Electronic Supplementary Information

Bridge-Driven Aggregation control in Dibenzofulvene-Naphthalimide Based Donor−Bridge−Acceptor Systems: Enabling Fluorescence Enhancement, Blue to Red Emission and Solvatochromism

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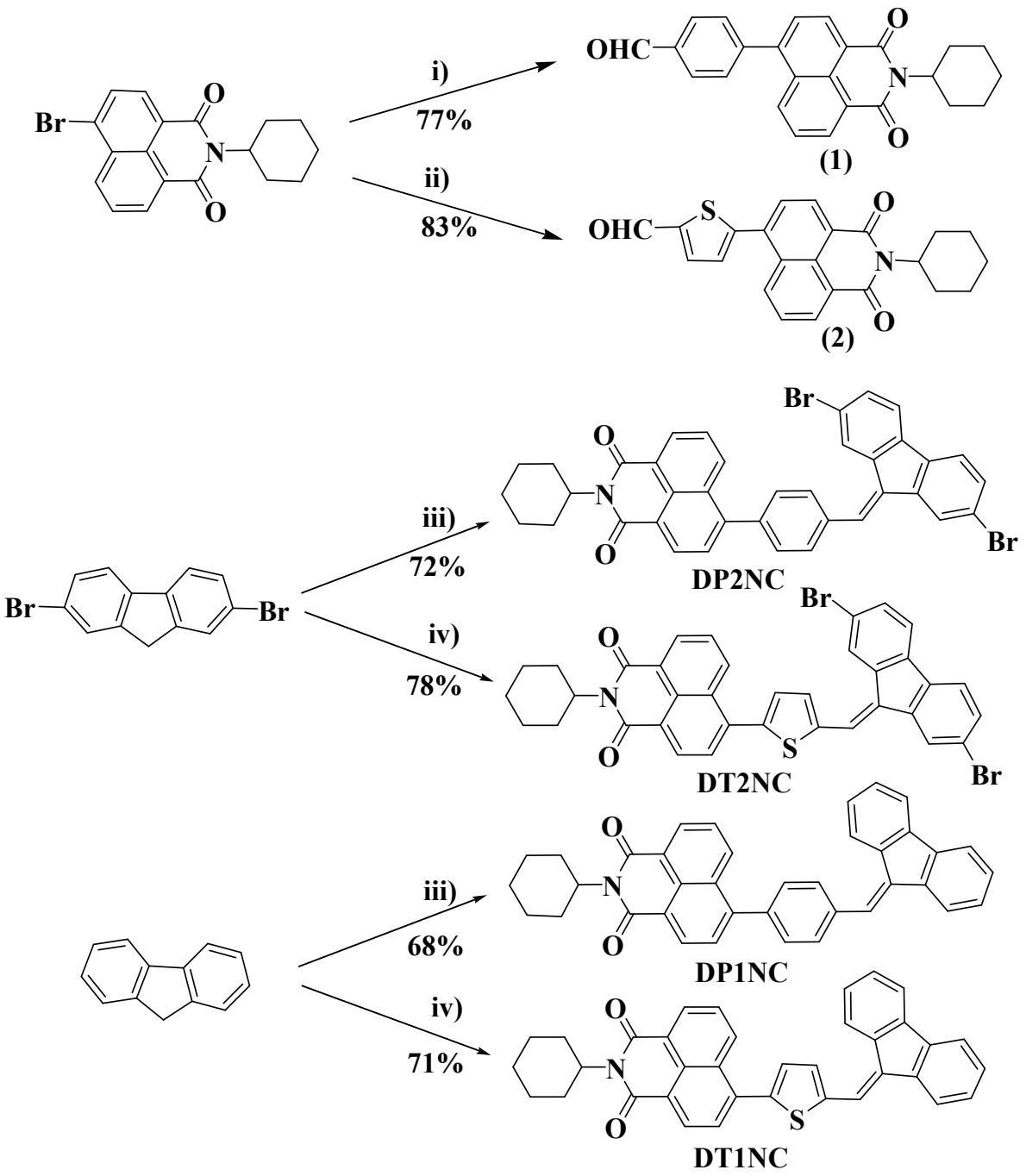


Scheme 1. Synthetic route for Monomers.

i) 4-Formylphenylboronic acid, $Pd(PPh_3)_4$, 2M K_2CO_3, THF, 12 h, 80 °C ii) 5-Formylthiophene-2-boronic acid, $Pd(PPh_3)_4$, 2M K_2CO_3, THF, 12 h. 80 °C iii) Compound (1) and EtOH, Potassium tert-butoxide, Reflux, 12 h. iv) Compound (2) and EtOH, Potassium tert-butoxide, Reflux, 12 h.

Synthetic procedure of Monomers:

Synthesis of 4-(2-Cyclohexyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-benzaldehyde (1): A mixture of N-cyclohexy6-Bromo-2-cyclohexyl-benzo[de]isoquinoline-

1,3-dione (1.eq), 4-Formylphenylboronic acid (1.2 eq), 12 mL of Tetrahydrofuran (THF) and tetrakis(triphenyl phosphine)palladium(0) (0.015 eq) were added into a dry two neck round bottom flask. Subsequently 4 mL 2M aqueous potassium carbonate were added to the flask. The reaction mixture was stirred at 80 °C for 12 hours under argon atmosphere. The reaction mixture was then cooled to room temperature. After work up, the mixture was purified by column chromatography to give white color **Compound 1**. (yield: 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.15 (s, 1H), 8.62 (dd, *J*=6 Hz, 6 Hz 2H), 8.14 (d, *J*=6 Hz, 1H), 8.07 (d, *J*=12 Hz, 2H), 7.70 (m, 4H), 5.04 (m, 1H), 2.56 (m, 2H), 1.89 (m, 2H), 1.75 (m, 2H), 1.45 (m, 2H), 1.33 (m, 2H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.86, 164.73, 164.53, 145.23, 144.91, 136.30, 131.71, 130.81, 130.72, 130.15, 129.74, 128.87, 128.02, 127.49, 123.87, 123.39, 54.11, 29.33, 26.75, 25.65. HRMS (ESI): m/z $[M + H]^+$ calcd: 384.1600; found: 384.1606.

Synthesis of 5-(2-Cyclohexyl-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-thiophene-2-carbaldehyde (2): A mixture of 6-Bromo-2-cyclohexyl-benzo[de]isoquinoline-1,3-dione (1.eq), 5-formylthiophene-2-boronic acid (1.2 eq), 12 mL of Tetrahydrofuran (THF) and tetrakis(triphenyl phosphine)palladium(0) (0.015 eq) were added into a dry two neck round bottom flask. Subsequently 4 mL 2M aqueous potassium carbonate were added to the flask. The reaction mixture was stirred at 80 °C for 12 hours under argon atmosphere. The reaction mixture was then cooled to room temperature. After work up, the mixture was purified by column chromatography to give light green color solid **Compound 2**. (yield: 83%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 10.01 (s, 1H), 8.64 (d, *J*=6 Hz, 1H), 8.60 (d, *J*=6 Hz, 1H), 8.49 (d, *J*=6 Hz, 1H), 7.89 (d, *J*=6 Hz, 1H), 7.84 (d, *J*=6 Hz, 1H), 7.79 (t, 1H), 7.43 (d, *J*= 6 Hz, 1H), 5.03 (m, 1H), 2.55 (m, 2H), 1.90 (m, 2H), 1.75 (m, 2H), 1.44 (m, 2H), 1.34 (m, 2H),^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 182.85, 164.51, 164.23, 149.59, 145.24, 137.13, 136.39, 131.65, 131.23, 130.48, 129.76, 129.05, 128.95, 127.95, 126.64, 124.17, 124.00, 54.23, 29.33, 26.73, 25.63. HRMS (ESI): m/z $[M + H]^+$: calcd: 390.1164; found: 390.1153.

Synthesis of 2-Cyclohexyl-6-[4-(2,7-dibromo-fluoren-9-ylidenemethyl)-phenyl]-benzo[de]isoquinoline-1,3-dione (DP2NC): A mixture of potassium tert-butoxide (1.2 eq) and 2,7-Dibromo-9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 hour than compound 1 (1 eq) was added into reaction mixture and again refluxed for 24 hours. The solvent was removed, and the residue was extracted with Chloroform. The solvent was evaporated. The residue was purified by column chromatography to give product as a yellow color solid compound **DP2NC**. (yield: 72%); ^{1}H

NMR (600 MHz, $CDCl_3$) δ (ppm): 8.66 (d, *J*=6 Hz, 1H), 8.63 (d, *J*=6 Hz, 1H), 8.34 (d, *J*=6 Hz, 1H), 7.94 (s, 1H), 7.79 (m, 2H), 7.74 (m, 4H), 7.64 (d, 2H), 7.57 (d, *J*=6 Hz, 2H), 7.53 (d, *J*=6 Hz, 1H), 7.47 (d, *J*=6 Hz, 1H), 5.07 (m, 1H), 2.59 (m, 2H), 2.04 (m, 2H), 1.93 (m, 2H), 1.49 (m, 4H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.89, 164.70, 139.55, 139.48, 138.16, 137.34, 136.28, 132.20, 131.69, 131.34, 130.87, 130.51, 129.68, 129.09, 128.05, 127.72, 127.30, 124.03, 121.58, 121.39, 121.28, 121.01, 114.26, 54.07, 29.36, 26.78, 25.69. HRMS (ESI): m/z $[M + H]^+$: calcd: 690.0466; found: 690.0455.

Synthesis of 2-Cyclohexyl-6-[5-(2,7-dibromo-fluoren-9-ylidenemethyl)-thiophen-2-yl]-benzo[de]isoquinoline-1,3-dione (DT2NC): A mixture of potassium tert-butoxide (1.2 eq) and 2,7-Dibromo-9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 hour than compound 2 (1 eq) was added into reaction mixture and again refluxed for 18 hours. The solvent was removed, and the residue was extracted with Chloroform. The solvent was evaporated. The residue was purified by column chromatography to give product as a orange color solid compound **DT2NC.** (yield: 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.71 (d, *J*= 12 Hz, 1H), 8.65 (d, *J*= 12 Hz, 1H), 8.61 (d, *J*= 12 Hz, 1H), 8.43 (s, 1H), 7.89 (m, 2H), 7.82 (t, 1H), 7.64 (s, 1H), 7.54 (m, 4H), 7.43 (d, *J*= 6 Hz, 1H), 5.05 (m, 1H), 2.57 (m, 2H), 1.90 (m, 2H), 1.75 (m, 2H), 1.43 (m, 4H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.73, 164.49, 143.00, 140.48, 139.46, 137.86, 137.05, 135.11, 132.16, 131.81, 131.69, 131.57, 131.28, 130.71, 129.87, 129.68, 129.10, 128.88, 127.73, 127.67, 123.88, 121.58, 121.45, 121.30, 121.24, 120.78, 54.12, 29.33, 26.76, 25.66. HRMS (ESI): m/z $[M + H]^+$: calcd: 696.0030; found: 696.0033.

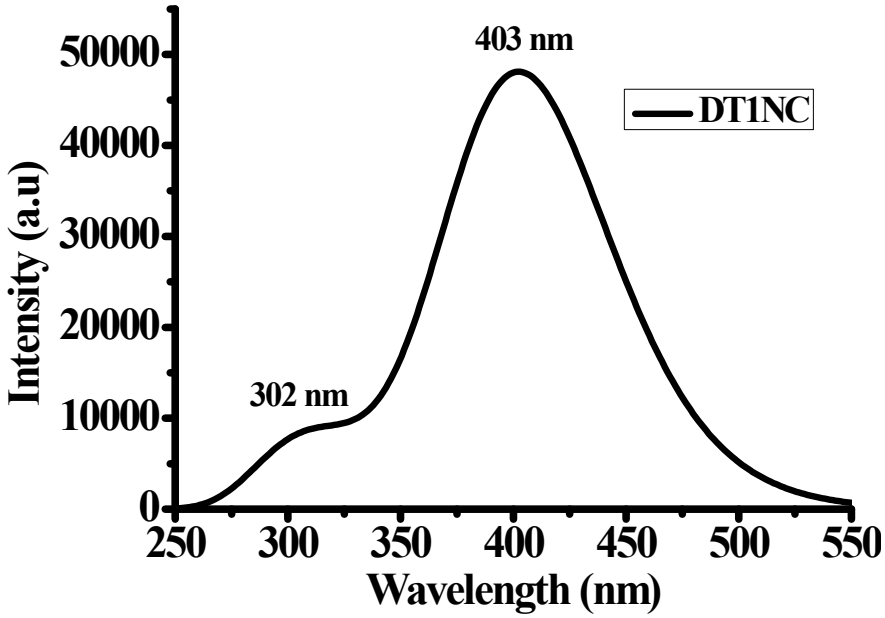
Synthesis of 2-Cyclohexyl-6-(4-fluoren-9-ylidenemethyl-phenyl)-benzo[de]isoquinoline-1,3-dione (DP1NC): A mixture of potassium tert-butoxide (1.2 eq) and 9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 hour than compound 1 (1 eq) was added into reaction mixture and again refluxed for 18 hours. The solvent was removed, and the residue was extracted with Chloroform. The solvent was evaporated. The residue was purified by column chromatography to give product as a yellow color solid compound **DP1NC**. (yield: 68%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.66-8.63 (dd, *J*= 6 Hz, *J*= 6 Hz, 2H), 8.34 (d, *J*= 12 Hz, 1H), 7.83 (d, 1H), 7.77 (m, 3H), 7.75 (m, 5H), 7.60 (d, *J*= 6 Hz, 2H), 7.40 (t, 1H), 7.36 (m, 2H), 7.13 (t, 1H), 5.07 (m, 1H), 2.59 (m, 2H), 1.91 (m, 2H), 1.77 (m, 2H), 1.45 (m, 4H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.92, 164.73, 146.14, 139.61, 139.45, 138.75, 137.35, 136.58, 134.88, 132.27, 131.31, 130.90, 130.28, 130.02, 129.92, 129.28, 129.08, 128.69, 128.12, 127.32, 127.19, 126.94, 126.37,

124.53, 120.52, 120.11, 119.88, 54.05, 29.36, 26.79, 25.70. HRMS (ESI): m/z $[M + H]^+$: calcd: 532.2277; found: 532.2301.

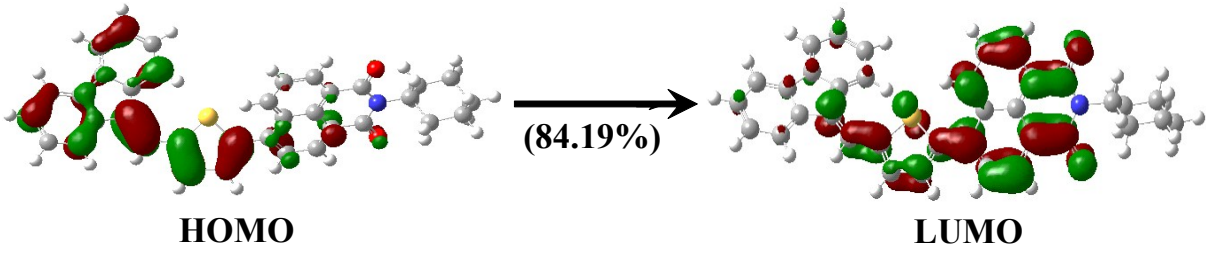
Synthesis of 2-Cyclohexyl-6-(5-fluoren-9-ylidenemethyl-thiophen-2-yl)-benzo[de]isoquinoline-1,3-dione (DT1NC): A mixture of potassium tert-butoxide (1.2 eq) and 9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 hour than compound 2 (1 eq) was added into reaction mixture and again refluxed for 18 hours. The solvent was removed, and the residue was extracted with Chloroform. The solvent was evaporated. The residue was purified by column chromatography to give product as a orange solid compound **DT1NC.** (yield: 71%);^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.72 (d, *J*= 12 Hz, 1H), 8.63 (d, *J*= 12 Hz, 1H), 8.61 (d, *J*= 12 Hz, 1H), 8.30 (d, *J*= 12 Hz, 1H), 7.89 (d, *J*= 12 Hz, 1H), 7.75 (m, 4H), 7.64 (s, 1H), 7.59 (d, *J*= 6 Hz, 1H), 7.37 (m, 4H), 7.25 (m, 1H), 5.05 (m, 1H), 2.58 (m, 2H), 1.88 (m, 2H), 1.77 (m, 2H), 1.42 (m, 4H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 164.76, 164.50, 141.85, 141.73, 139.67, 138.27, 136.21, 131.94, 131.51, 131.48, 130.74, 130.70, 130.53, 130.48, 129.45, 129.31, 129.15, 128.79, 128.73, 127.55, 127.34, 127.14, 124.66, 120.48, 120.16, 119.19, 118.12, 118.08, 54.13, 29.36, 26.77, 25.67. HRMS (ESI): m/z calcd: 538.1841; found: 538.1844.

Table S1. TD-DFT calculations of the luminogens.

Monomers	**TD-DFT**		
	λ_{theory} (nm)	**f**	**Composition**
DT1NC	302 ($S_0 \rightarrow S_{11}$) 403 ($S_0 \rightarrow S_5$)	0.11, 1.17	H→L+1 (72.13%) = π-π* H→L (84.19%) = π-π* (ICT)
DT2NC	323 ($S_0 \rightarrow S_9$) 399 ($S_0 \rightarrow S_5$)	0.09, 1.23	H→L+1 (65.45%) = π-π* H-2→L (25.0%) = π-π*, H→L (89.65%) = π-π* (ICT)
DP1NC	339 ($S_0 \rightarrow S_6$)	1.26	H→L (60.05%) = π-π* H→L+1 (16.83%) = π-π*
DP2NC	328 ($S_0 \rightarrow S_8$)	1.04	H→L+1 (55.77%) = π-π* H→L (23.43%) = π-π*



Excitation transition at 403 nm ($S_0 \rightarrow S_5$)



Excitation transition at 302 nm ($S_0 \rightarrow S_{11}$)

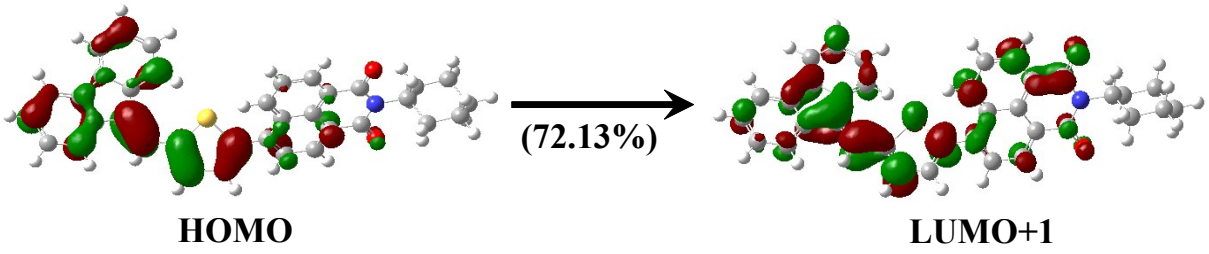
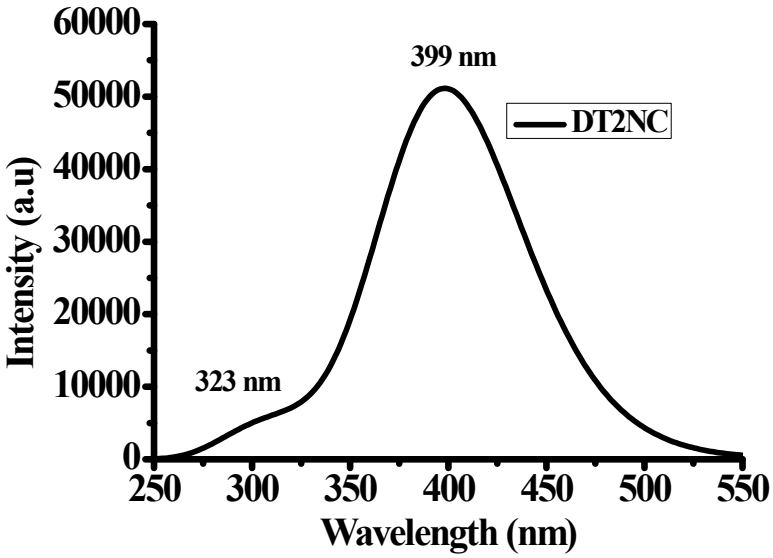
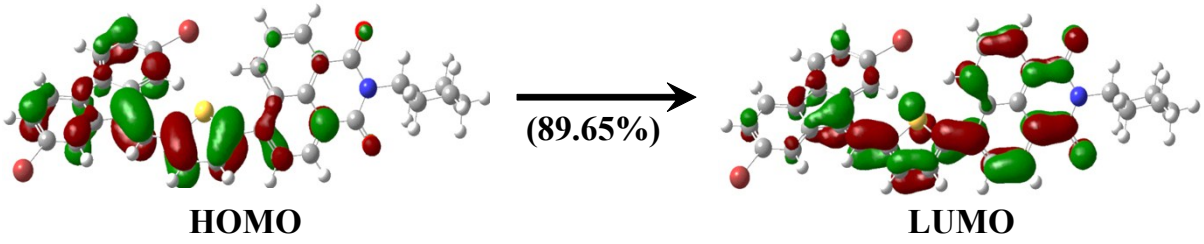


Figure S1. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DT1NC** luminogen.



Excitation transition at 399 nm ($S_0 \rightarrow S_3$)



Excitation transition at 323 nm ($S_0 \rightarrow S_9$)

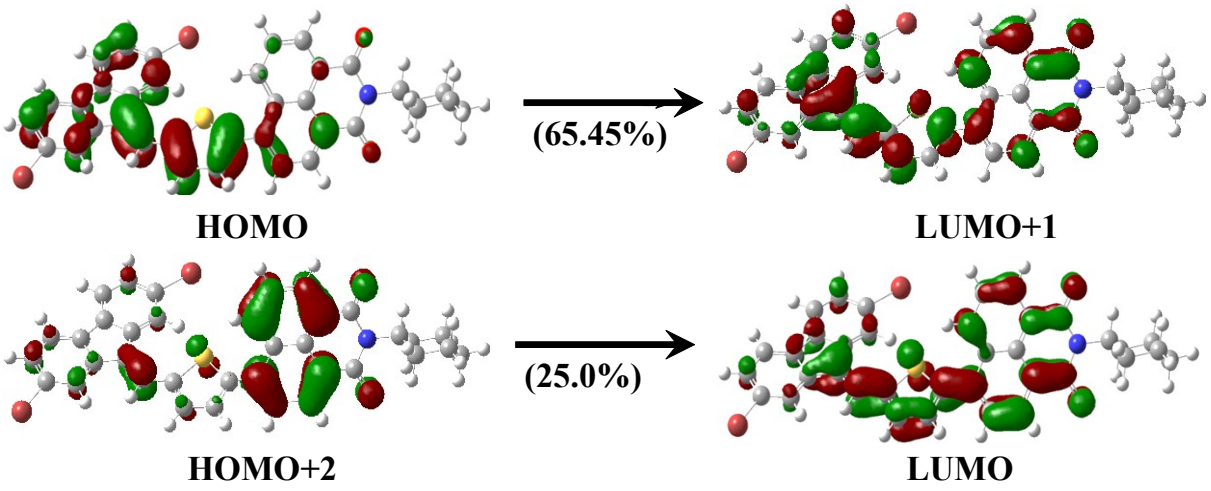
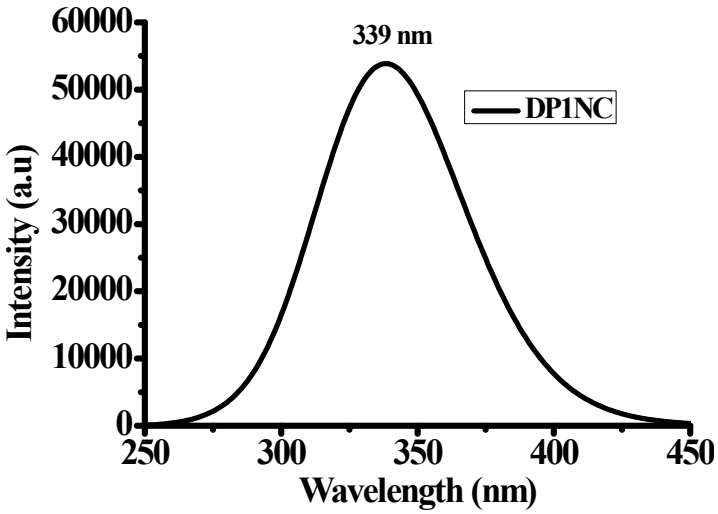


Figure S2. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DT2NC** luminogen.



Excitation transition at 339 nm ($S_0 \rightarrow S_6$)

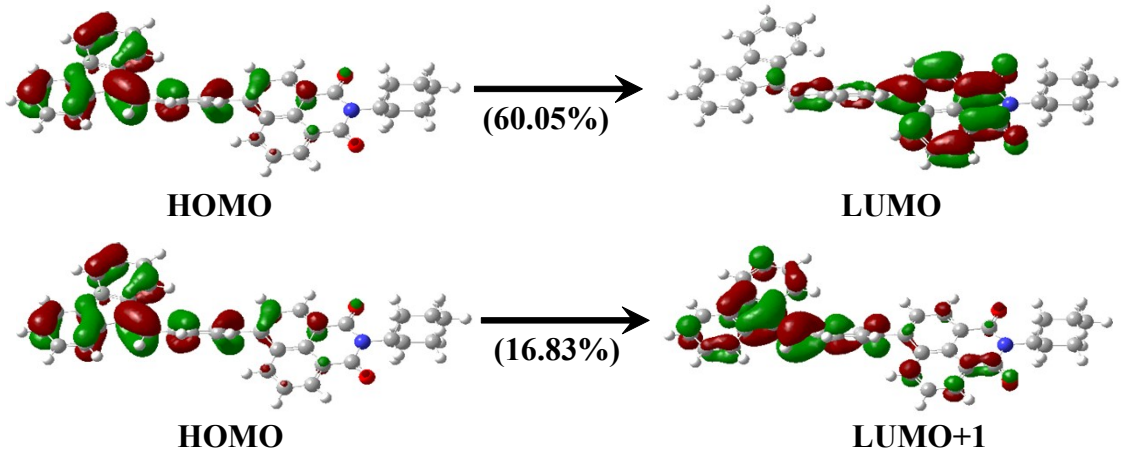
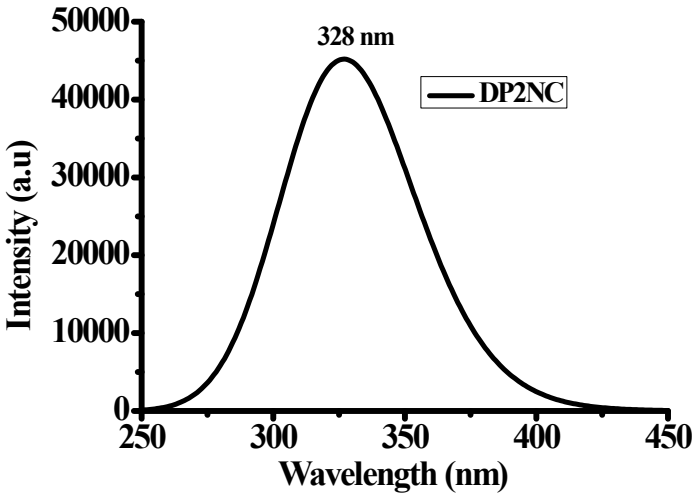


Figure S3. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DP1NC** luminogen.



Excitation transition at 328 nm ($S_0 \rightarrow S_8$)

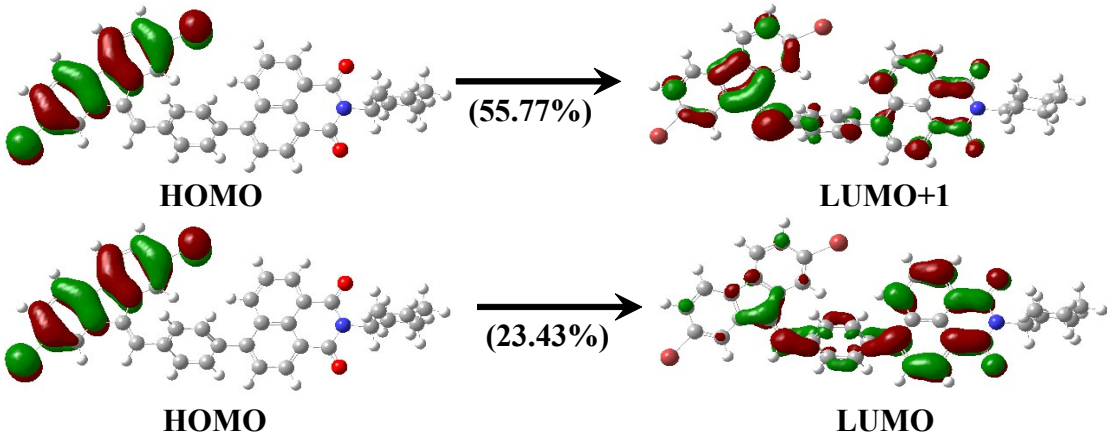


Figure S4. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DP2NC** luminogen.

Crystal Data:

Table S2. Structure determination summary of **DP1NC** and **DP2NC.**

Compound	**DP1NC**	**DP2NC**
Empirical formula	$C_{38}H_{29}NO_2$	$C_{38}H_{27}Br_2NO_2$
CCDC NO	1525968	1525969
Formula weight	531.62	689.41
Temperature/K	296 (2)	296 (2)
Crystal system	monoclinic	monoclinic
Space group	P 2_1/c	C 2/c
a/Å	11.2762(6)	19.610(2)
b/Å	13.9376(8)	15.469(2)
c/Å	17.8045(11)	20.516(2)
α/°	90.00	90.00
β/°	101.143(4)	107.135(11)

γ/°	90.00	90.00
Volume/Å^3	2745.5(3)	5947.2(12)
Z	4	8
ρ_{calc}mg/mm^3	1.286	1.540
m/mm^{-1}	0.079	2.763
F(000)	1120.0	2784.0
Crystal size/mm^3	0.28 × 0.24 × 0.21	0.28 × 0.24 × 0.21
2Θ range for data collection	3.74 to 50°	3.42 to 50°
Index ranges	-13 ≤ h ≤ 12, -16 ≤ k ≤ 16, -21 ≤ l ≤ 20	-17 ≤ h ≤ 23, -18 ≤ k ≤ 18, -24 ≤ l ≤ 24
Reflections collected	26930	32449
Independent reflections	4837[R(int) = 0.0712]	5249[R(int) = 0.0866]
Data/restraints/parameters	4837/0/370	5249/0/388
Goodness-of-fit on F^2	0.978	0.985
Final R indexes [I>=2σ (I)]	R1 = 0.0545, wR2 = 0.1472	R1 = 0.0436, wR2 = 0.1186
Final R indexes [all data]	R1 = 0.1213, wR2 = 0.1844	R1 = 0.1421, wR2 = 0.1870

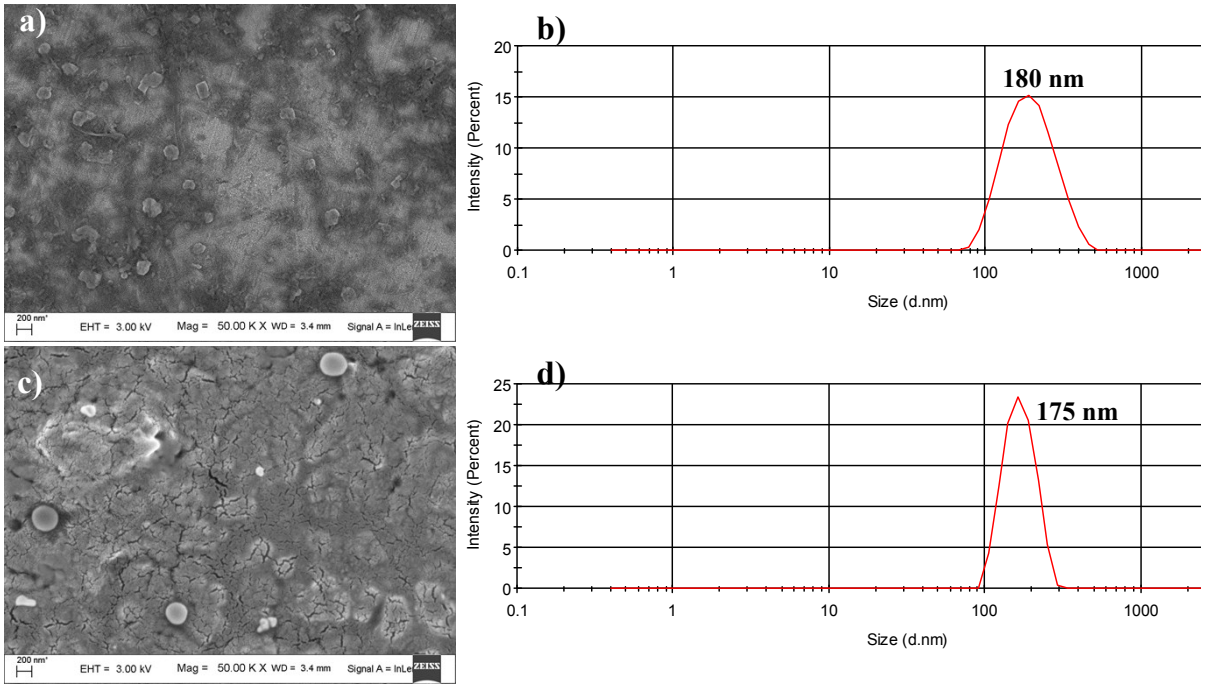


Figure S5. FE-SEM images and Dynamic Light Scattering (DLS) curves of DT1NC (a) & (b) and DT2NC (c) & (d).

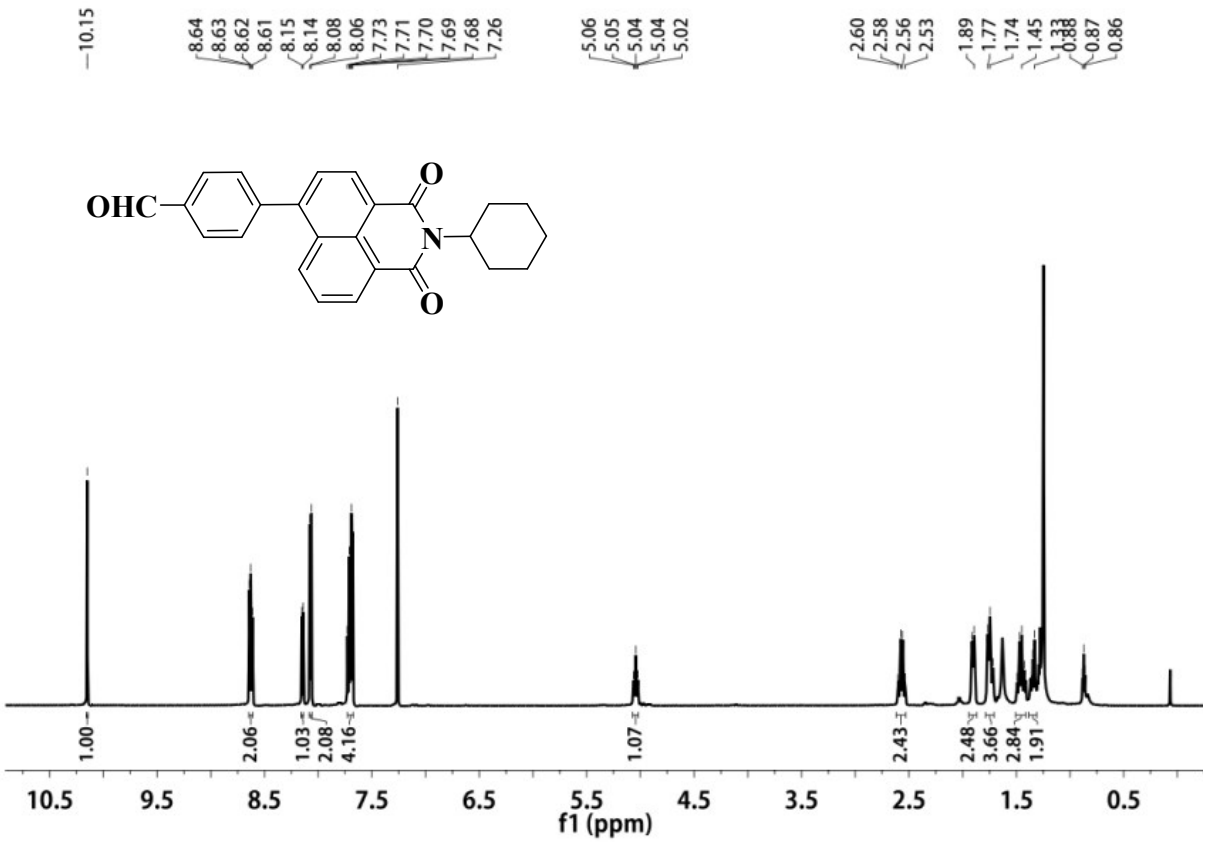


Figure S6. The ^{1}H NMR of the **Compound-1** in $CDCl_3$.

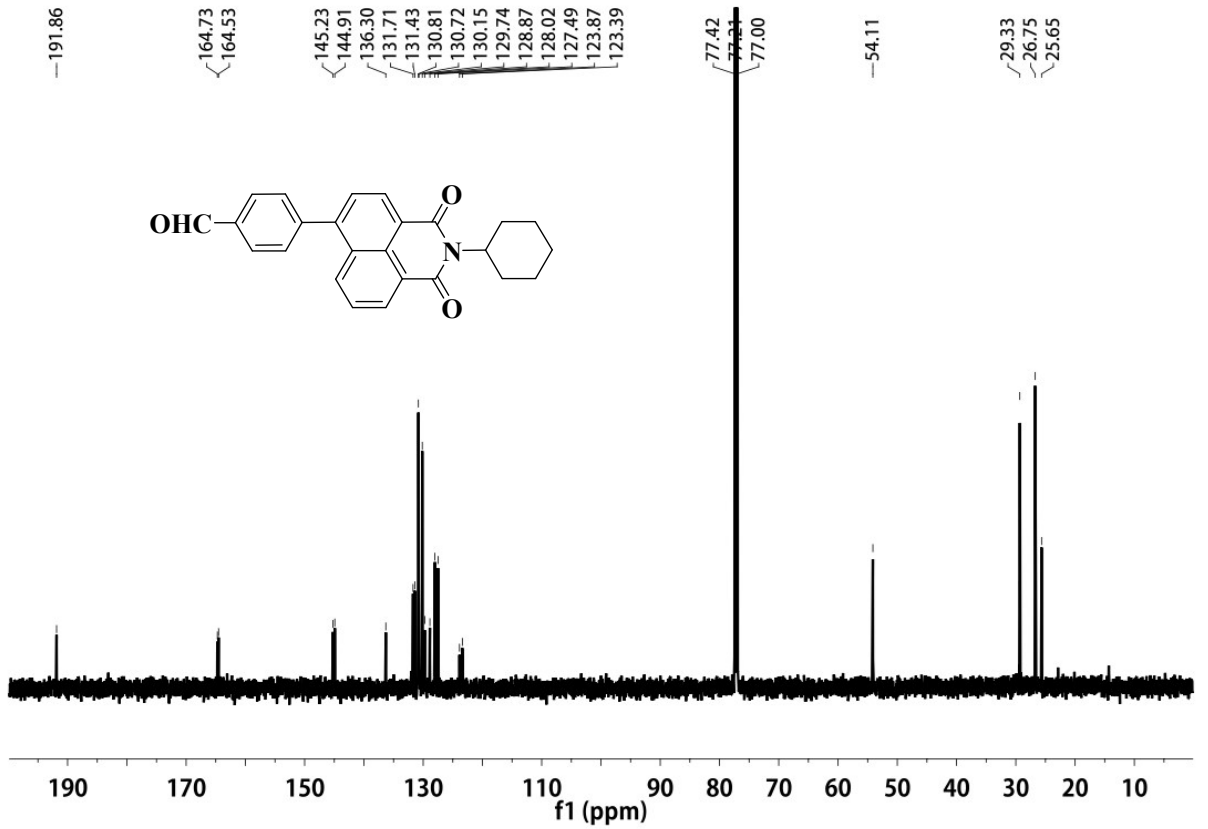


Figure S7. The ^{13}C NMR of the **Compound-1** in $CDCl_3$.

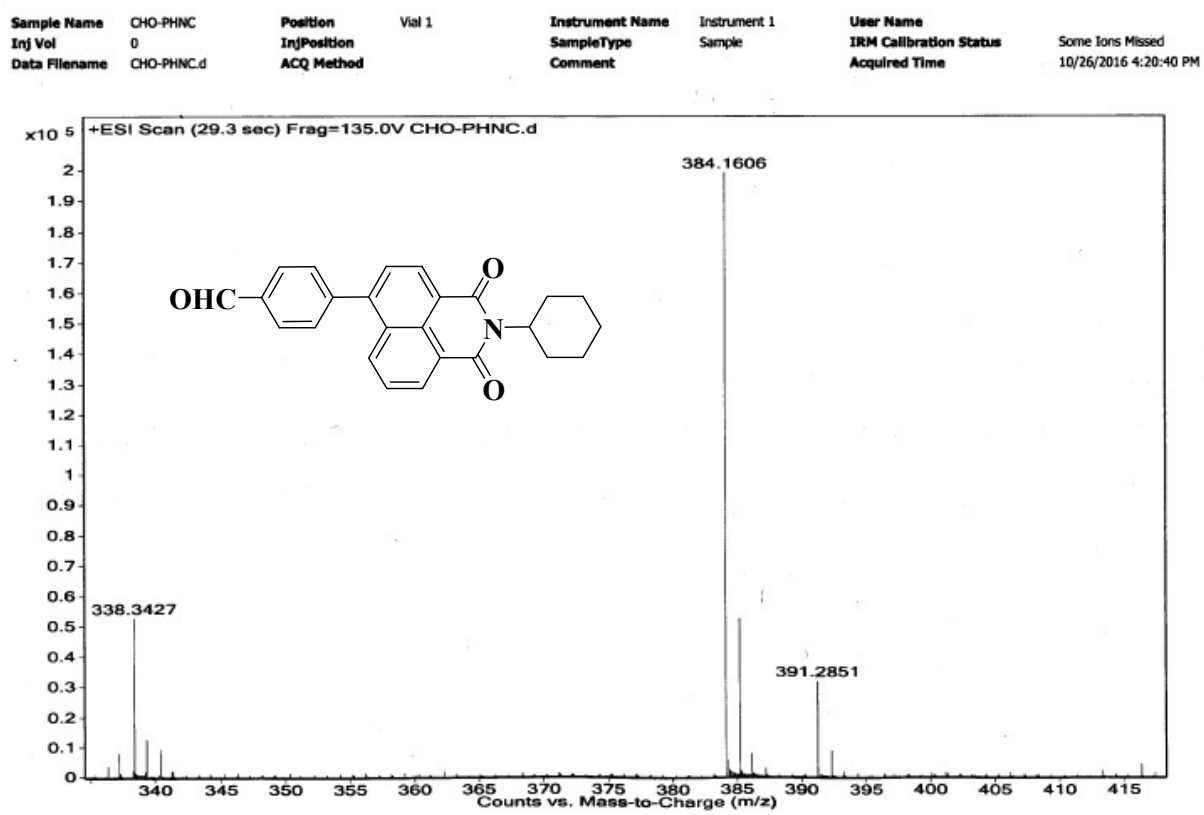


Figure S8. HRMS of the **Compound-1**.

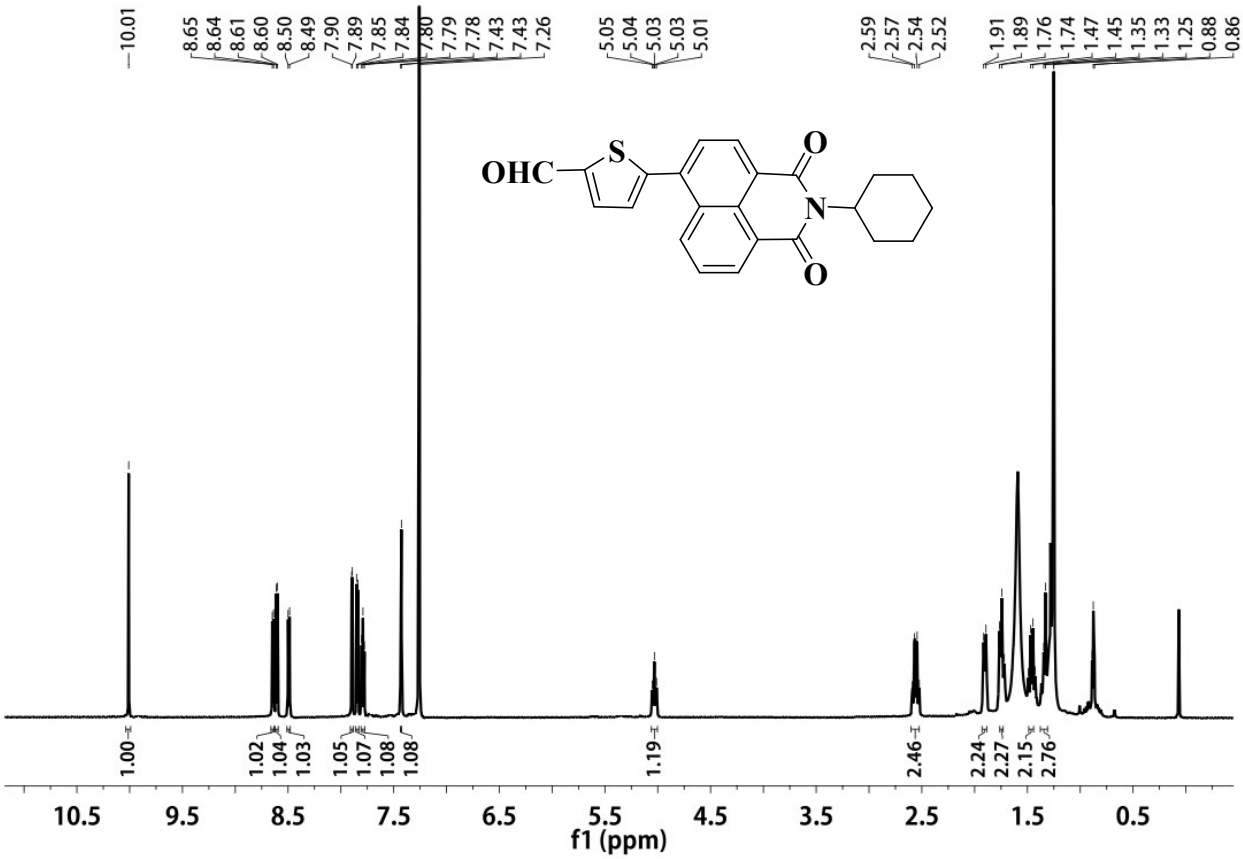


Figure S9. The ^{1}H NMR of the **Compound-2** in $CDCl_3$.

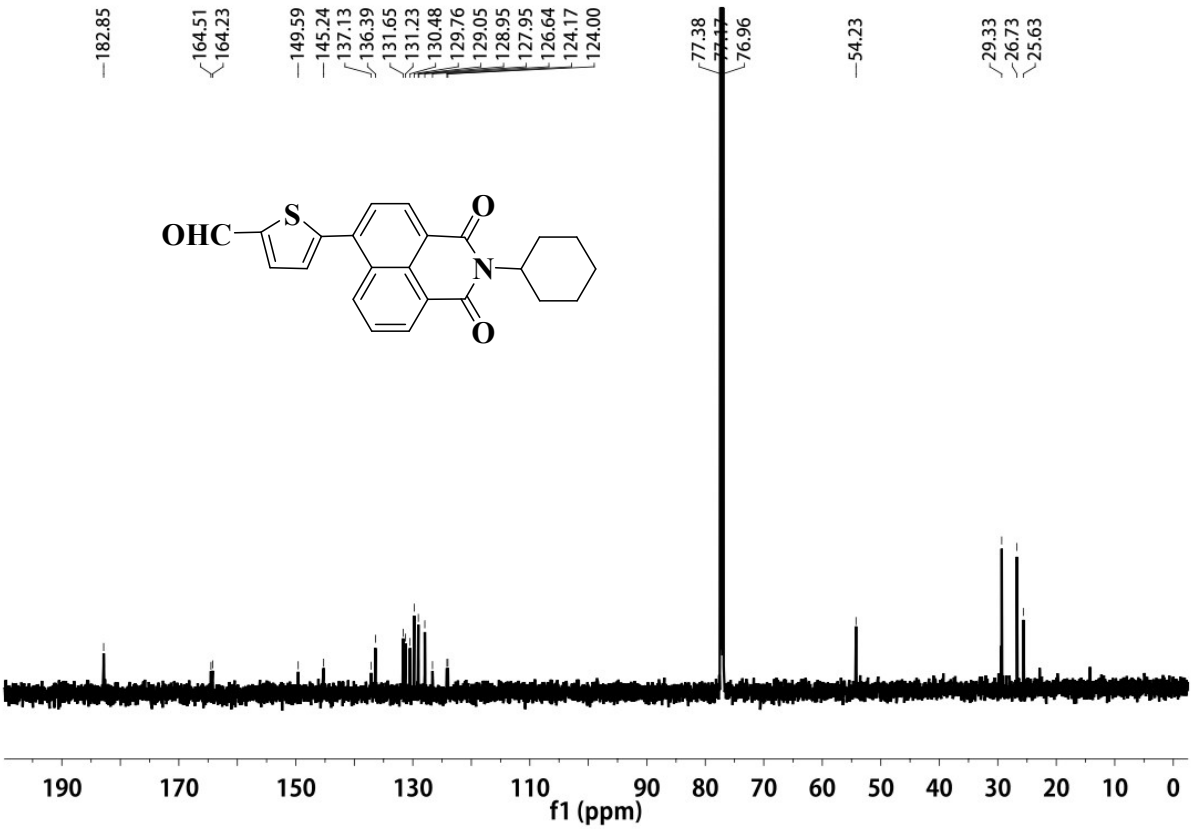


Figure S10. The ^{13}C NMR of the **Compound-2** in $CDCl_3$.

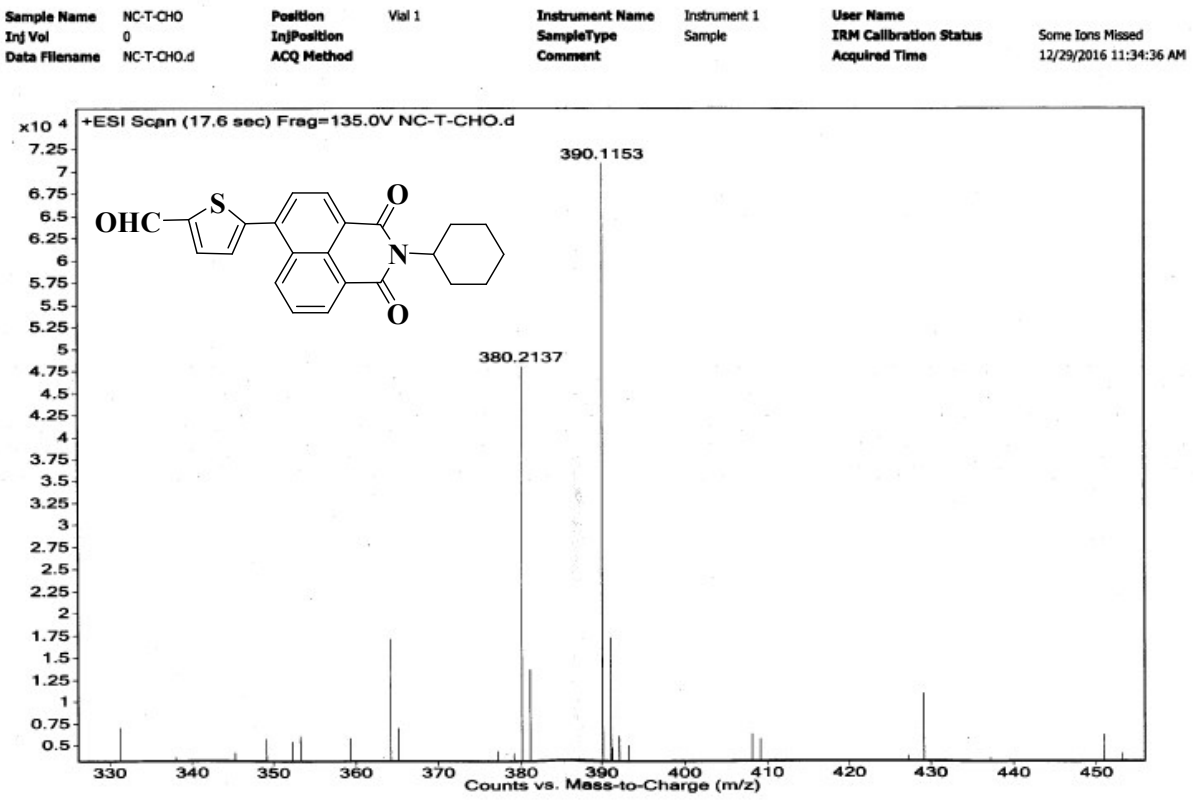


Figure S11. HRMS of the **Compound-2**.

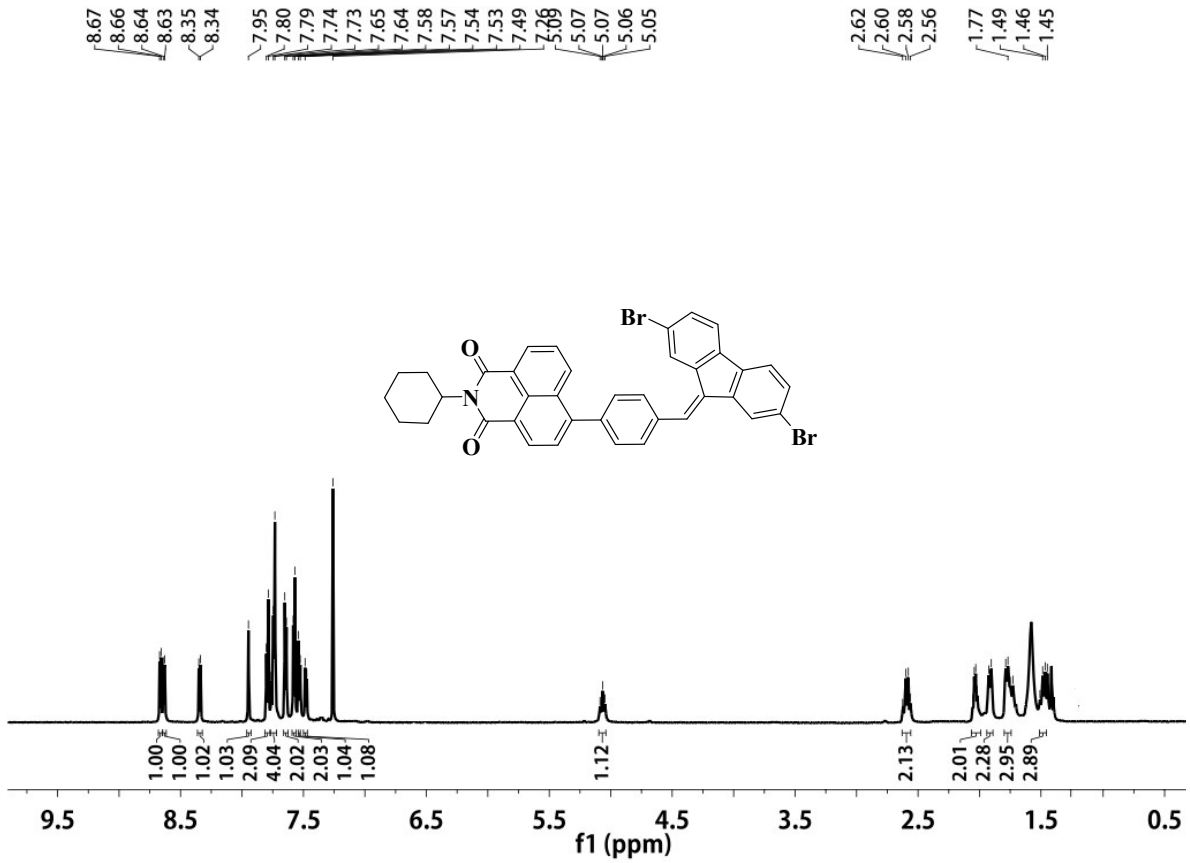


Figure S12. The ^{1}H NMR of the **DP2NC** in $CDCl_3$.

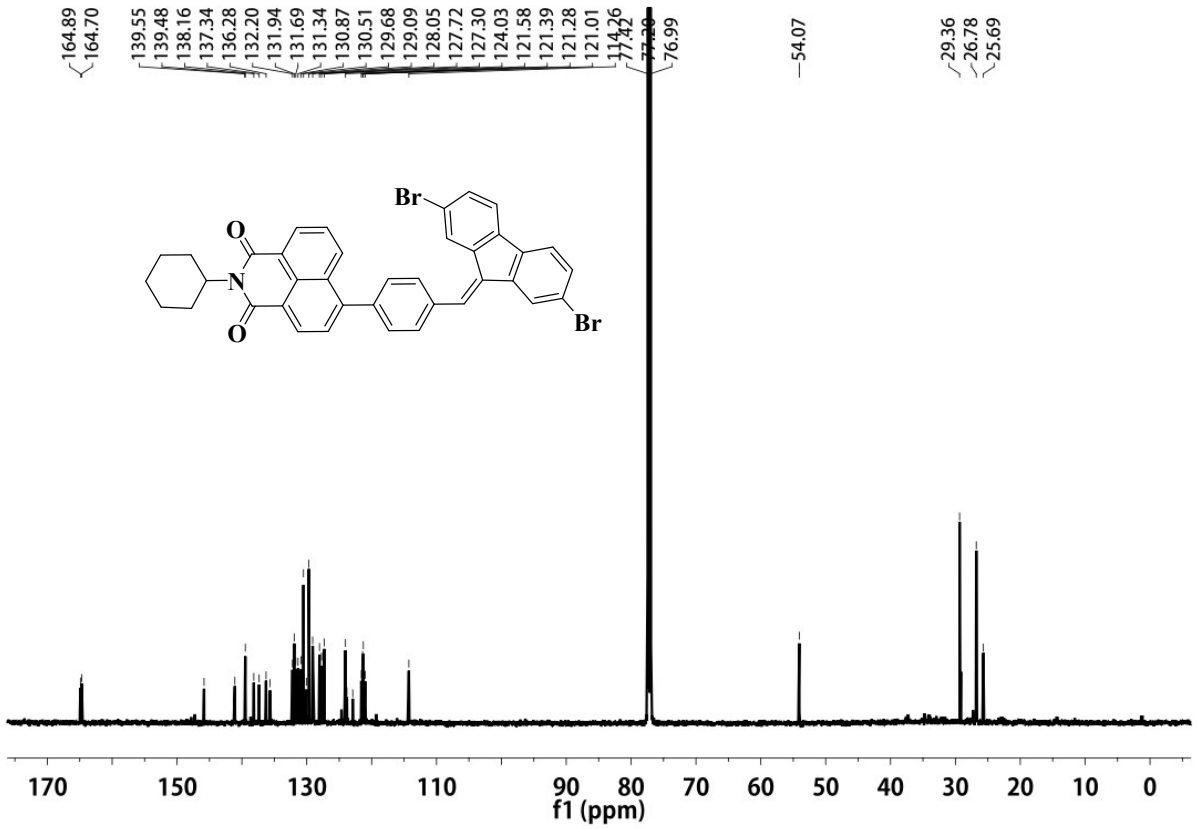


Figure S13. The ^{13}C NMR of the **DP2NC** in $CDCl_3$.

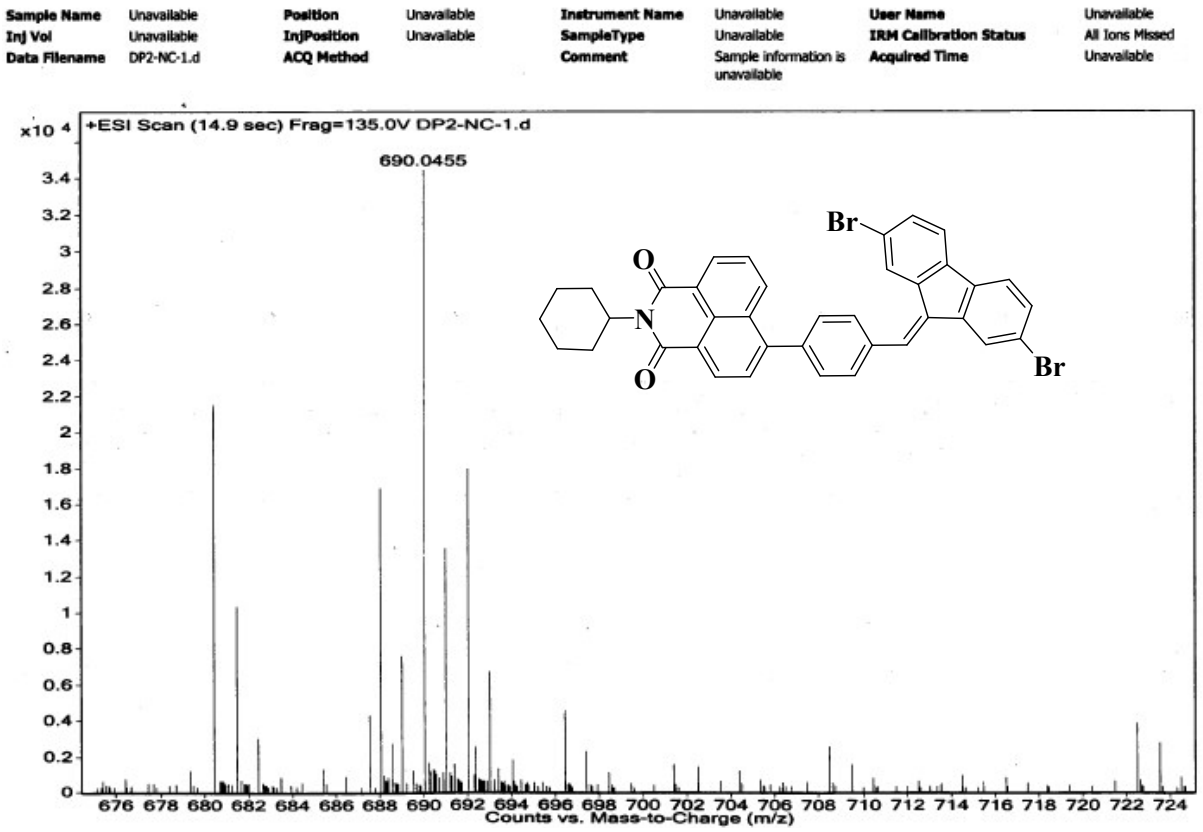


Figure S14. HRMS of the **DP2NC**.

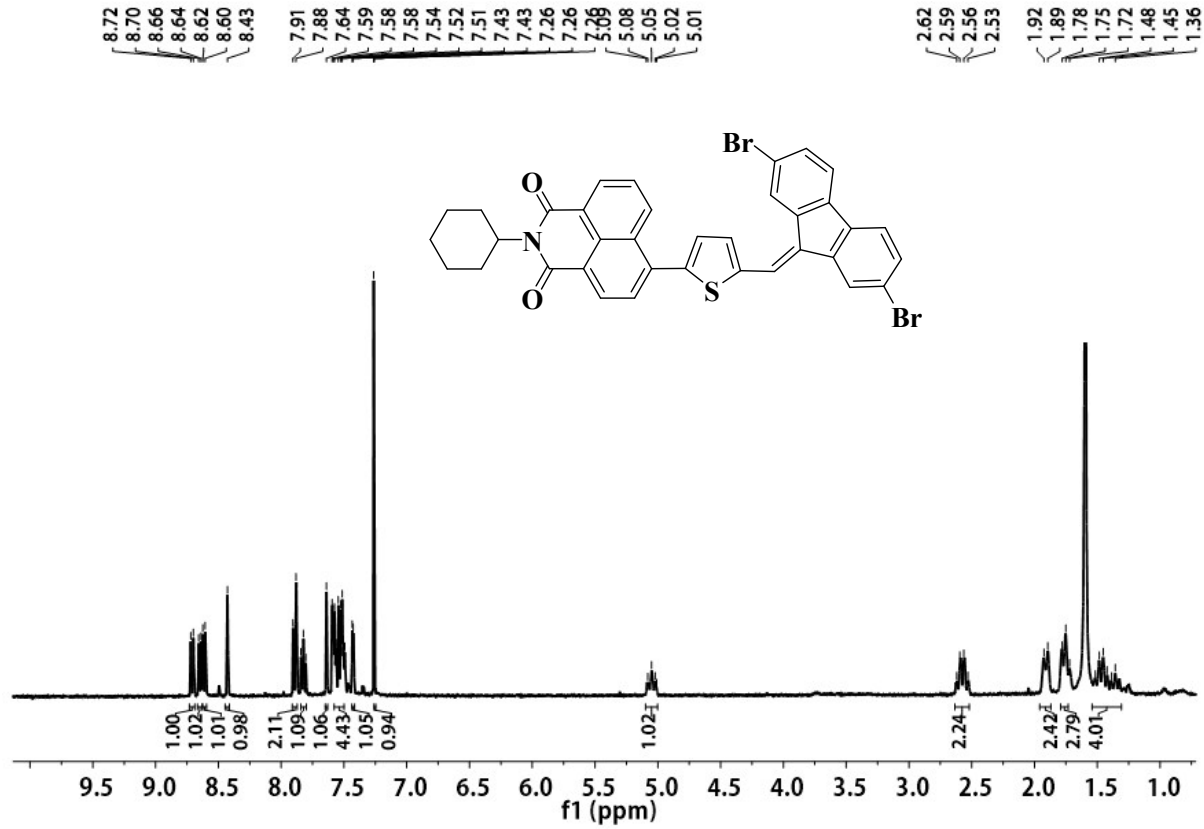


Figure S15. The ^{1}H NMR of the **DT2NC** in $CDCl_3$.

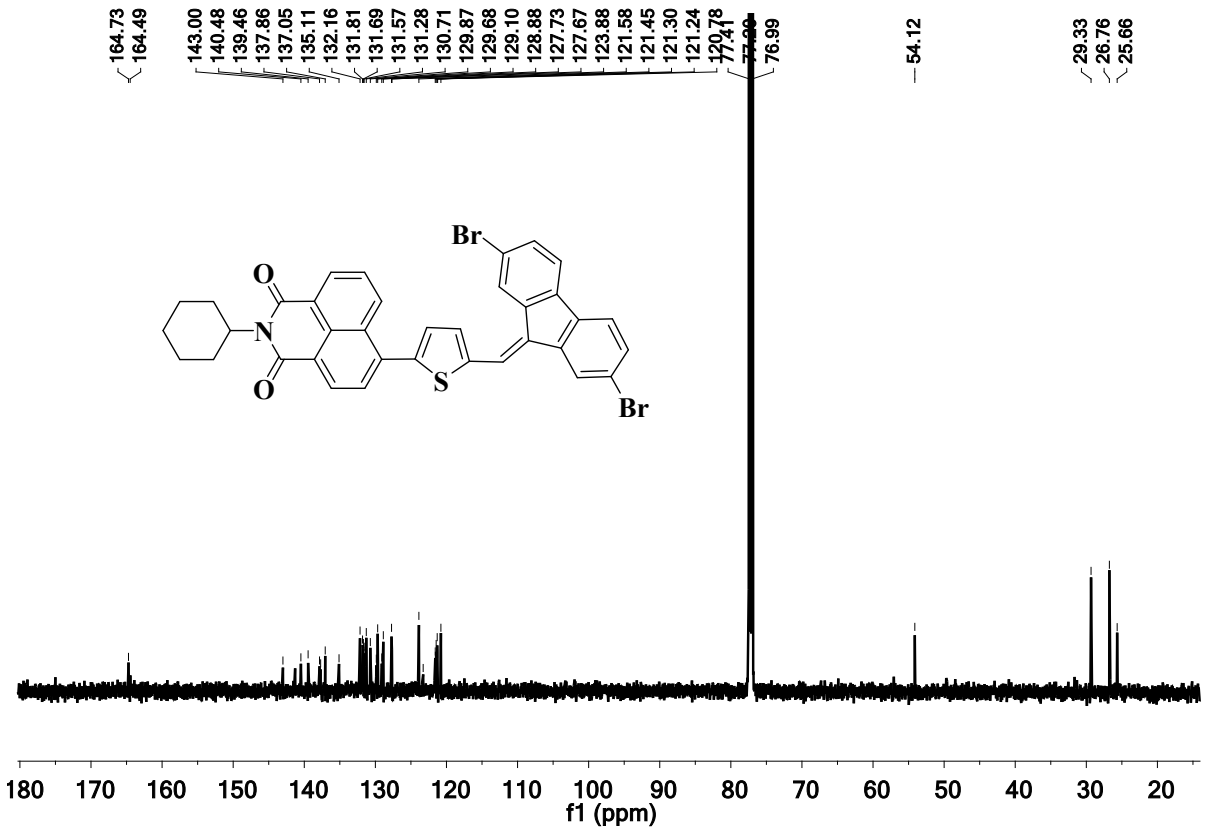


Figure S16. The ^{13}C NMR of the **DT2NC** in $CDCl_3$.

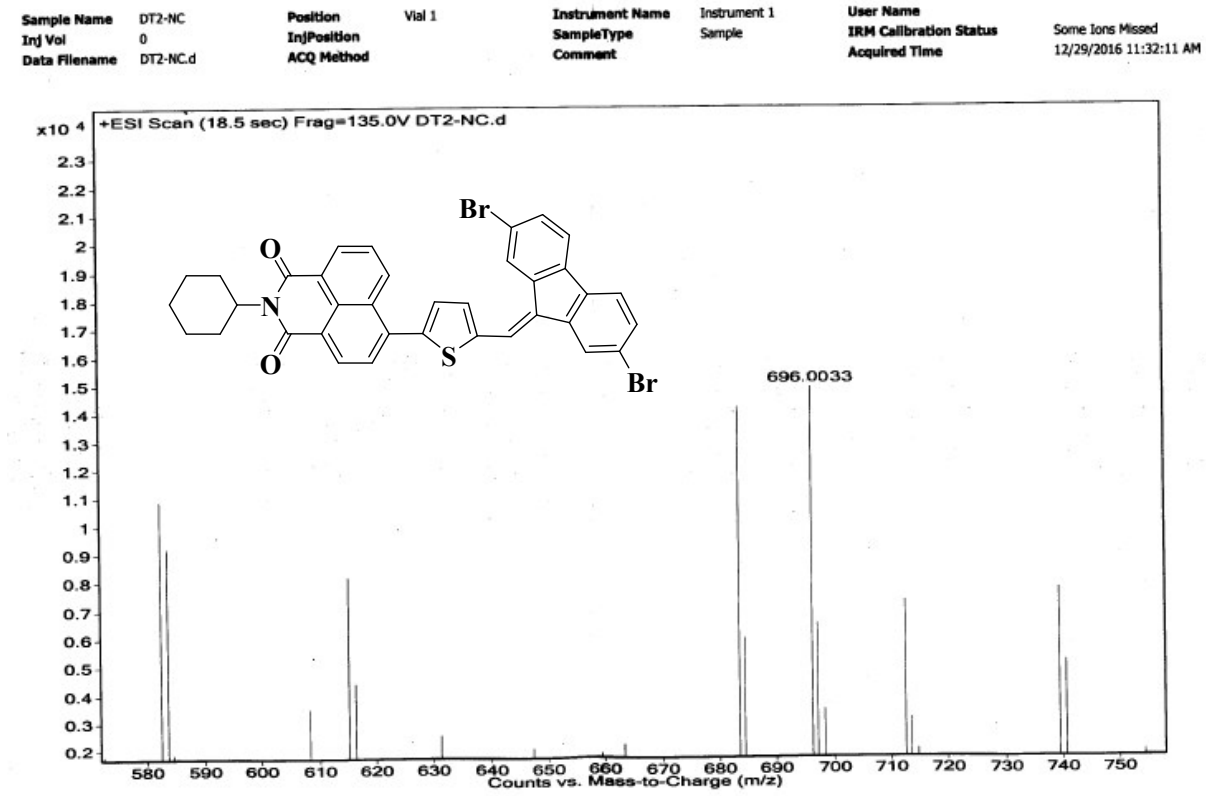


Figure S17. HRMS of the **DT2NC**.

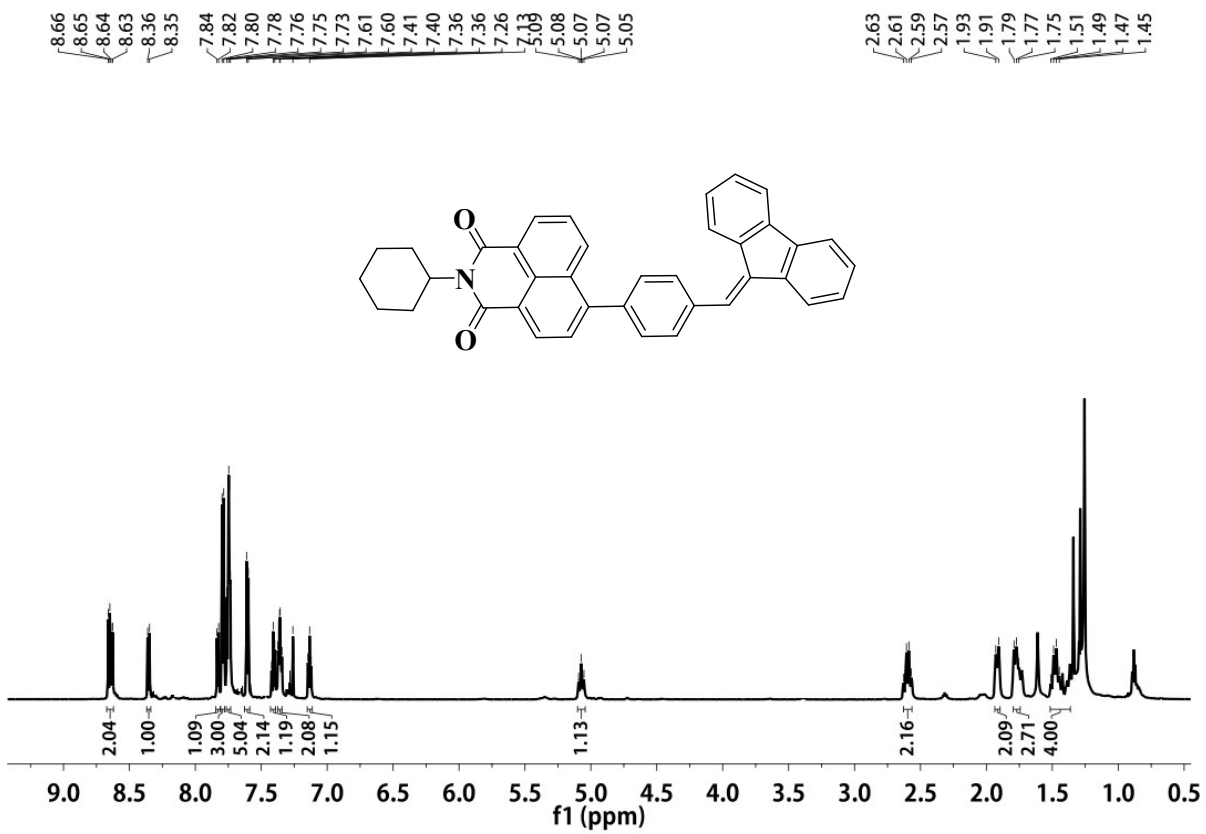


Figure S18. The ^{1}H NMR of the **DP1NC** in $CDCl_3$.

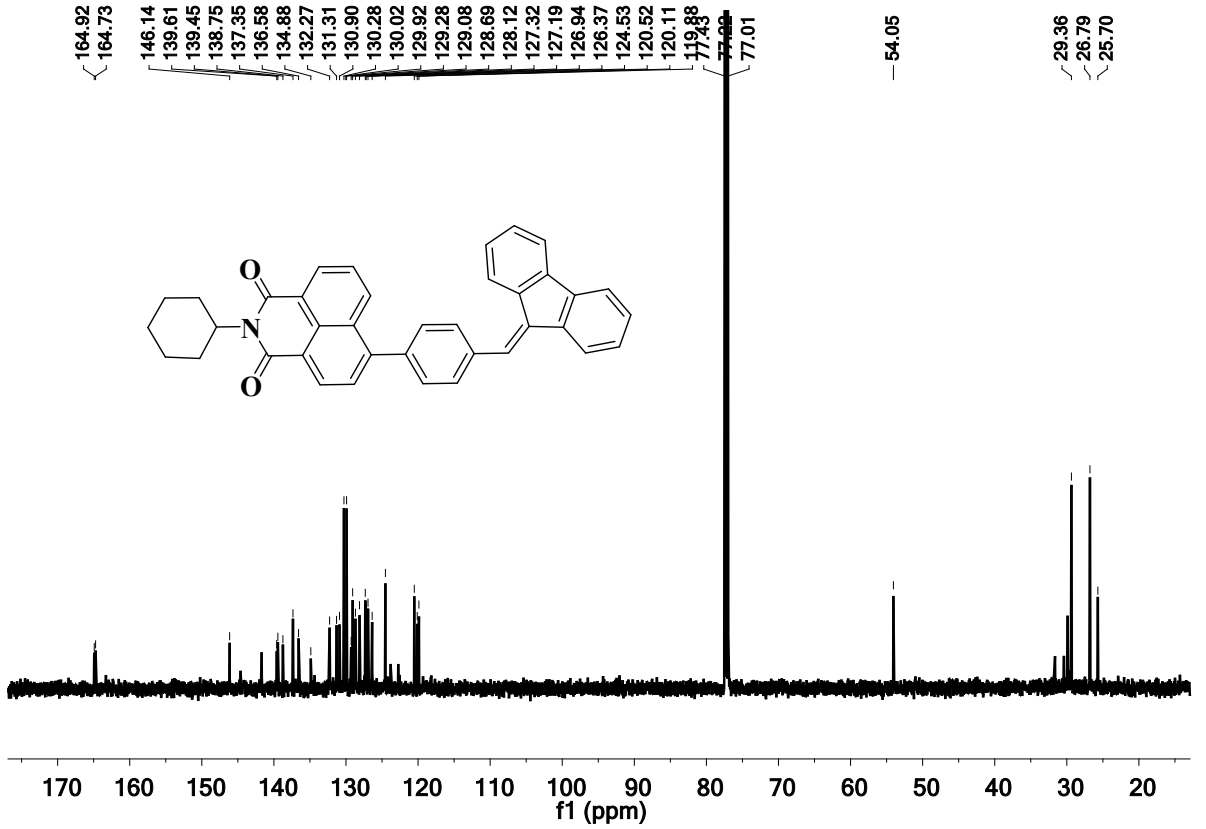


Figure S19. The ^{13}C NMR of the **DP1NC** in $CDCl_3$.

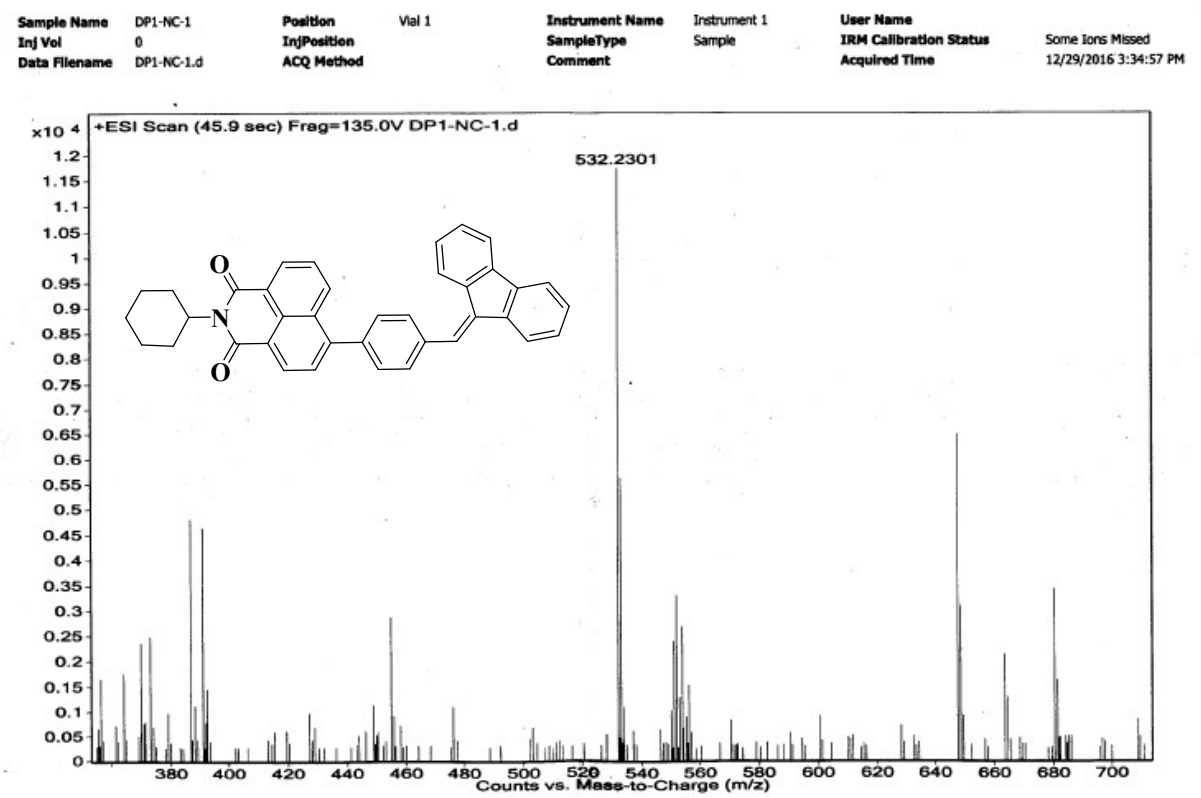


Figure S20. HRMS of the **DP1NC**.

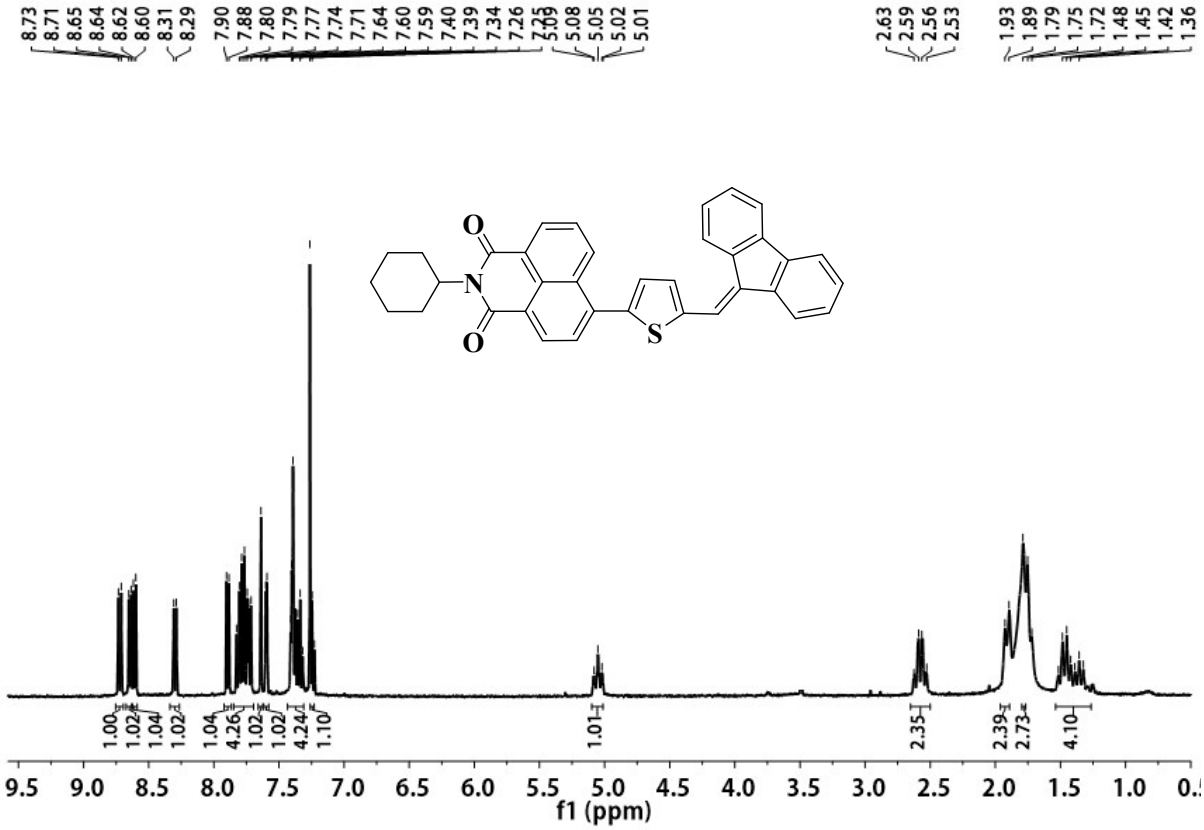


Figure S21. The ^{1}H NMR of the **DT1NC** in $CDCl_3$.

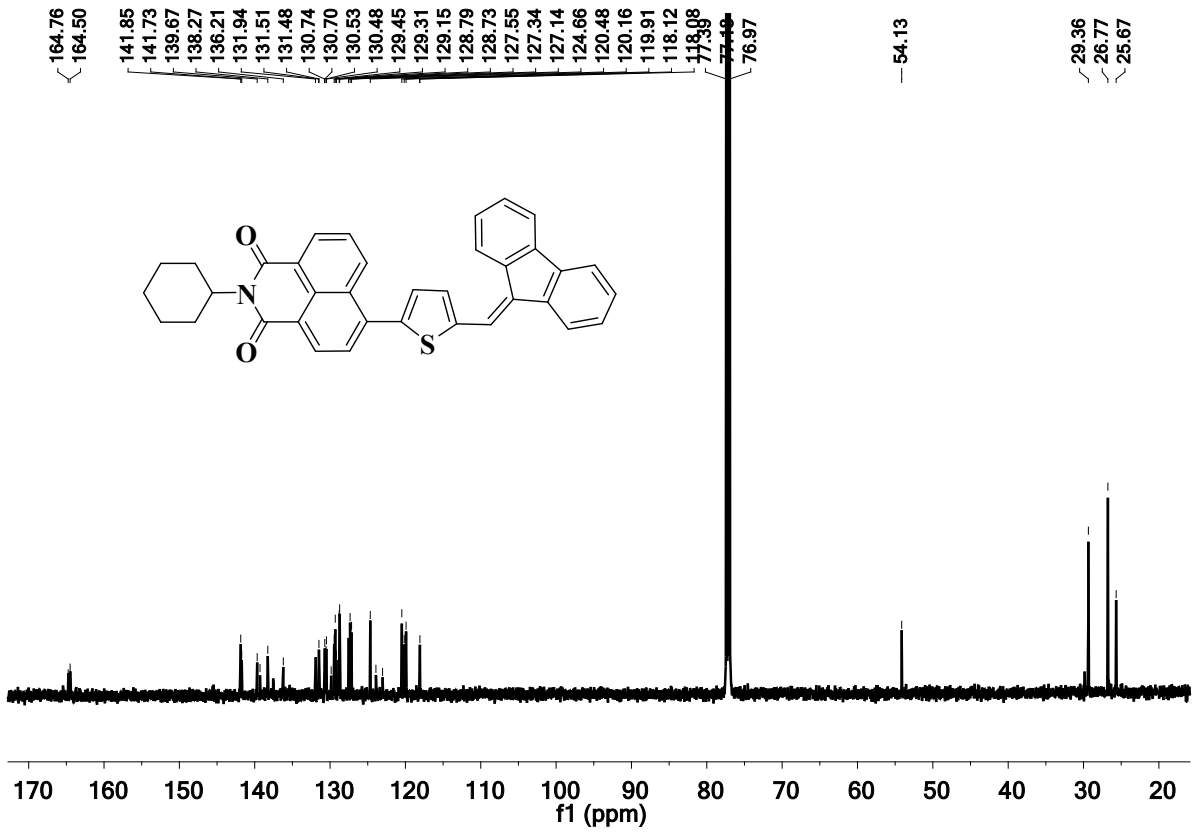


Figure S22. The ^{13}C NMR of the **DT1NC** in $CDCl_3$.

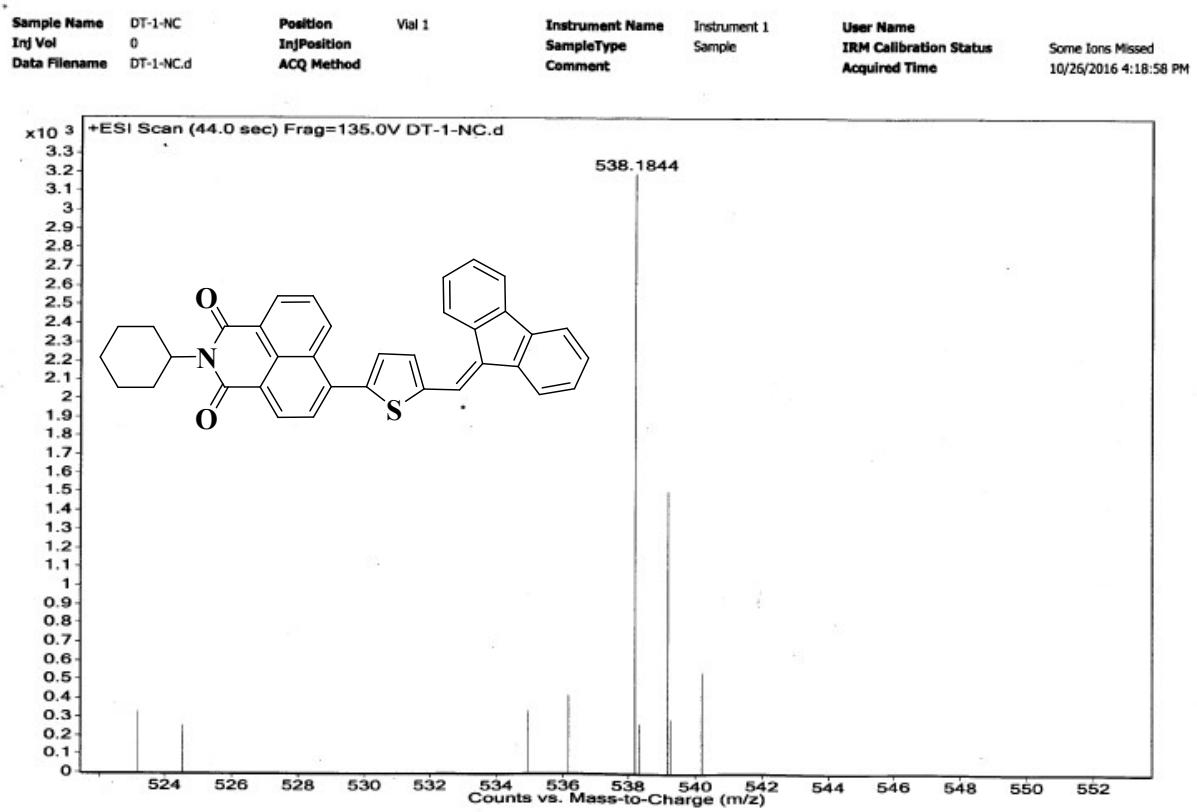


Figure S23. HRMS of the **DT1NC**.