Supporting Information

High-Efficiency Thermally Activated Delayed Fluorescence Emitters by a High Horizontal Dipole Ratio and Controlled Dual Emission

*Youngnam Lee, Jong-In Hong**

Y. Lee, Prof. J.-I. Hong
Department of Chemistry
Seoul National University
Seoul 08826, Republic of Korea
E-mail: jihong@snu.ac.kr

1. General methods

1.1. Quantum chemical calculations

Density functional theory (DFT) calculations were performed to predict optimized molecular structures and orbital distributions of frontier orbitals. Time-dependent density functional theory (TD-DFT) calculations were performed to calculate energies of excited states. All calculations were employed using Gaussian 09 software at the B3LYP/6-31G(d) level.

1.2. Photophysical property analysis

UV-visible spectra were recorded on a Jasco V-730 spectrophotometer. Fluorescence and phosphorescence spectra were recorded on a Jasco FP-8300 spectrophotometer. Absolute quantum efficiency was obtained with a PTI QuantaMaster 40 spectrofluorometer using a 3.2 in. integrating sphere at room temperature. Transient photoluminescence (PL) was measured with time-correlated single photon counting (TCSPC) techniques by using a PicoQuant, FluoTime 250 instrument. A 377 nm pulsed laser was used as an excitation source. For angle-dependent PL (ADPL) measurements, *p*-polarized light emitted from PL samples was measured by attaching the film substrate to a half-cylinder lens with index-matching oil and

changing the angle between the sample and the detector from –90° to 90° using a motorized rotational stage.

1.3. Electrochemical and thermal analysis

Cyclic voltammetry (CV) experiments were conducted in DMF solution (1.00 mM) with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte. A glassy carbon electrode was employed as the working electrode and referenced to an Ag reference electrode. All potential values were calibrated against the ferrocene/ferrocenium (Fc/Fc^+) redox couple. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed with a TA instrument DSC Q10 and TGA Q50 in a nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

1.4. Device fabrication and measurements

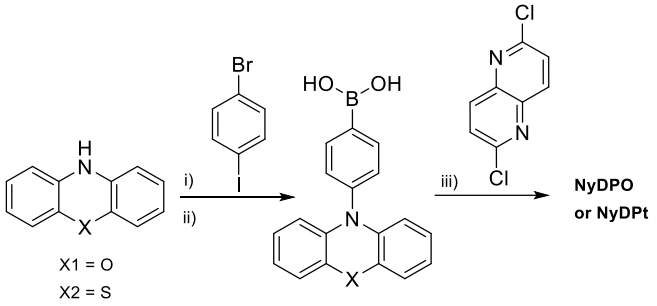
The patterned indium-tin-oxide (ITO, 70 nm) substrates were washed with water and isopropyl alcohol, followed by 10 min UV-ozone treatment. Organic layers, LiF, and Al were thermally evaporated at a deposition rate of 1−2 Å s^{-1} for organic layers, 0.1 Å s^{-1} for LiF, and 3−5 Å s^{-1} for the Al electrode. OLED properties were measured using a Keithley source meter 2400 and a PR-650 spectrascan colorimeter.

1.5. Synthesis and characterization

Commercially available reagents and solvents were used without further purification unless otherwise noted. ^{1}H-spectra were recorded using an Agilent 400-MR DD2 400 MHz or Varian/Oxford As-500 500 MHz in $CDCl_3$ and DMSO-d_6. ^{1}H-NMR chemical shifts were

referenced to $CHCl_3$ (7.26 ppm) and DMSO (2.50 ppm). ^{13}C-NMR spectra could not be obtained because NyDPO and NyDPt have very low solubility in all NMR solvents. Mass spectra were recorded on a matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) Microflex instrument from Bruker. Elemental analysis (EA) data (Thermo Fisher Scientific, Flash2000) and high-resolution mass spectrometric (HRMS) data (JEOL, JMS-700) with fast atom bombardment (FAB) positive mode were received directly from the National Center for Inter-University Research Facilities (NCIRF).

2. Synthesis



i) $CuSO_4 \cdot 5H_2O$, K_2CO_3, *o*-dichlorobenzene, reflux; ii) *n*-BuLi, trimethylborate, THF, -78°C → rt; iii) $Pd(PPh_3)_4$, K_2CO_3, Toluene/H_2O, reflux

2.1. Synthesis of 10-(4-bromophenyl)-10*H*-phenoxazine.

A mixture of phenoxazine (200 mg, 1.09 mmol), 1-bromo-4-iodobenzene (339 mg, 1.20 mmol), $CuSO_4 \cdot 5H_2O$ (29 mg, 0.11 mmol) and K_2CO_3 (301 mg, 2.18 mmol) in *o*-dichlorobenzene (5 mL) was stirred at 180°C overnight. After cooling down to room temperature, the solvent was removed under reduced pressure and filtered through silica pad. The crude product was purified by column chromatography (SiO_2, dichloromethane:hexane = 1:10) to afford compound 10-(4-bromophenyl)-10*H*-phenoxazine (255 mg, 69%) as a white

solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.75 – 6.65 (m, 4H), 6.65 – 6.59 (m, 2H), 5.94 (d, *J* = 7.8 Hz, 2H).

2.2. Synthesis of 10-(4-bromophenyl)-10*H*-phenothiazine

A mixture of phenothiazine (2.0 g, 10 mmol), 1-bromo-4-iodobenzene (3.1 g, 11 mmol), $CuSO_4 \cdot 5H_2O$ (249 mg, 1.0 mmol) and K_2CO_3 (2.76 g, 20 mmol) in *o*-dichlorobenzene (20 mL) was stirred at 180°C overnight. After cooling down to room temperature, the solvent was removed under reduced pressure and filtered through silica pad. The crude product was purified by column chromatography (SiO_2, hexane only) to afford compound 10-(4-bromophenyl)-10*H*-phenothiazine (1.4 g, 40%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 7.15 (dd, *J* = 7.4, 1.6 Hz, 2H), 6.96 (dd, *J* = 16.4, 8.8 Hz, 4H), 6.36 (d, *J* = 8.0 Hz, 2H).

2.3. Synthesis of (4-(10*H*-phenoxazin-10-yl)phenyl)boronic acid

*n*BuLi (11 mL, 17.7 mmol) was added dropwise to a solution of 10-(4-bromophenyl)-10*H*-phenoxazine (4.0 g, 11.8 mmol) in dry THF (60 mL) at -78°C under a nitrogen atmosphere. After the solution was stirred for 1 hour, trimethylborate (2.6 mL, 23.6 mmol) was added. The mixture was stirred at room temperature overnight. After 1N HCl solution was poured into the mixture, the organic phase was extracted with dichloromethane and washed with brine. The crude product was precipitated using dichloromethane and hexane, which was used for the next step without further purification. MS (MALDI-TOF): calcd. for $C_{18}H_{14}BNO_3$ $[M]^+$: 303.1067; found: 303.032.

2.4. Synthesis of (4-(10*H*-phenothiazin-10-yl)phenyl)boronic acid

*n*BuLi (13 mL, 21.2 mmol) was added dropwise to a solution of 10-(4-bromophenyl)-10*H*-phenothiazine (5.0 g, 14.1 mmol) in dry THF (70 mL) at -78°C under a nitrogen atmosphere. After the solution was stirred for 1 hour, trimethylborate (3.1 mL, 28.2 mmol) was added. The mixture was stirred at room temperature overnight. After 1N HCl solution was poured into the mixture, and the organic phase was extracted with dichloromethane and washed with brine. The crude product was precipitated using dichloromethane and hexane, which was used for the next step without further purification. MS (MALDI-TOF): calcd. for $C_{18}H_{14}BNO_2S$ $[M]^+$: 319.0838; found: 319.075.

2.5. Synthesis of 2,6-bis(4-(10*H*-phenoxazin-10-yl)phenyl)-1,5-naphthyridine (NyDPO)

A mixture of 2,6-dichloro-1,5-naphthyridine (330 mg, 1.66 mmol), (4-(10*H*-phenoxazin-10-yl)phenyl)boronic acid (1.3 g, 4.32 mmol), $Pd(PPh_3)_4$ (196 mg, 0.17 mmol) and K_2CO_3 (917 mg, 6.64 mmol) in toluene (16 mL) and water (6 mL) was stirred at 100°C overnight. After cooling down to room temperature, the solid was filtered and purified by recrystallization from chloroform and ethanol to afford **NyDPO** (967 mg, 90%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.67 – 8.52 (m, 8H), 7.65 (d, J = 8.5 Hz, 4H), 6.81 – 6.75 (m, 4H), 6.74 – 6.67 (m, 8H), 6.04 – 5.97 (m, 4H). HRMS (FAB+): calcd for $C_{44}H_{28}N_4O_2$ $[M]^+$: 644.2212; found: 644.2212. Elem. Anal.: calcd for $C_{44}H_{28}N_4O_2$ C 81.97, H 4.38, N 8.69; found C 82.15, H 4.48, N 8.58.

2.6. Synthesis of 2,6-bis(4-(10H-phenothiazin-10-yl)phenyl)-1,5-naphthyridine (NyDPt)

A mixture of 2,6-dichloro-1,5-naphthyridine (400 mg, 2.00 mmol), (4-(10*H*-phenothiazin-10-yl)phenyl)boronic acid (1.6 g, 5.01 mmol), $Pd(PPh_3)_4$ (231 mg, 0.20 mmol) and K_2CO_3 (1.4

g, 10.31 mmol) in toluene (20 mL) and water (10 mL) was stirred at 100°C overnight. After cooling down to room temperature, the solid was filtered and purified by recrystallization from chloroform and ethanol to afford **NyDPt** (1.0 g, 74%) as a pale red solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.55 (dt, J = 18.7, 9.4 Hz, 8H), 7.56 (d, J = 8.6 Hz, 4H), 7.21 (dd, J = 7.6, 1.5 Hz, 4H), 7.11 – 7.02 (m, 4H), 6.97 (td, J = 7.5, 1.1 Hz, 4H), 6.53 (dd, J = 8.1, 1.0 Hz, 4H). HRMS (FAB+): calcd for $C_{44}H_{28}N_4S_2$ [M]$^+$: 676.1755; found: 676.1760. Elem. Anal.: calcd for $C_{44}H_{28}N_4S_2$ C 78.08, H 4.17, N 8.28, S 9.47; found C 78.48, H 4.29, N 8.23, S 9.64.

3. Supplementary figures

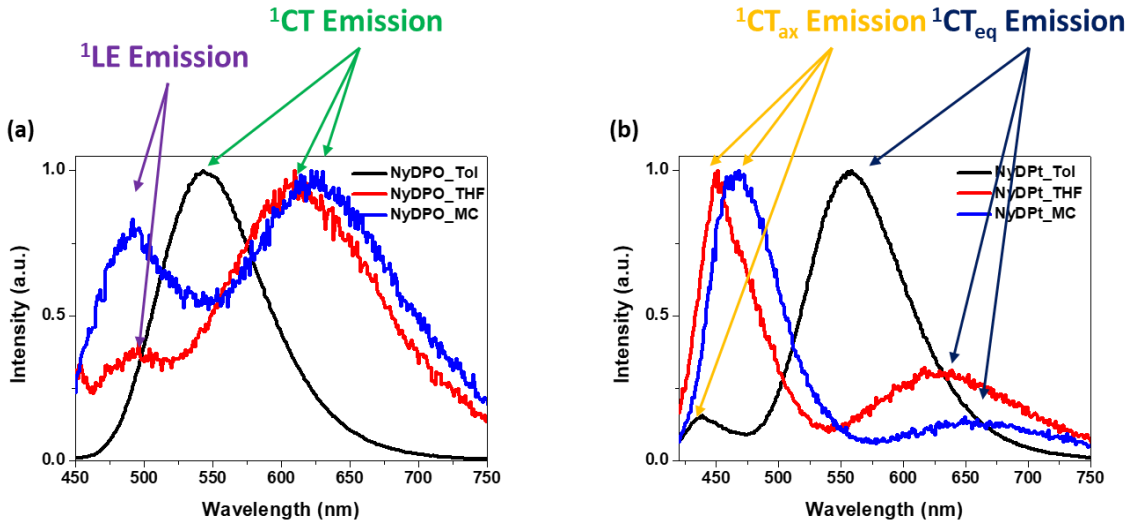


Fig. S1. Effects of solvent polarity on PL spectra of (a) **NyDPO** and (b) **NyDPt**.

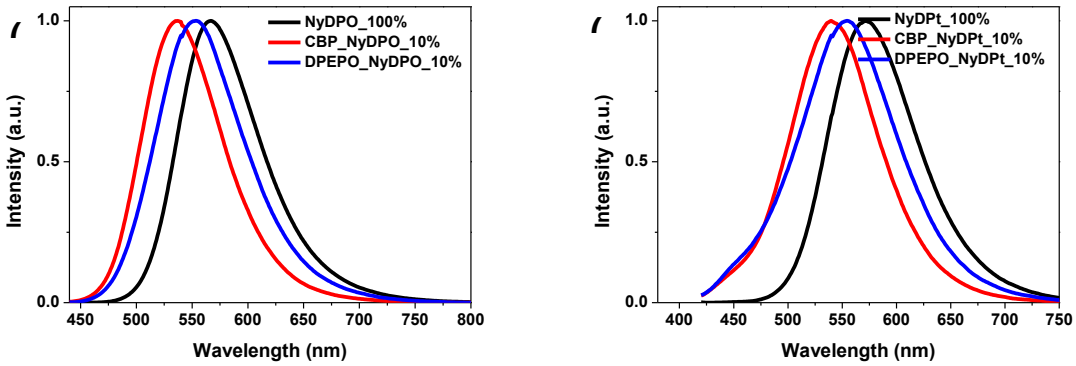


Fig. S2. PL spectra of neat film and doped film. (a) **NyDPO** and (b) **NyDPt**.

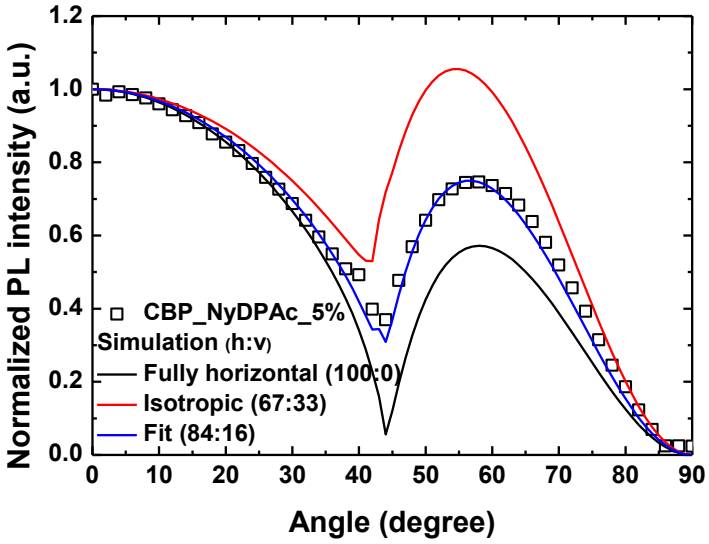


Fig. S3. Angle-dependent PL spectra of 5 wt% doped film of **NyDPAc** in CBP.

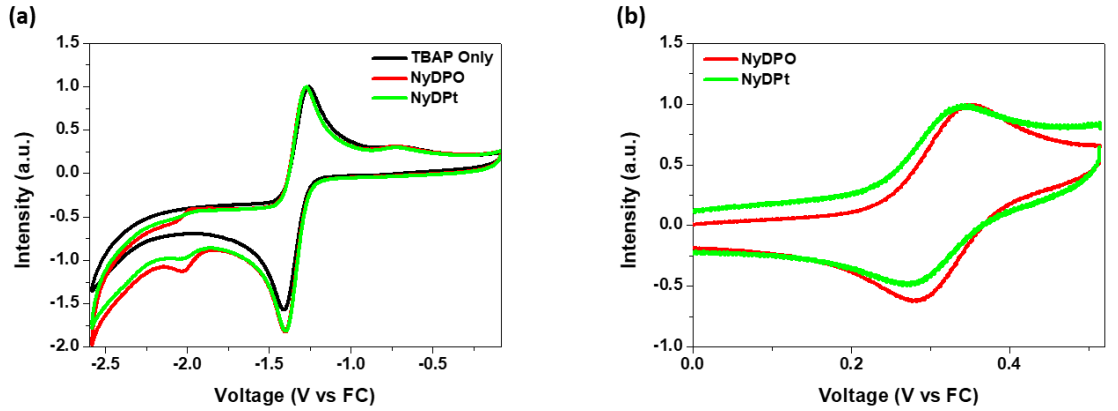


Fig. S4. Cyclic voltammograms of **NyDPO** and **NyDPt**. (a) reduction and (b) oxidation.

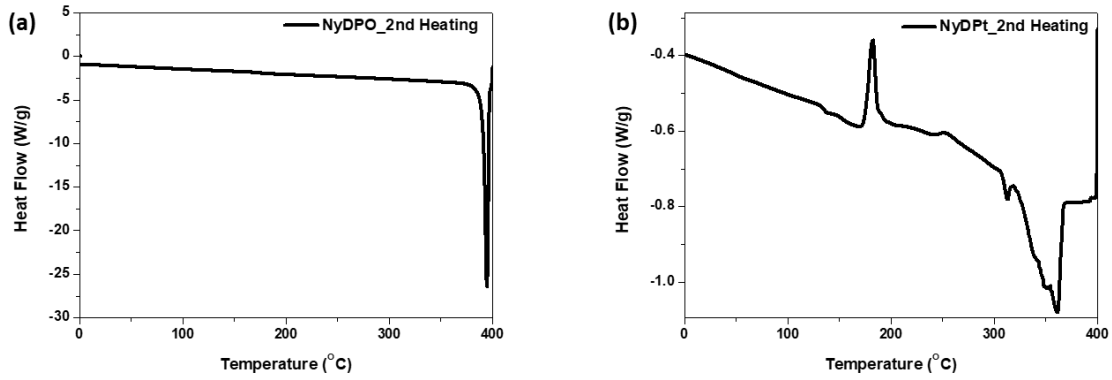


Fig. S5. DSC thermograms of (a) **NyDPO** and (b) **NyDPt**.

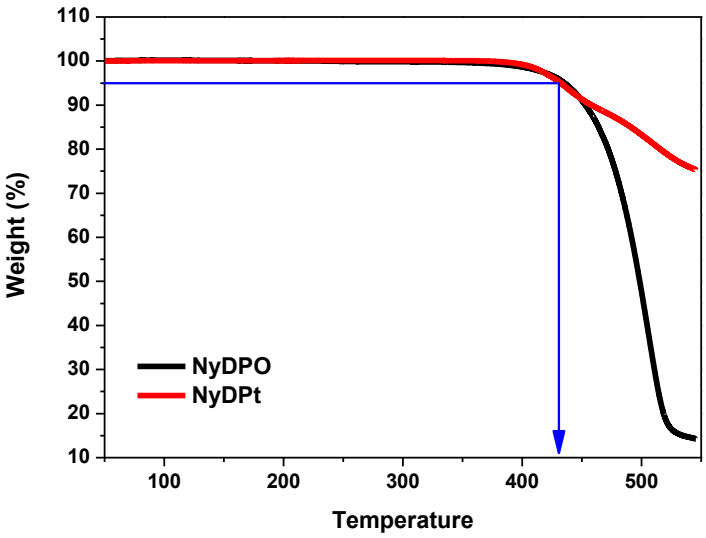


Fig. S6. TGA thermograms of **NyDPO** and **NyDPt**.

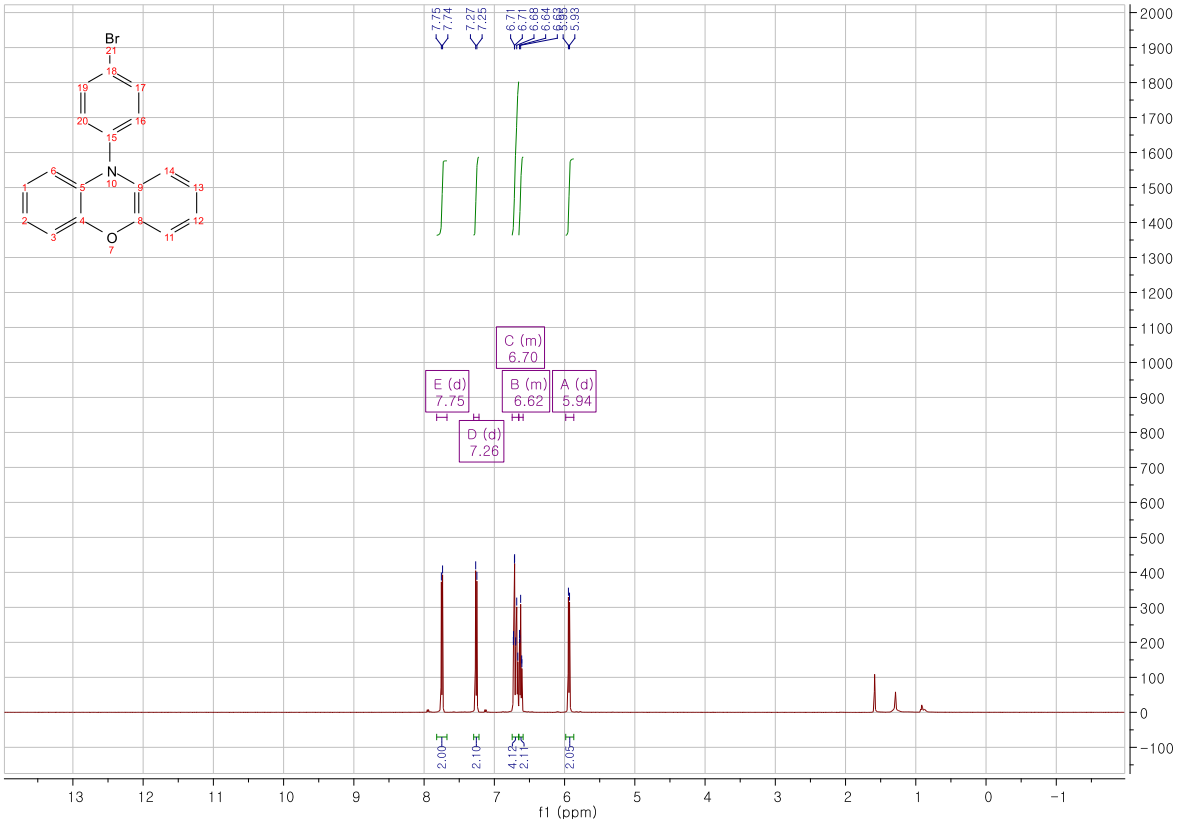


Fig. S7. ^{1}H NMR spectrum of 10-(4-bromophenyl)-10*H*-phenoxazine in $CDCl_3$.

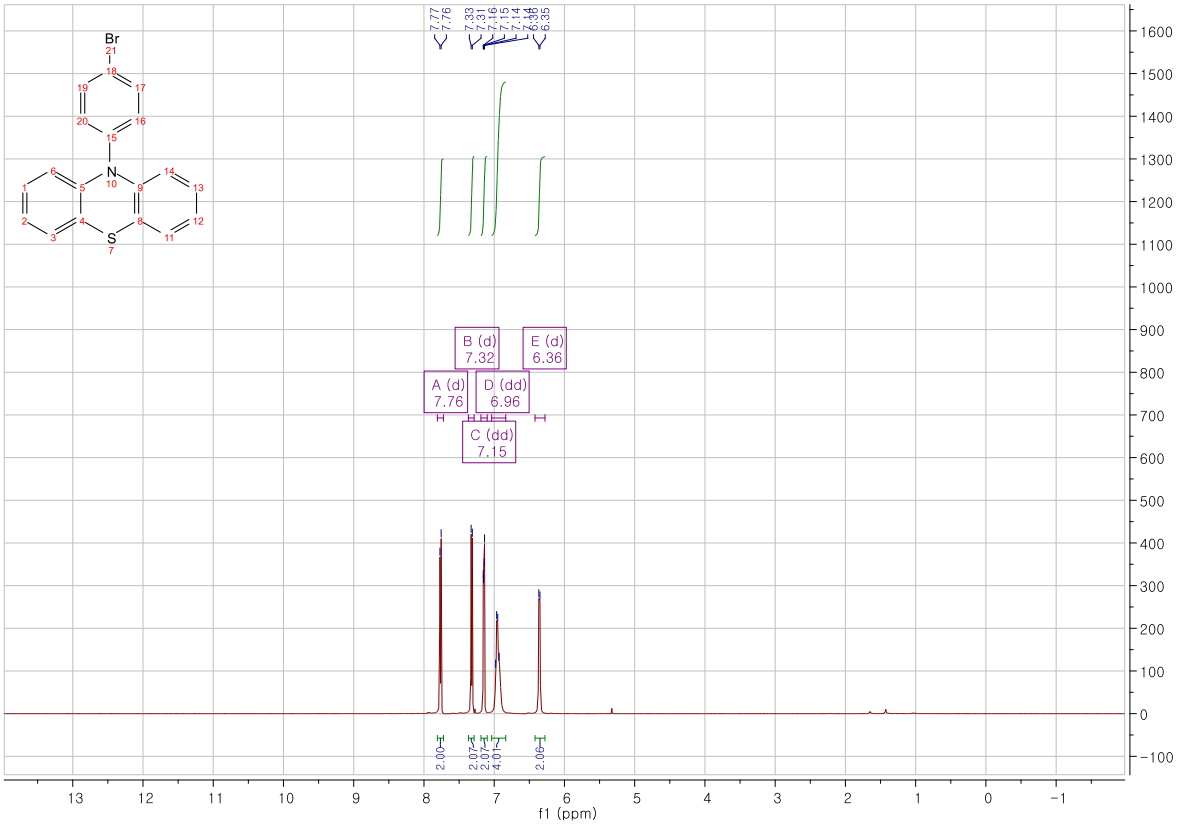


Fig. S8. ^{1}H NMR spectrum of 10-(4-bromophenyl)-10*H*-phenothiazine in $CDCl_3$.

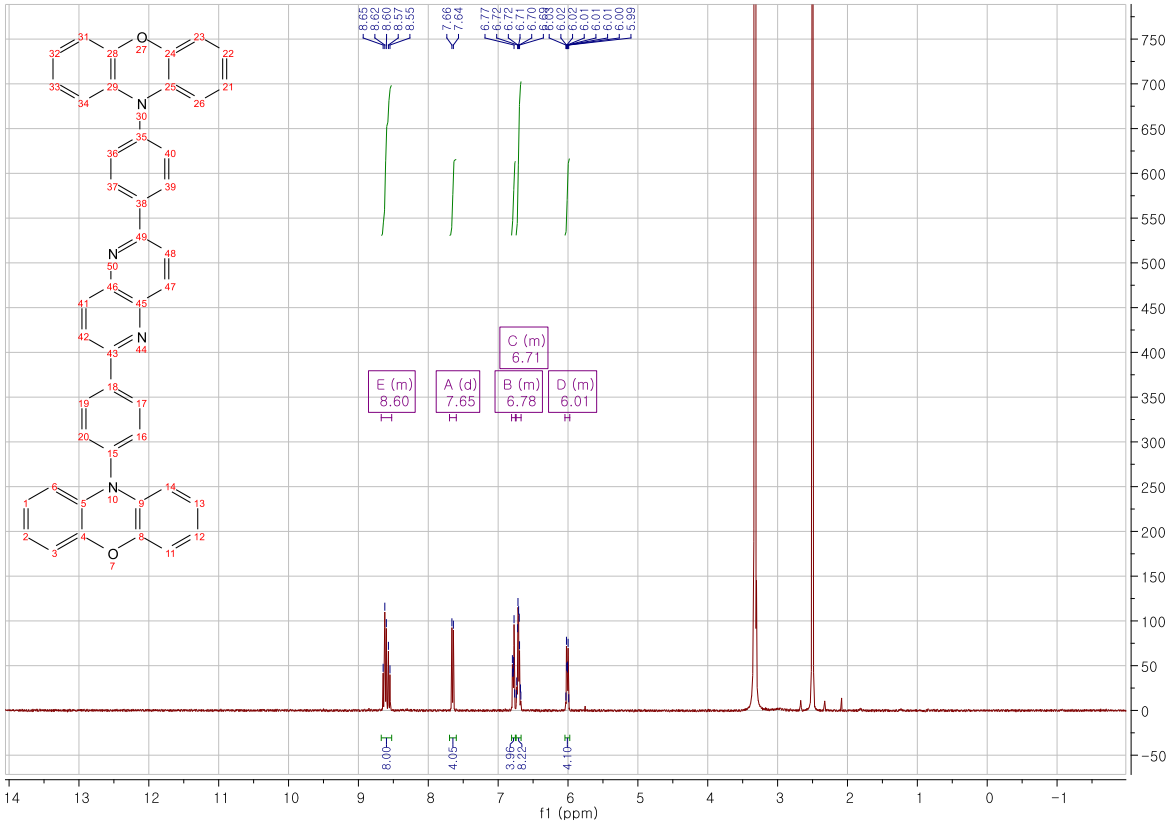


Fig. S9. ^{1}H NMR spectrum of **NyDPO** in DMSO-d_6.

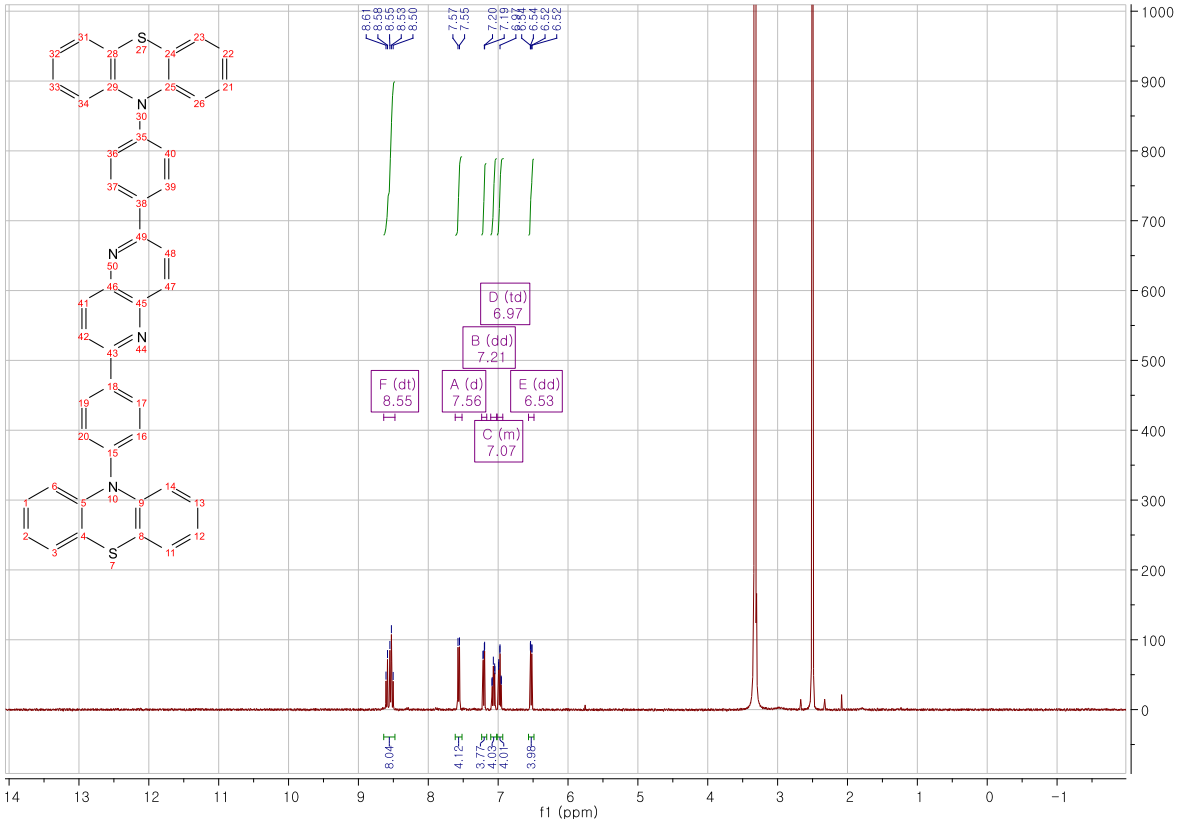


Fig. S10. ^{1}H NMR spectrum of **NyDPt** in DMSO-d_6.