-2.600343	2.342494	0.593292
14	6	0	-0.697456	2.960780	1.829862
15	6	0	-1.424294	3.196944	0.593292
16	6	0	1.424294	1.960373	2.594105
17	6	0	0.697456	2.960780	1.829862
18	6	0	1.424294	3.196944	0.593292

19	6	0	2.600343	1.578251	1.829862
20	6	0	2.600343	2.342494	0.593292
21	6	0	-0.000000	-2.423154	2.594105
22	6	0	1.176049	-2.805275	1.829862
23	6	0	0.726838	-3.423561	0.593292
24	6	0	-1.176049	-2.805275	1.829862
25	6	0	-0.726838	-3.423561	0.593292
26	6	0	2.304556	-0.748796	2.594105
27	6	0	3.031395	0.251611	1.829862
28	6	0	3.480605	-0.366674	0.593292
29	6	0	2.304556	-1.985367	1.829862
30	6	0	3.031395	-1.749203	0.593292
31	6	0	1.176049	0.382121	-3.327454
32	6	0	0.000000	1.236571	-3.327454
33	6	0	-1.176049	0.382121	-3.327454
34	6	0	0.726838	-1.000407	-3.327454
35	6	0	-0.726838	-1.000407	-3.327454
36	6	0	2.304556	0.748796	-2.594105
37	6	0	3.031395	-0.251611	-1.829862
38	6	0	3.480605	0.366674	-0.593292
39	6	0	2.304556	1.985367	-1.829862
40	6	0	3.031395	1.749203	-0.593292
41	6	0	0.000000	2.423154	-2.594105
42	6	0	1.176049	2.805275	-1.829862
43	6	0	0.726838	3.423561	-0.593292
44	6	0	-1.176049	2.805275	-1.829862
45	6	0	-0.726838	3.423561	-0.593292
46	6	0	-2.304556	0.748796	-2.594105
47	6	0	-2.304556	1.985367	-1.829862
48	6	0	-3.031395	1.749203	-0.593292
49	6	0	-3.031395	-0.251611	-1.829862
50	6	0	-3.480605	0.366674	-0.593292
51	6	0	1.424294	-1.960373	-2.594105
52	6	0	0.697456	-2.960780	-1.829862
53	6	0	1.424294	-3.196944	-0.593292
54	6	0	2.600343	-1.578251	-1.829862
55	6	0	2.600343	-2.342494	-0.593292
56	6	0	-1.424294	-1.960373	-2.594105

57	6	0	-2.600343	-1.578251	-1.829862
58	6	0	-2.600343	-2.342494	-0.593292
59	6	0	-0.697456	-2.960780	-1.829862
60	6	0	-1.424294	-3.196944	-0.593292

Table S11. Cartesian Coordinates of **1a'**⊃C_{60} at the B3LYP-D3/6-31G(d,p) Level
Electronic energy = –8007.642893 hartree
Charge = 0 Multiplicity = 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	5.450137	-3.785025	1.933712
2	6	0	5.435239	-5.400658	1.176425
3	6	0	6.957736	-3.209731	1.171636
4	6	0	6.654411	-6.093645	1.036087
5	6	0	8.031855	-4.111430	1.031658
6	7	0	7.859608	-5.460609	1.417938
7	6	0	4.238152	-5.975056	0.766162
8	6	0	7.078626	-1.888266	0.758694
9	6	0	4.201512	-7.271527	0.225766
10	6	0	8.280430	-1.403601	0.215570
11	6	0	5.414938	-7.962564	0.106217
12	6	0	9.350407	-2.300749	0.095225
13	6	0	6.621289	-7.384697	0.493387
14	6	0	9.229397	-3.632036	0.485215
15	16	0	-0.553139	-6.611975	-1.932824
16	6	0	-1.959589	-7.406587	-1.174935
17	6	0	0.699096	-7.629877	-1.170946
18	6	0	-1.950114	-8.808888	-1.034192
19	6	0	0.455178	-9.010871	-1.030472
20	7	0	-0.799488	-9.536262	-1.416329
21	6	0	-3.055653	-6.657019	-0.764899
22	6	0	1.904118	-7.073853	-0.758440
23	6	0	-4.196650	-7.273499	-0.224267
24	6	0	2.924702	-7.872198	-0.215061
25	6	0	-4.188198	-8.669814	-0.104014

26	6	0	2.682631	-9.247344	-0.094251
27	6	0	-3.084552	-9.425641	-0.490999
28	6	0	1.469122	-9.808200	-0.483955
29	16	0	-6.004981	-2.827012	1.934605
30	6	0	-7.396083	-2.006338	1.176113
31	6	0	-6.259596	-4.420144	1.171880
32	6	0	-8.605543	-2.715877	1.034326
33	6	0	-7.577342	-4.899697	1.030580
34	7	0	-8.660146	-4.076186	1.415931
35	6	0	-7.294866	-0.682299	0.766260
36	6	0	-5.175097	-5.185235	0.759643
37	6	0	-8.398864	-0.002497	0.224740
38	6	0	-5.355553	-6.468237	0.216011
39	6	0	-9.603736	-0.708078	0.103658
40	6	0	-6.667305	-6.946516	0.094451
41	6	0	-9.706605	-2.041818	0.490516
42	6	0	-7.760208	-6.176390	0.483653
43	16	0	-5.450063	3.785200	-1.933641
44	6	0	-5.435186	5.400745	-1.176168
45	6	0	-6.957706	3.209844	-1.171702
46	6	0	-6.654356	6.093733	-1.035828
47	6	0	-8.031828	4.111540	-1.031708
48	7	0	-7.859536	5.460757	-1.417830
49	6	0	-4.238115	5.975084	-0.765775
50	6	0	-7.078632	1.888345	-0.758885
51	6	0	-4.201486	7.271501	-0.225251
52	6	0	-8.280474	1.403641	-0.215881
53	6	0	-5.414912	7.962537	-0.105685
54	6	0	-9.350459	2.300781	-0.095541
55	6	0	-6.621249	7.384724	-0.492978
56	6	0	-9.229415	3.632102	-0.485403
57	16	0	0.553258	6.611772	1.933118
58	6	0	1.959646	7.406435	1.175162
59	6	0	-0.699032	7.629740	1.171414
60	6	0	1.950167	8.808748	1.034534
61	6	0	-0.455116	9.010741	1.031029
62	7	0	0.799580	9.536097	1.416842
63	6	0	3.055666	6.656894	0.764959

64	6	0	-1.904077	7.073747	0.758927
65	6	0	4.196616	7.273408	0.224266
66	6	0	-2.924677	7.872131	0.215637
67	6	0	4.188158	8.669734	0.104124
68	6	0	-2.682612	9.247289	0.094931
69	6	0	3.084555	9.425536	0.491278
70	6	0	-1.469088	9.808116	0.484628
71	16	0	6.004806	2.826997	-1.934909
72	6	0	7.395958	2.006329	-1.176502
73	6	0	6.259462	4.420126	-1.172186
74	6	0	8.605427	2.715871	-1.034812
75	6	0	7.577216	4.899681	-1.030977
76	7	0	8.659994	4.076179	-1.416430
77	6	0	7.294765	0.682302	-0.766605
78	6	0	5.174991	5.185198	-0.759838
79	6	0	8.398796	0.002513	-0.225141
80	6	0	5.355484	6.468179	-0.216169
81	6	0	9.603683	0.708091	-0.104175
82	6	0	6.667244	6.946463	-0.094703
83	6	0	9.706530	2.041820	-0.491075
84	6	0	7.760120	6.176359	-0.484026
85	6	0	9.045080	-6.284048	1.588413
86	6	0	-0.920003	-10.974667	-1.586444
87	6	0	-9.966130	-4.691326	1.584619
88	6	0	-9.044984	6.284229	-1.588314
89	6	0	0.920114	10.974487	1.587062
90	6	0	9.965964	4.691329	-1.585196
91	1	0	3.319139	-5.412930	0.895265
92	1	0	6.232251	-1.221800	0.889135
93	1	0	5.427817	-8.950342	-0.343324
94	1	0	10.280062	-1.969673	-0.356551
95	1	0	7.541414	-7.936504	0.341006
96	1	0	10.066716	-4.302822	0.332623
97	1	0	-3.028560	-5.580097	-0.894445
98	1	0	2.058215	-6.007701	-0.889233
99	1	0	-5.037107	-9.174741	0.345825
100	1	0	3.434126	-9.886838	0.357718
101	1	0	-3.102188	-10.498348	-0.338215

102	1	0	1.306807	-10.868694	-0.331100
103	1	0	-6.348857	-0.167227	0.896595
104	1	0	-4.174933	-4.785244	0.890919
105	1	0	-10.465195	-0.225451	-0.346810
106	1	0	-6.844863	-7.917055	-0.357766
107	1	0	-10.644267	-2.562947	0.337001
108	1	0	-8.759556	-6.566310	0.330006
109	1	0	-3.319103	5.412957	-0.894884
110	1	0	-6.232255	1.221882	-0.889329
111	1	0	-5.427802	8.950270	0.343955
112	1	0	-10.280148	1.969667	0.356138
113	1	0	-7.541377	7.936523	-0.340583
114	1	0	-10.066742	4.302880	-0.332813
115	1	0	3.028571	5.579963	0.894414
116	1	0	-2.058155	6.007585	0.889651
117	1	0	5.037026	9.174693	-0.345756
118	1	0	-3.434122	9.886816	-0.356965
119	1	0	3.102183	10.498255	0.338580
120	1	0	-1.306778	10.868622	0.331850
121	1	0	6.348741	0.167235	-0.896846
122	1	0	4.174820	4.785204	-0.891044
123	1	0	10.465173	0.225473	0.346243
124	1	0	6.844835	7.916983	0.357539
125	1	0	10.644207	2.562948	-0.337645
126	1	0	8.759477	6.566280	-0.330447
127	1	0	9.501357	-6.603378	0.638604
128	1	0	9.788333	-5.721941	2.157662
129	1	0	8.778637	-7.174833	2.161082
130	1	0	-0.968094	-11.529302	-0.636518
131	1	0	-1.824873	-11.189357	-2.158766
132	1	0	-0.061789	-11.337411	-2.155931
133	1	0	-10.605187	-4.015334	2.156523
134	1	0	-10.469508	-4.926730	0.634093
135	1	0	-9.851584	-5.616101	2.153915
136	1	0	-9.501338	6.603462	-0.638508
137	1	0	-9.788197	5.722190	-2.157683
138	1	0	-8.778485	7.175072	-2.160866
139	1	0	0.968139	11.529199	0.637177

140	1	0	1.825027	11.189127	2.159334
141	1	0	0.061942	11.337190	2.156639
142	1	0	10.604984	4.015352	-2.157158
143	1	0	10.469405	4.926715	-0.634699
144	1	0	9.851373	5.616115	-2.154465
145	6	0	2.927341	-0.686464	1.891564
146	6	0	1.997933	-1.676557	2.410909
147	6	0	1.029902	-0.986787	3.248780
148	6	0	2.534183	0.614426	2.408617
149	6	0	1.361856	0.428566	3.248036
150	6	0	3.411635	-0.800768	0.587171
151	6	0	3.523711	0.382356	-0.251971
152	6	0	3.167330	0.003778	-1.610256
153	6	0	2.985361	-1.909645	-0.251415
154	6	0	2.833123	-1.412466	-1.608415
155	6	0	1.589625	-2.741600	1.606574
156	6	0	2.093449	-2.860568	0.247404
157	6	0	1.011278	-3.354714	-0.590048
158	6	0	0.196013	-3.160245	1.606977
159	6	0	-0.160743	-3.540217	0.250482
160	6	0	-0.306137	-1.389402	3.250127
161	6	0	-0.732270	-2.498697	2.412708
162	6	0	-2.056094	-2.189468	1.896784
163	6	0	-1.365927	-0.394325	3.250899
164	6	0	-2.448296	-0.888883	2.414904
165	6	0	2.641600	1.749348	1.603055
166	6	0	1.582179	2.746890	1.604774
167	6	0	1.431056	3.243131	0.246046
168	6	0	3.146785	1.630888	0.245688
169	6	0	2.398808	2.553524	-0.593303
170	6	0	0.345188	1.384339	3.248786
171	6	0	-1.046458	0.963990	3.249937
172	6	0	-1.795000	1.886576	2.412189
173	6	0	0.457082	2.567850	2.411026
174	6	0	-0.865915	2.877779	1.893978
175	6	0	-2.927325	0.686500	-1.891630
176	6	0	-2.534165	-0.614392	-2.408682
177	6	0	-1.361837	-0.428531	-3.248101

178	6	0	-1.997915	1.676592	-2.410976
179	6	0	-1.029883	0.986822	-3.248846
180	6	0	-3.411616	0.800803	-0.587233
181	6	0	-2.985341	1.909682	0.251351
182	6	0	-2.833101	1.412503	1.608351
183	6	0	-3.523694	-0.382320	0.251909
184	6	0	-3.167308	-0.003740	1.610192
185	6	0	-2.641583	-1.749314	-1.603120
186	6	0	-3.146770	-1.630855	-0.245750
187	6	0	-2.398790	-2.553492	0.593239
188	6	0	-1.582161	-2.746857	-1.604838
189	6	0	-1.431035	-3.243094	-0.246110
190	6	0	-0.345168	-1.384305	-3.248850
191	6	0	-0.457062	-2.567815	-2.411091
192	6	0	0.865936	-2.877740	-1.894043
193	6	0	1.046478	-0.963954	-3.250002
194	6	0	1.795021	-1.886538	-2.412253
195	6	0	-1.589602	2.741633	-1.606641
196	6	0	-0.195991	3.160281	-1.607045
197	6	0	0.160766	3.540251	-0.250549
198	6	0	-2.093425	2.860601	-0.247473
199	6	0	-1.011254	3.354748	0.589979
200	6	0	0.306157	1.389437	-3.250193
201	6	0	1.365948	0.394361	-3.250963
202	6	0	2.448317	0.888919	-2.414967
203	6	0	0.732291	2.498733	-2.412774
204	6	0	2.056115	2.189503	-1.896849

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6. Job's Plot Experiments by NMR

A solution of **1a** in toluene-d_8 (1.00×10^{-3} mol L^{-1}, **A**) and a solution of C_{60} in toluene-d_8 (1.00×10^{-3} mol L^{-1}, **B**) were prepared. Mixing the two solutions **A** and **B** gave a solution of **1a** and C_{60} at the constant total concentration C (= 1.00×10^{-3} mol L^{-1}) with variable molar fractions of **1a** (x).

Total concentration: [**1a**] + [C_{60}] = C

Molar fraction of **1a**: [**1a**]/([**1a**] + [C_{60}]) = [**1a**]/C = x

Molar fraction of C_{60}: [C_{60}]/([**1a**] + [C_{60}]) = [C_{60}]/C = 1 – x

^{1}H NMR of the mixed solutions were measured at 298 K. The observed chemical shifts were referenced to the residual solvent signal of toluene at δ 2.08 (Figure S11a and Table S2). From the observed spectra, the differences of the chemical shifts $\Delta\delta$ (= $\delta - \delta_0$), where δ and δ_0 are the chemical shifts at [**1a**]/C = x and 0, respectively, were read for the signals derived from the H_1, H_2, and H_3 protons. The Job's plot for the H_3 signal was obtained by plotting $\Delta\delta \times x$ versus x (Figure S11b). The Job's plot shows a maximum at x = 0.5 all for H_1, H_2, and H_3, indicating the stoichiometric ratio of **1a** and C_{60} is 1:1. The parameters obtained from H_3 proton were adopted because of the largest changes in chemical shifts.

7. Titration Experiments by UV–vis

A solution of C_{60} in toluene (0.50×10^{-3} mol L^{-1}, **A**) and a mixture solution of C_{60} and **1a** in toluene (0.50×10^{-3} mol L^{-1} for C_{60} and 10×10^{-3} mol L^{-1} for **1a**, **B**) were prepared. To the solution **A** (3.0 mL), the solution **B** (0–1.0 mL) was added giving the sample solution, in which the concentration of C_{60} was fixed at 0.50×10^{-3} mol L^{-1} with various concentrations of **1a** (0–2.5×10^{-3} mol L^{-1}), and the UV–vis spectra of the resulting mixtures were measured at 298 K (Fig. S12). The absorbances at 540, 600, and 611 nm were monitored (Table S3): A is the absorbance of the mixture of **1a** and C_{60}, A_0 is the absorbance of only C_{60}, and ΔA (= A − A_0) is the differences between A and A_0. The binding constant (K_a) at 298 K was estimated by curve fitting method (Fig. S13) using the results of the UV–vis measurements, and the following K_a values were obtained:

$K_a = (2.0 \pm 0.2) \times 10^2$ L mol^{-1} (540 nm) (Fig. S14)

$K_a = (1.9 \pm 0.2) \times 10^2$ L mol^{-1} (600 nm) (Fig. S15)

$K_a = (2.1 \pm 0.2) \times 10^2$ L mol^{-1} (611 nm) (Fig. S16)

We adopted the value obtained at 540 nm in the main text because of the largest changes in absorbance.

8. ^{1}H and ^{13}C NMR Spectra

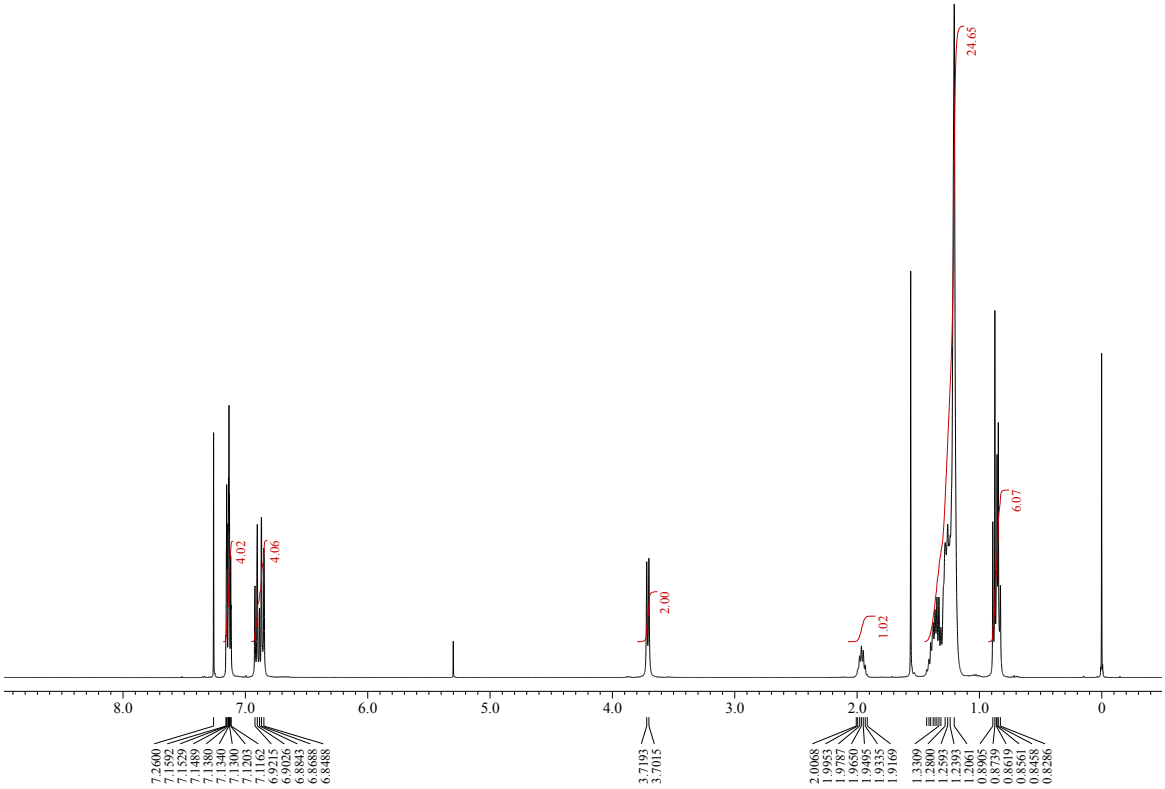

Figure S20. ^{1}H spectrum of *N*-(2-hexyldecyl)phenothiazine in $CDCl_3$ solution (400 MHz).

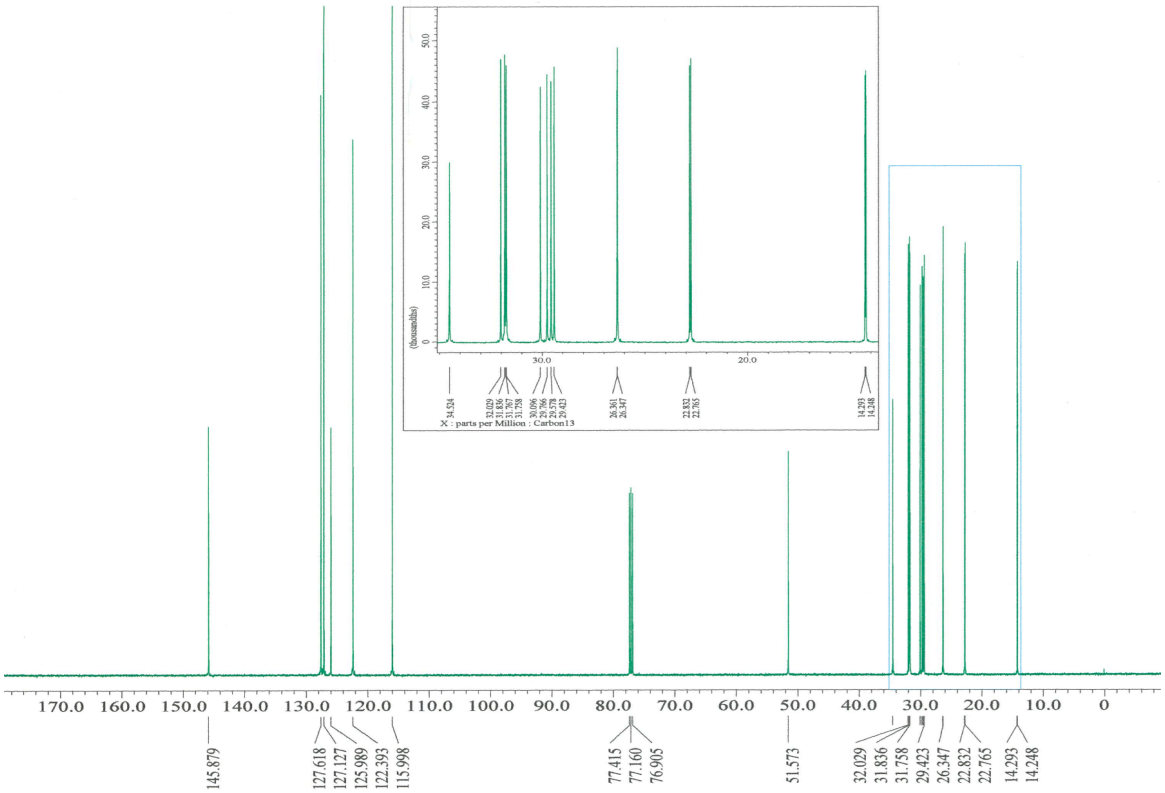

Figure S21. ^{13}C{^{1}H} spectrum of *N*-(2-hexyldecyl)phenothiazine in $CDCl_3$ solution (125 MHz).

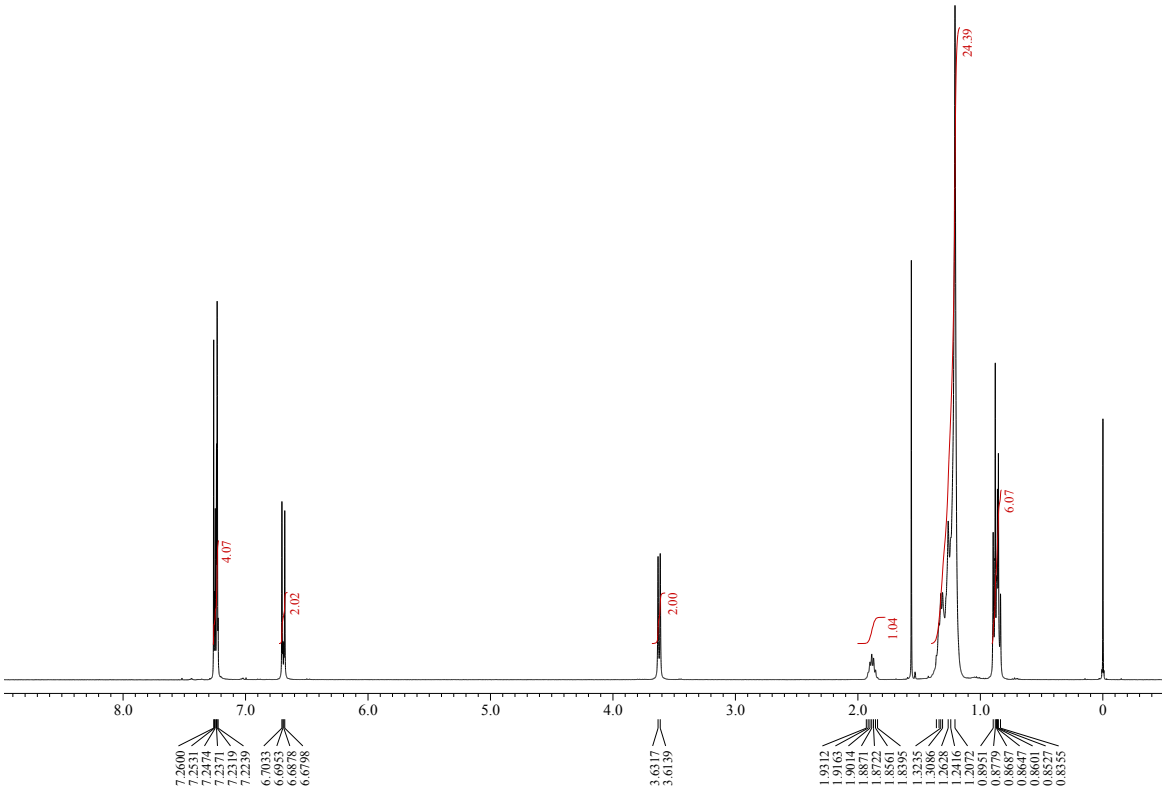

Figure S22. ^{1}H spectrum of **5a** in $CDCl_3$ solution (400 MHz).

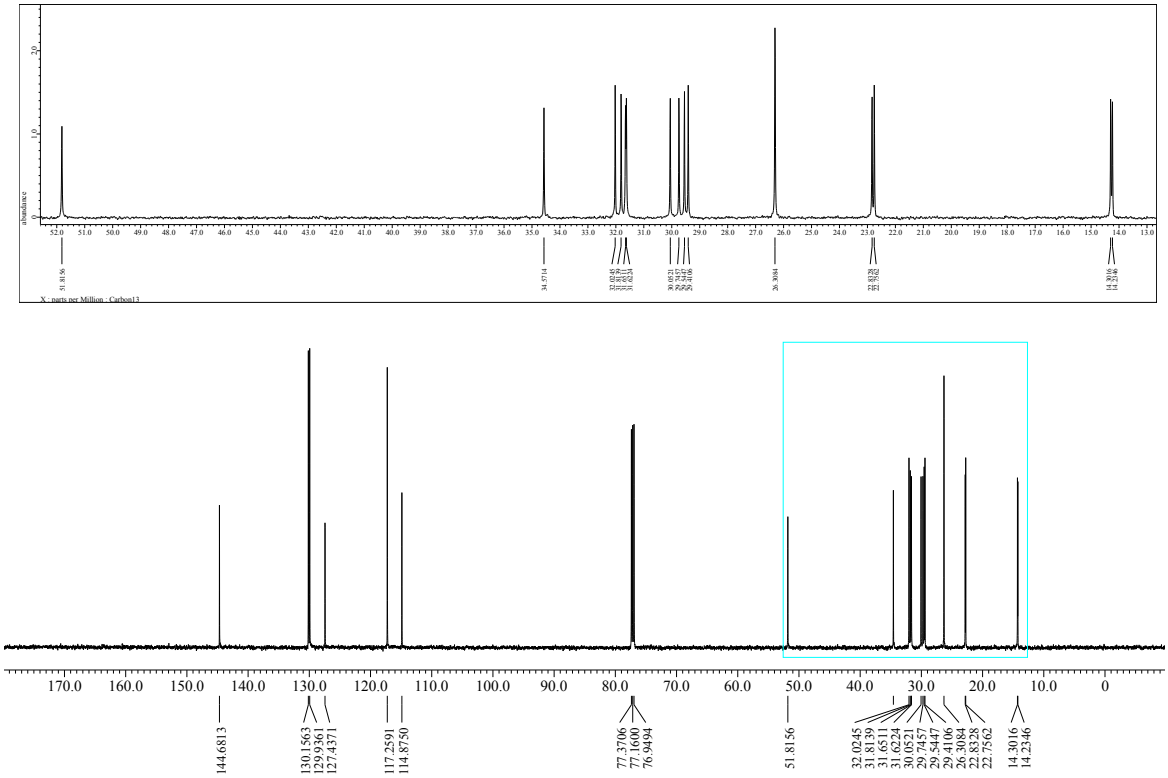

Figure S23. $^{13}C\{^{1}H\}$ spectrum of **5a** in $CDCl_3$ solution (150 MHz).

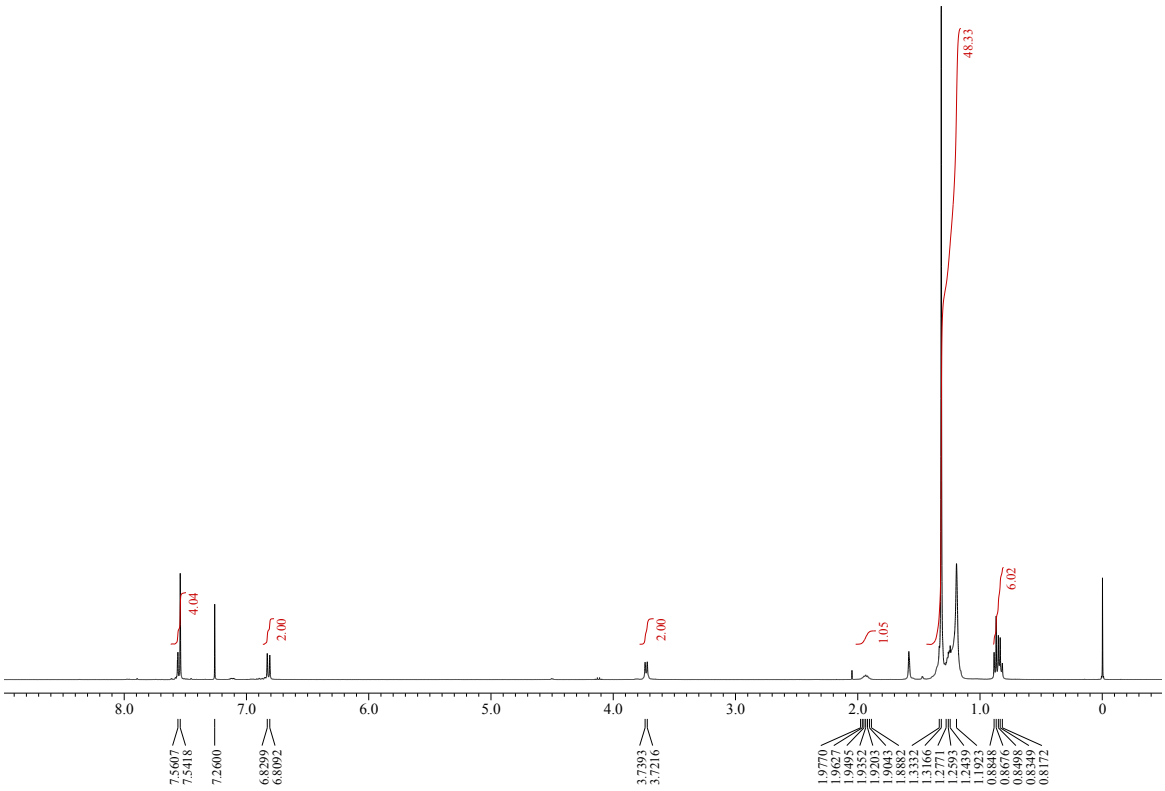

Figure 24. ^{1}H spectrum of **6a** in $CDCl_3$ solution (400 MHz).

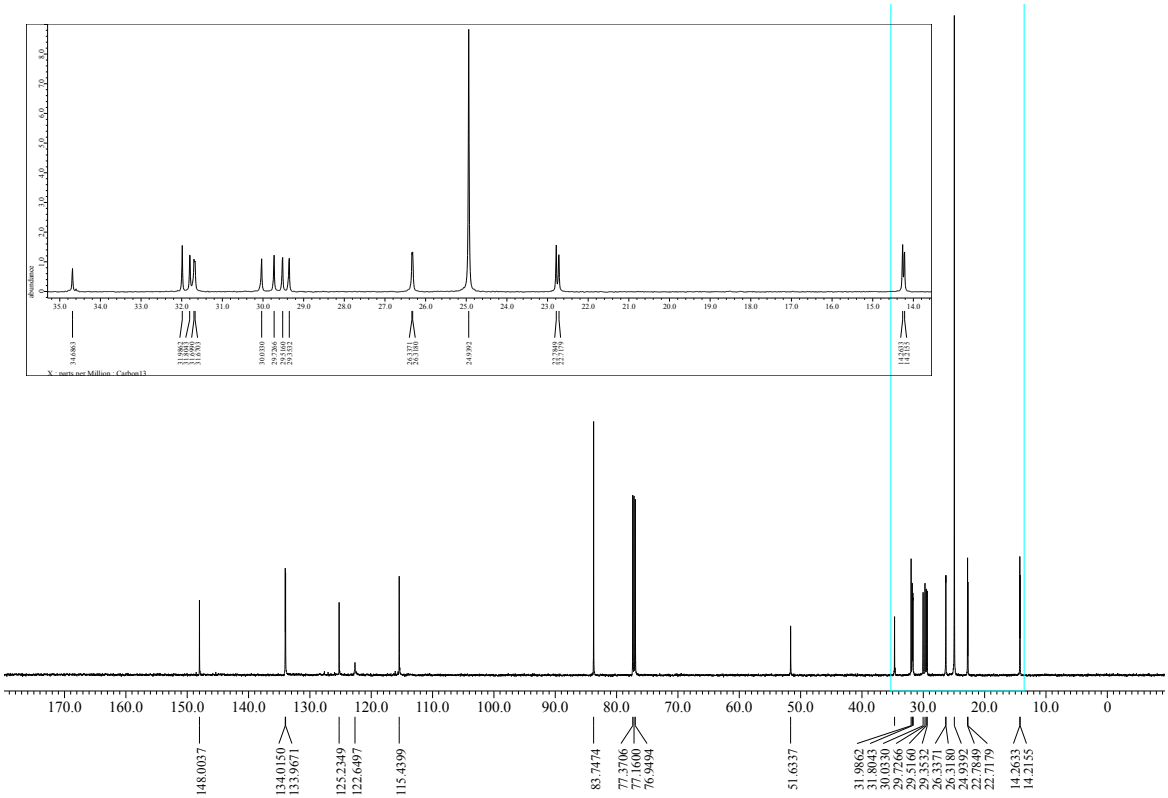

Figure S25. $^{13}C\{^{1}H\}$ spectrum of **6a** in $CDCl_3$ solution (150 MHz).

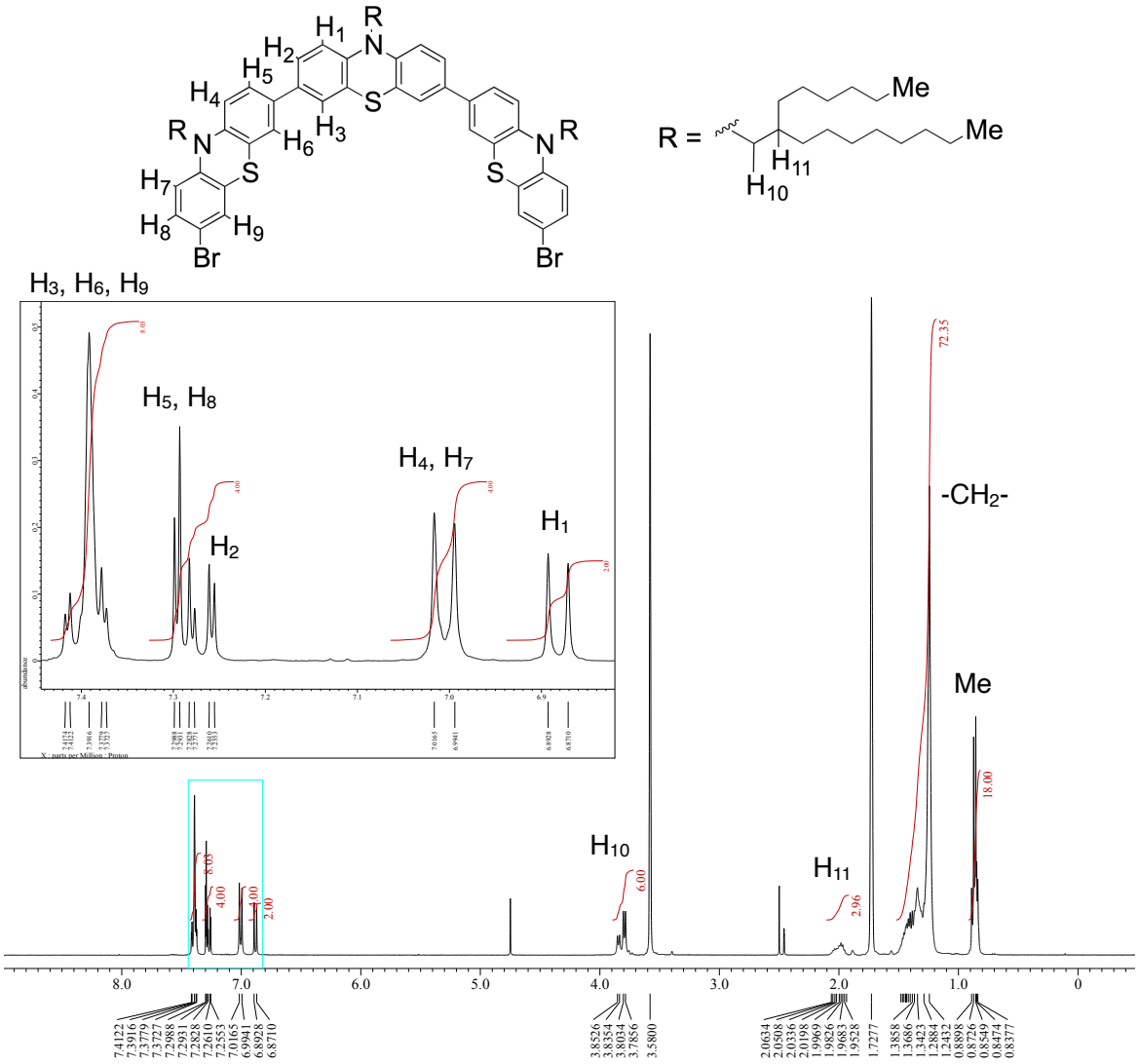

Figure S26. ^{1}H spectrum of **7a** in THF-d_8 solution (400 MHz). The structure of **7a** is also shown.

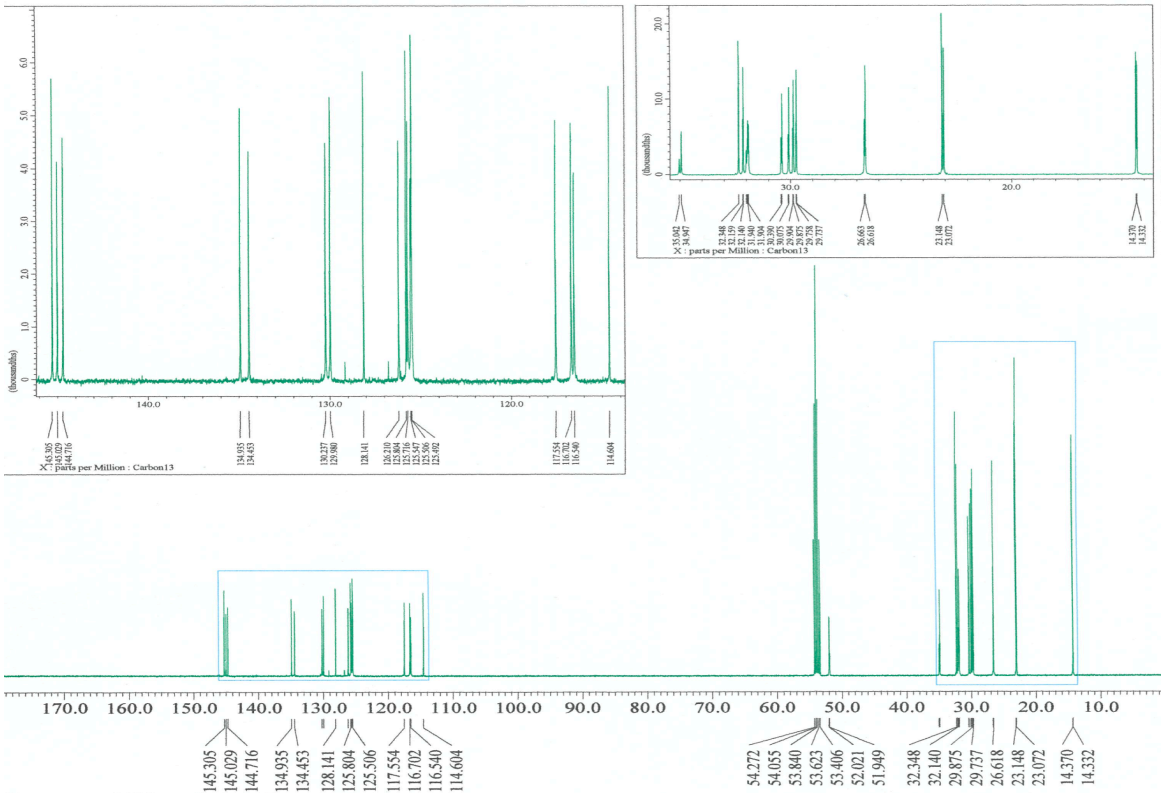

Figure S27. $^{13}C\{^{1}H\}$ spectrum of **7a** in CD_2Cl_2 solution (125 MHz).

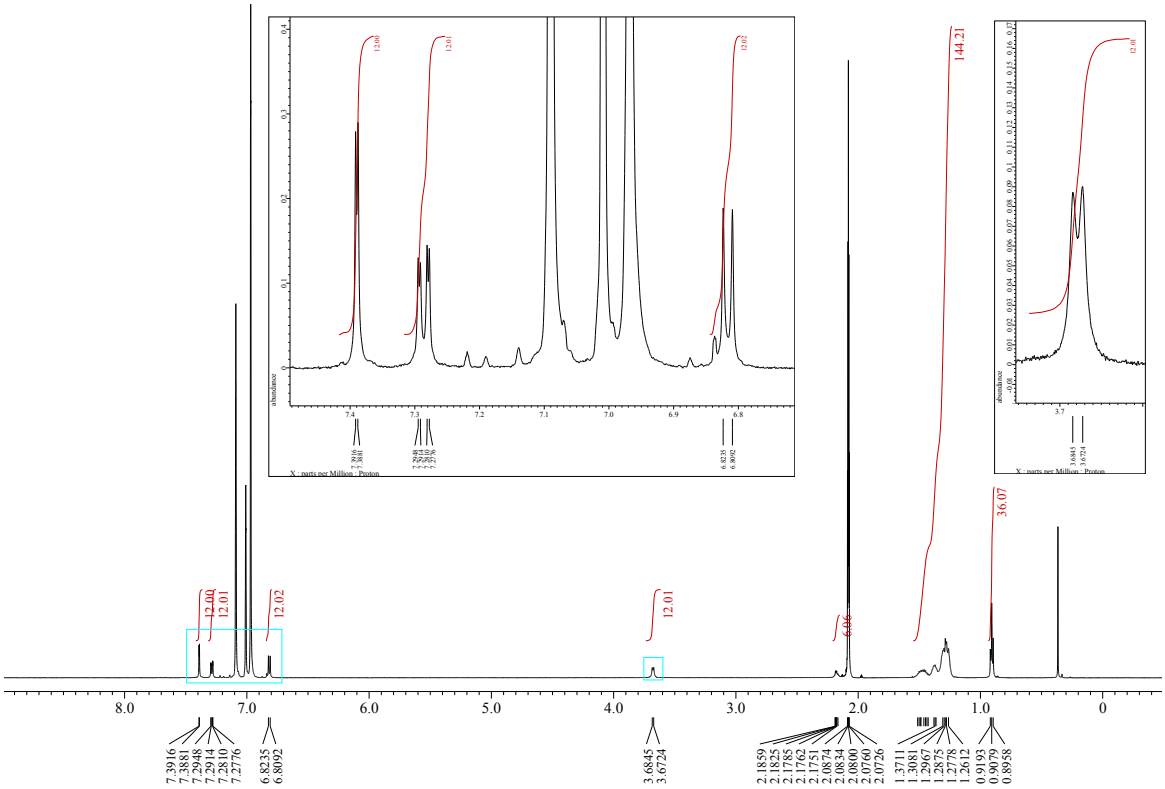

Figure S28. ^{1}H spectrum of **1a** in toluene-d_8 solution (600 MHz).

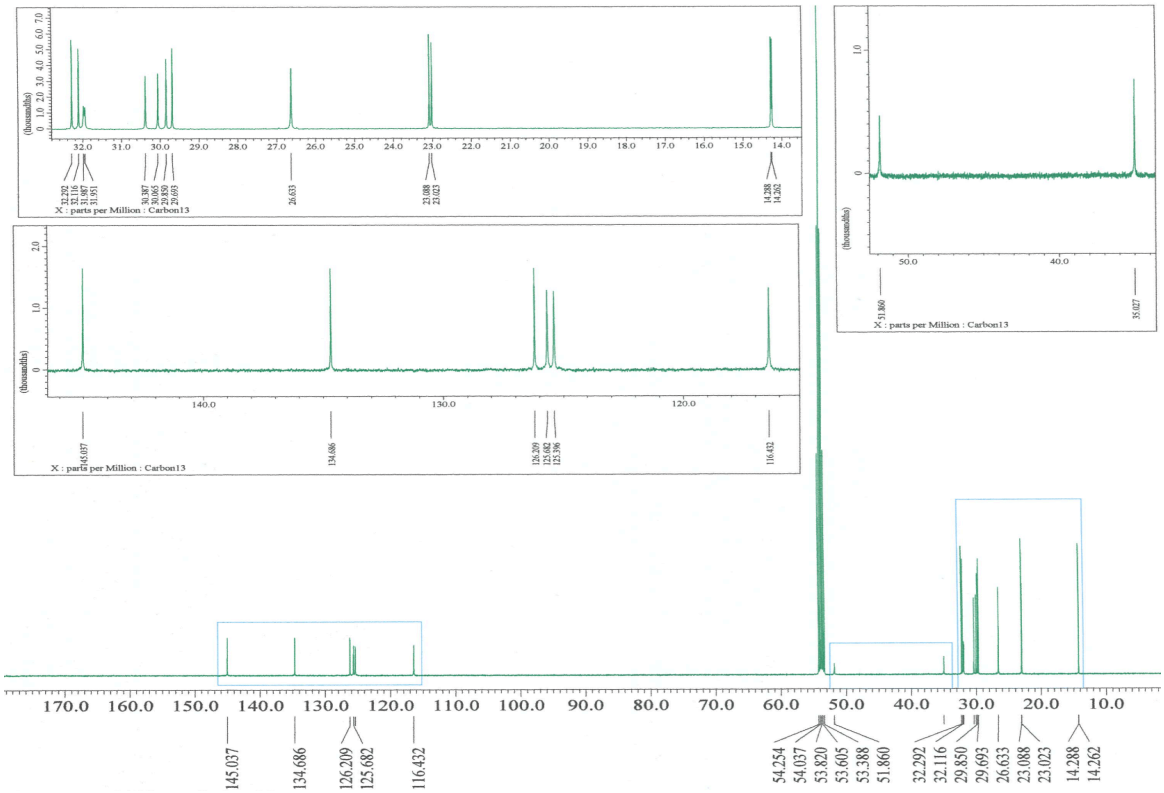

Figure S29. $^{13}C\{^{1}H\}$ spectrum of **1a** in CD_2Cl_2 solution (125 MHz).

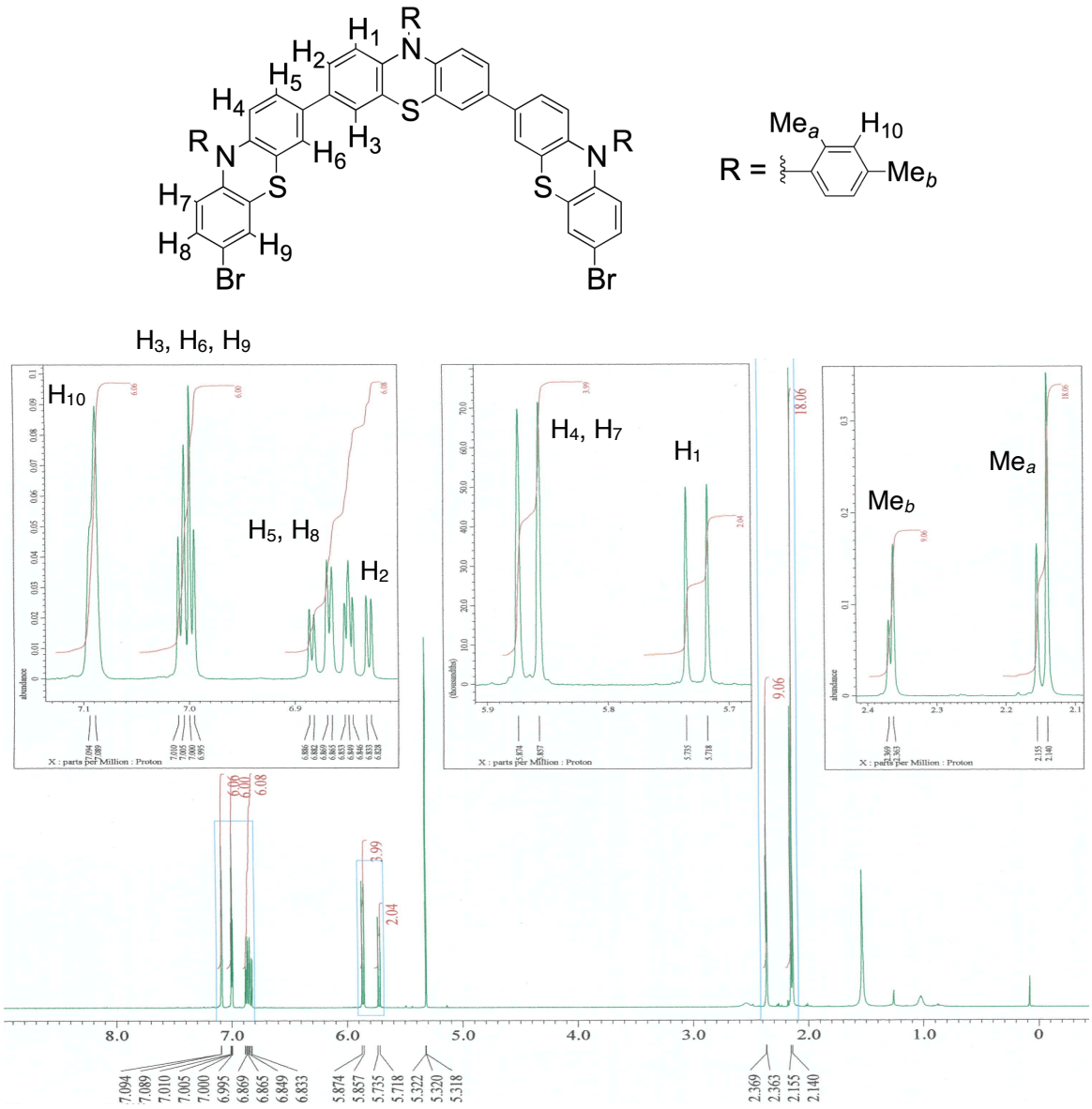

Figure S30. ^{1}H spectrum of **7b** in CD_2Cl_2 solution (500 MHz). The structure of **7b** is also shown.

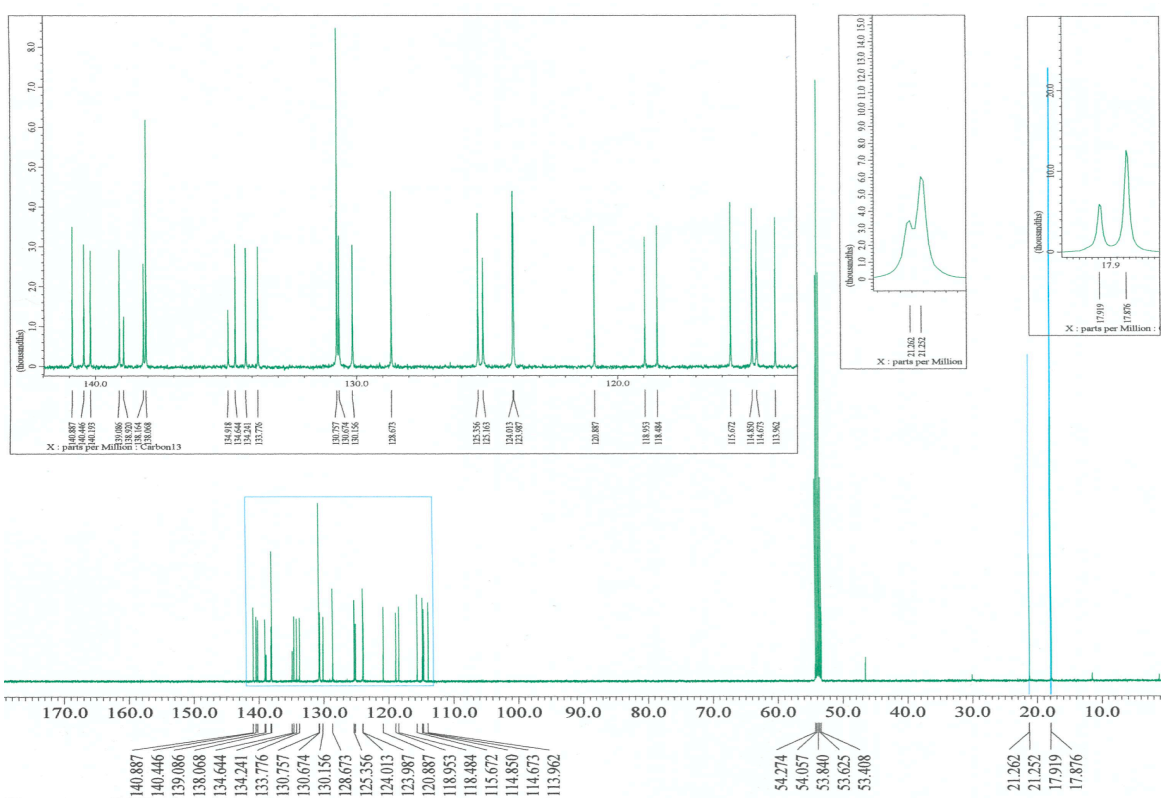

Figure S31. $^{13}C\{^{1}H\}$ spectrum of **7b** in CD_2Cl_2 solution (125 MHz).

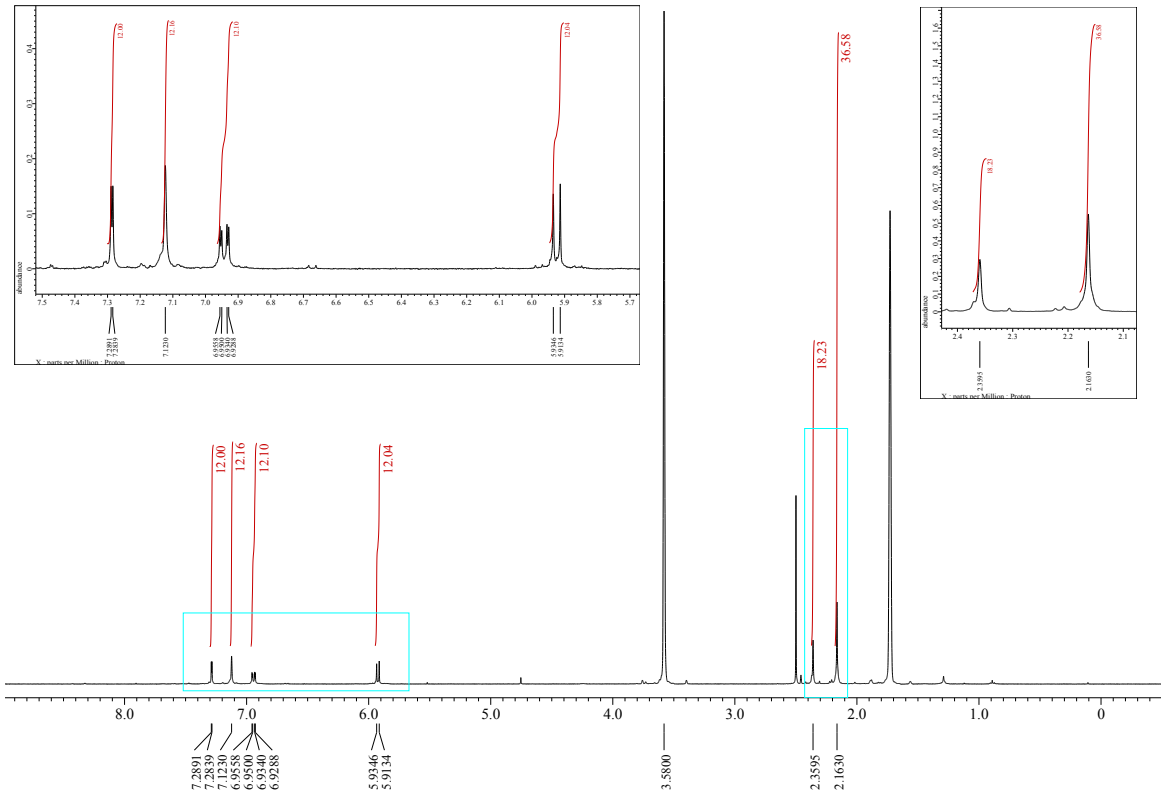

Figure S32. ^{1}H spectrum of **1b** in THF-d_8 solution (400 MHz).

9. ESI- and MALDI-TOF-MS Spectra

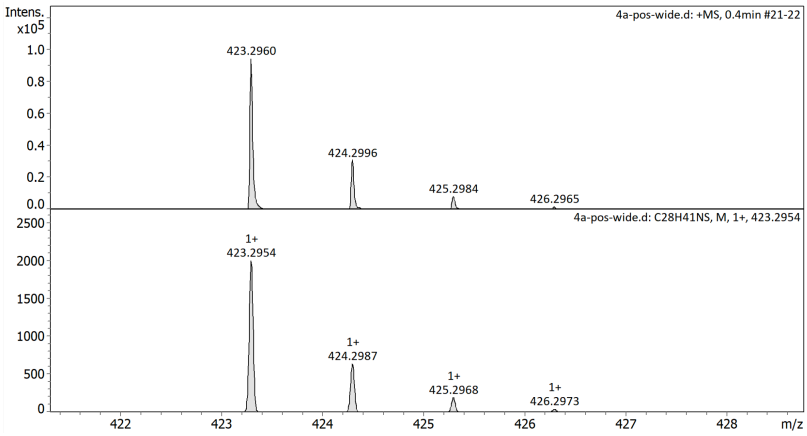

Figure S33. ESI-TOF-MS spectra (positive) of *N*-(2-hexyldecyl)phenothiazine (upper: found [M^+], bottom: calculated for $C_{28}H_{41}NS^+$).

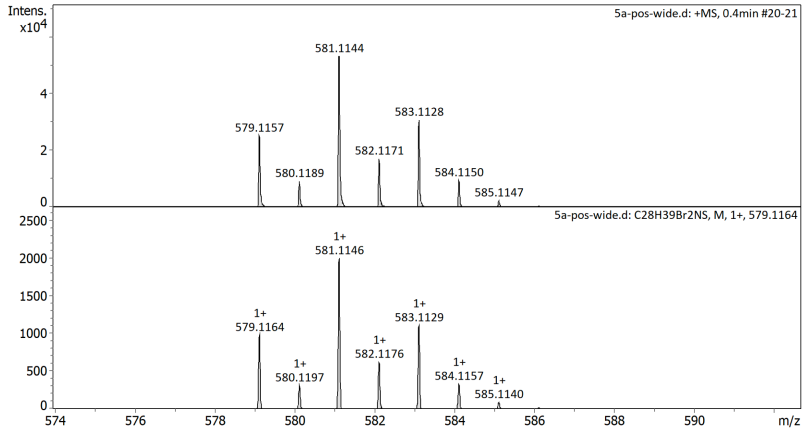

Figure S34. ESI-TOF-MS spectra (positive) of **5a** (upper: found [M^+], bottom: calculated for $C_{28}H_{39}Br_2NS^+$).

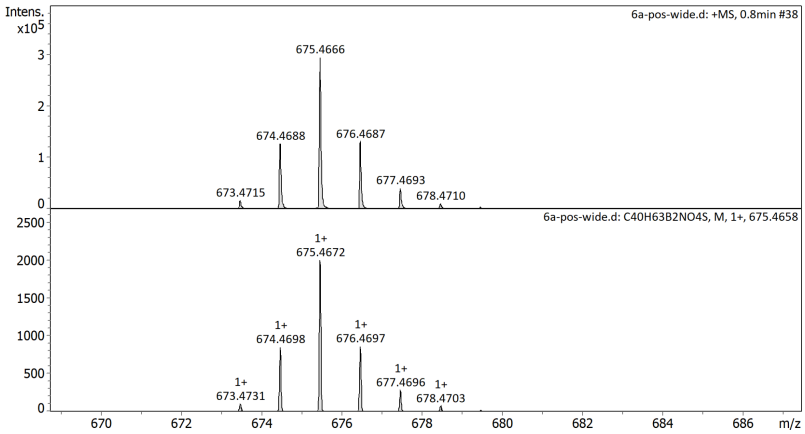

Figure S35. ESI-TOF-MS spectra (positive) of **6a** (upper: found [M^+], bottom: calculated for $C_{40}H_{63}B_2NO_4S^+$).

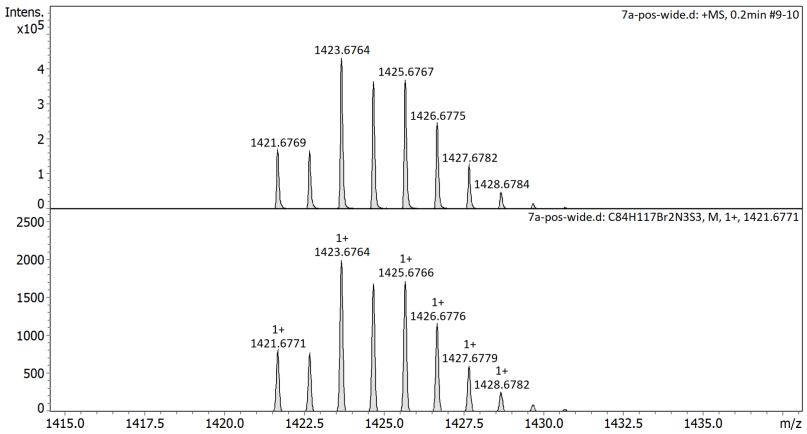

Figure S36. ESI-TOF-MS spectra (positive) of **7a** (upper: found [M^+], bottom: calculated for $C_{84}H_{117}Br_2N_3S_3^+$).

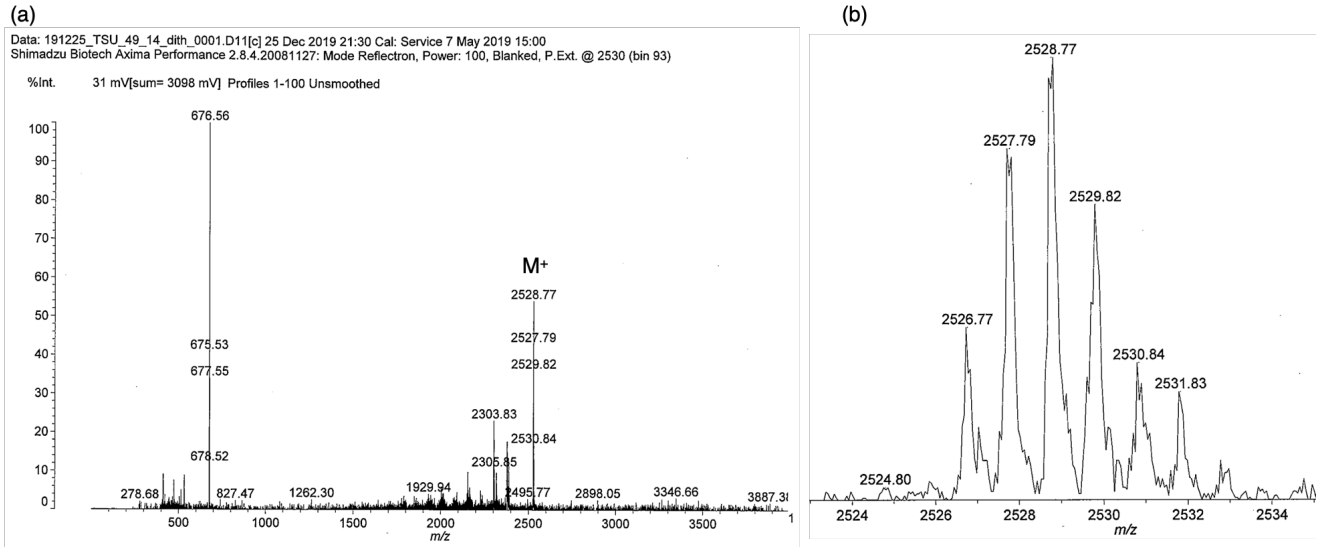

Figure S37. (a) MALDI-TOF-MS spectrum (positive) of **1a** (found for [M^+]) and (b) the expansion around [M^+].

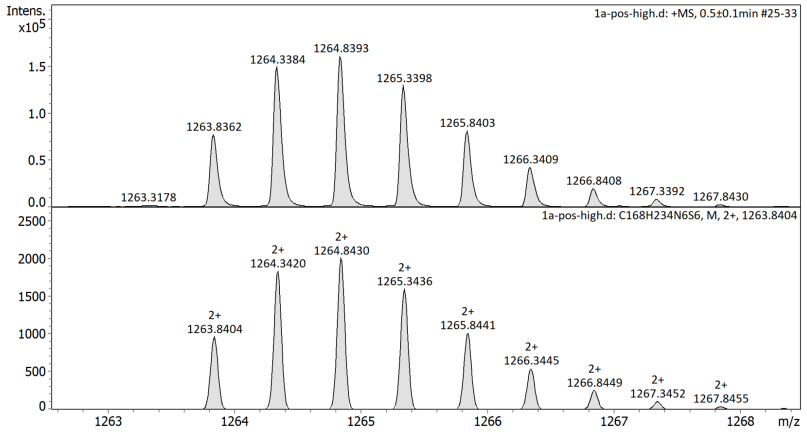

Figure S38. ESI-TOF-MS spectra (positive) of **1a** (upper: found [M^{2+}], bottom: calculated for $C_{168}H_{234}N_6S_6^{2+}$).

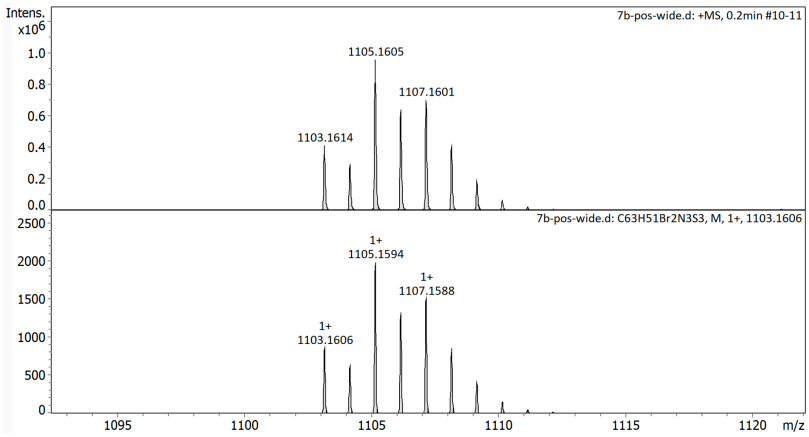

Figure S39. ESI-TOF-MS spectra (positive) of **7b** (upper: found [M^+], bottom: calculated for $C_{63}H_{51}Br_2N_3S_3{}^+$).

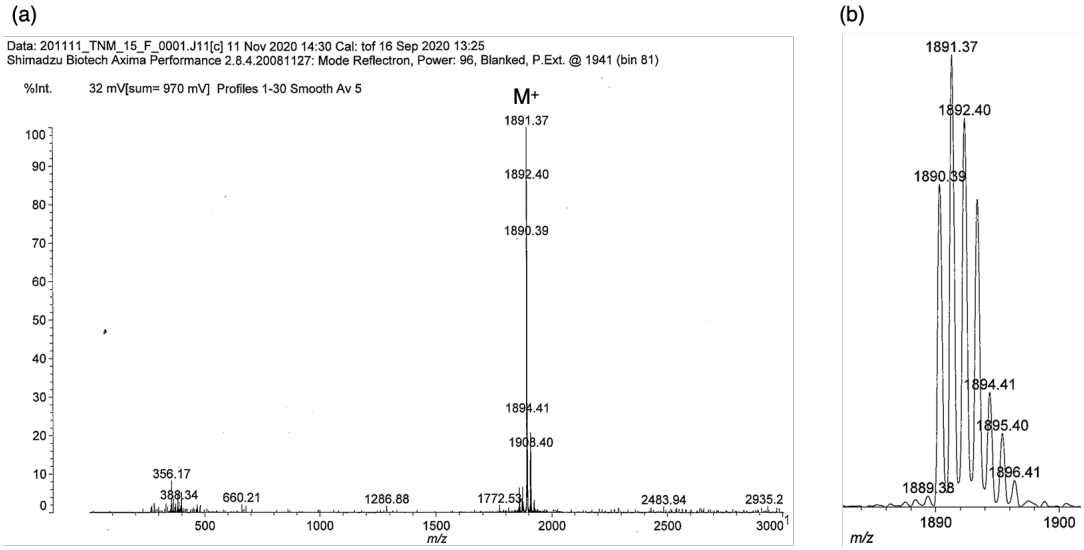

Figure S40. (a) MALDI-TOF-MS spectrum (positive) of **1b** (found for [M^+]) and (b) the expansion around [M^+].

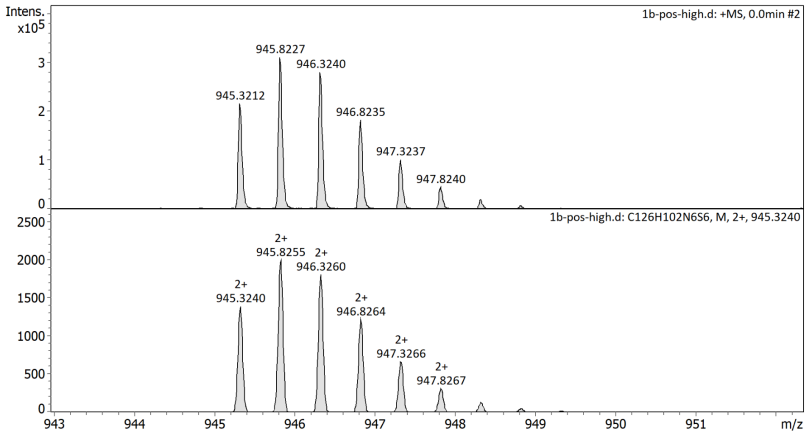

Figure S41. ESI-TOF-MS spectra (positive) of **1b** (upper: found [M^{2+}], bottom: calculated for $C_{126}H_{102}N_6S_6{}^{2+}$).

10. References

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