

Supporting Information

Red fluorescent zwitterionic naphthalenediimides with di/mono-benzimidazolium and a negatively-charged oxygen substituent

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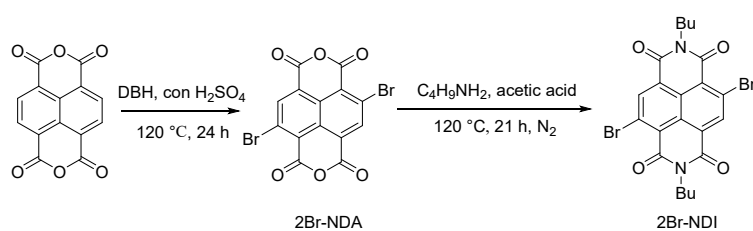
I. General Remarks

Unless otherwise noted, all commercially available reagents and solvents were of reagent grade and used without further purification. DMF was dried through the manual solvent purification system from Innovative Technology. The solvents for the spectroscopic measurements were of spectroscopic grade. 1,3-Dibromo-5,5-dimethylhydantoin (DBH) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA) were purchased from Energy Chemical. 1,3-Diethylbenzimidazolium bromide was prepared according to the literature procedures.¹

NMR spectra were obtained on a Bruker AV II-400 MHz. The ¹H NMR (400 MHz) chemical shifts were recorded relative to CDCl₃ or (CD₃)₂SO as the internal reference (CDCl₃: δ = 7.26 ppm; (CD₃)₂SO: δ = 2.50 ppm). The ¹³C NMR (100 MHz) chemical shifts were given using CDCl₃ or (CD₃)₂SO as the internal standard (CDCl₃: δ = 77.16 ppm; (CD₃)₂SO: δ = 39.52 ppm). High-resolution mass spectroscopy (HRMS) was measured on a Waters-Q-TOF-Premier (ESI). Absorption spectra were obtained on a HITACHI U-2910 spectrometer, Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. Cyclic voltammetric (CV) measurements were conducted on CHI660D.

II. Synthesis of 1-3

Synthesis of 2Br-NDI:²



2Br-NDA: 1,4,5,8-Naphthalenetetracarboxylic dianhydride (6.0 g, 22.39 mmol) was dissolved in concentrated sulfuric acid (100 mL), and the resultant solution was heated to 120 °C. 1,3-Dibromo-5,5-dimethylhydantoin (DBH) (8 g, 28.0 mmol) was added slowly, and the mixture was stirred at 120 °C overnight. The solution was poured into ice, and the solid was collected by filtration, washed with methanol, and air-dried to give 2Br-NDA (8.47 g, 90%) as a pale yellow solid.

2Br-NDI: 2Br-NDA (12 g, 28 mmol) was added into a flask with glacial acetic acid (120 mL), and then butylamine (11.6 mL, 4.2 equiv) was added dropwise while stirred. The resultant mixture was stirred at 120 °C for 21 h, and poured into 1 L of methanol after cooled down to room temperature. The solid was collected by filtration, washed with methanol, and dried under vacuum. The crude product was further purified by column chromatography (silica gel) using DCM: PE = 3: 2 to give 2Br-NDI (5.24 g, 35 %) as a yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.99 (s, 2H), 4.20 (t, *J* = 7.6 Hz, 4H), 1.76-1.68 (m, 4H), 1.50-1.41 (m, 4H), 0.99 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 173.3, 160.9, 160.8, 139.2, 128.5, 127.8, 125.4, 41.5, 30.0, 20.5, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₂₂H₂₁Br₂N₂O₄⁺ 536.9842, 534.9863, found 536.9835, 534.9874.

Synthesis of compound **1** and **2**:³

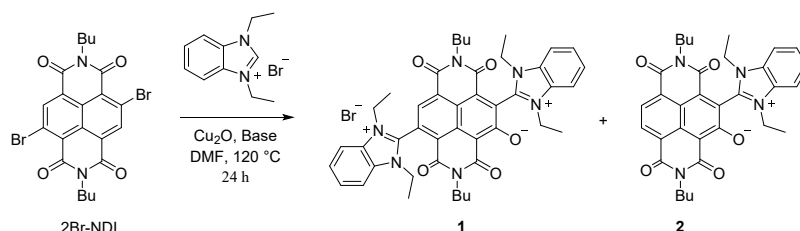


Table S1. Optimization of reaction conditions.

Entry	[Cu]	Base	Yield	
			1	2
1 ^a	Cu ₂ O	K ₂ CO ₃	trace	trace
2 ^b	Cu ₂ O	NaOAc	trace	14%
3 ^b	Cu ₂ O	K ₃ PO ₄	30%	6%
4 ^b	CuBr	NaOAc	trace	15%
5 ^b	CuBr	K ₃ PO ₄	12%	15%
6 ^b	Cu ₂ O	KOH	38%	7%
7 ^c	Cu ₂ O	NaOAc	trace	54%
8 ^c	Cu ₂ O	KOH	45%	11%

^a2Br-NDI (0.05 mmol), benzimidazolium salts (4 equiv), [Cu] (40 mol%), Base (2.0 equiv), DMF (0.5 mL), 120 °C, N₂, 24 h. ^b2Br-NDI (0.2 mmol), benzimidazolium salts (4 equiv), [Cu] (40 mol%), Base (2.0 equiv), DMF (2 mL), 120 °C, N₂, 24 h. ^c2Br-NDI (0.1 mmol), benzimidazolium salts (3 equiv), [Cu] (40 mol%), Base (3.0 equiv), DMF (1 mL), 120 °C, N₂, 24 h.

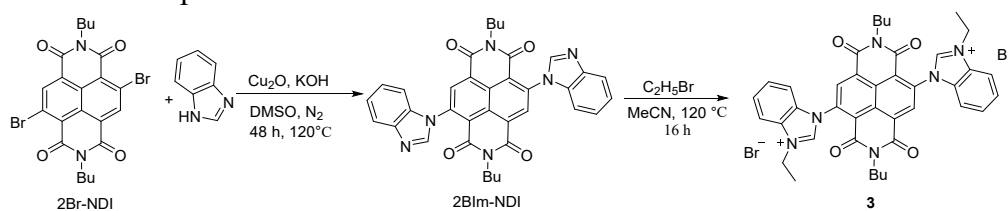
2,7-dibutyl-5,10-bis(1,3-diethyl-1*H*-benzo[*d*]imidazol-3-ium-2-yl)-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthroline-4-olate bromide (1**):**

A Schlenk tube with a magnetic stir bar was charged with the benzimidazolium salt (0.3 mmol), 2Br-NDI (0.1 mmol), Cu₂O (40 mol%), KOH (3.0 equiv) and DMF (1 mL).

The reaction mixture was stirred at 120 °C for 24 h under a N₂ atmosphere in an oil bath. After the volatiles were removed under reduced pressure, the residue was passed through a neutral Al₂O₃ column eluted with dichloromethane/methanol (v/v, 100/1–30/1) to afford **1** as a claret-colored solid with metallic luster (40.5 mg, 45% yield) (entry 8). M. p.: 236-239 °C, ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.39 (s, 2H), 7.84-7.82 (m, 2H), 7.76-7.72 (m, 4H), 7.65-7.62 (m, 2H), 4.60-4.51 (m, 4H), 4.42-4.24 (m, 2H), 4.12 (t, *J* = 7.2 Hz, 2H), 3.82 (t, *J* = 7.6 Hz, 2H), 1.72-1.66 (m, 4H), 1.48-1.38 (m, 16H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.76 (t, *J* = 7.6 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 163.1, 162.9, 162.6, 151.2, 131.7, 131.4, 131.2, 129.9, 128.3, 128.2, 127.2, 126.2, 122.4, 113.3, 113.0, 111.5, 110.1, 108.0, 107.8, 42.5, 42.3, 41.4, 40.0, 30.1, 29.7, 20.6, 20.3, 14.9, 14.6, 14.0, 13.8. HRMS (ESI) *m/z*: [M-Br]⁺ calcd for C₄₄H₄₇N₆O₅⁺ 739.3602, found 739.3608.

2,7-dibutyl-5-(1,3-diethyl-1*H*-benzo[*d*]imidazol-3-ium-2-yl)-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthrolin-4-olate (2). A Schlenk tube with a magnetic stir bar was charged with the benzimidazolium salt (0.3 mmol), 2Br-NDI (0.1 mmol), Cu₂O (40 mol%), NaOAc (3.0 equiv) and DMF (1 mL). The reaction mixture was stirred at 120 °C for 24 h under a N₂ atmosphere in an oil bath. After the volatiles were removed under reduced pressure, the residue was passed through a neutral Al₂O₃ column eluted with dichloromethane/methanol (v/v, 100/1–30/1) to afford **2** as a rust-colored solid (30.8 mg, 54% yield) (entry 7). M. p.: >250 °C, ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.66 (d, *J* = 8 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.75-7.71 (m, 2H), 7.67-7.64 (m, 2H), 4.27-4.10 (m, 6H), 3.97 (t, *J* = 7.6 Hz, 2H), 1.76-1.68 (m, 2H), 1.57-1.47 (m, 2H), 1.46-1.36 (m, 8H), 1.34-1.27 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H), 0.88 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 171.3, 163.7, 163.4, 162.5, 151.9, 134.3, 132.1, 131.6, 127.6, 126.3, 126.1, 125.3, 123.6, 123.0, 116.2, 112.8, 109.3, 41.7, 40.6, 39.9, 30.27, 30.20, 20.6, 20.3, 14.3, 14.0, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₃₃H₃₄N₄O₅ 567.2602, found 567.2600.

Synthesis of compound **3**:⁴



2BIm-NDI: A mixture of 2Br-NDI (53.5 mg, 0.1 mmol), benzimidazole (47.3 mg, 0.4 mmol), Cu₂O (5.7 mg, 40 mol%), and KOH (22.4 mg, 0.48 mmol) was stirred in DMSO (1 mL) at 120°C for 48 h under a N₂ atmosphere in an oil bath. The cooled reaction mixture was diluted with dichloromethane and filtered through Celite. The resulting solution was washed with brine and water, then dried with anhydrous MgSO₄ and evaporated to dryness. The crude product was purified by column chromatography on silica gel (dichloromethane/methanol, v/v, 30/1) to give 2BIm-NDI as a yellow solid (28 mg, 46% yield). M. p.: 216-218 °C, ¹H NMR (CDCl₃, 400 MHz): δ (ppm) = 8.92 (s, 2H), 8.16 (s, 2H), 7.98 (d, *J* = 8 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 8 Hz, 2H), 4.09 (t, *J* = 7.6 Hz, 4H) 1.67-1.58 (m, 4H), 1.39-1.34 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ (ppm) = 161.0, 160.2, 139.4, 132.7, 128.2, 127.9, 124.6, 123.8, 121.4, 120.0, 109.8, 41.3, 30.0, 20.3, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ calcd for C₃₆H₃₁N₆O₄⁺ 611.2401, found 611.2399.

1,1'-(2,7-dibutyl-1,3,6,8-tetraoxo-1,2,3,6,7,8 hexahydrobenzo[*lmn*][3,8] phenanthroline-4,9-diyl)bis(3-ethyl-1*H*-benzo[*d*]imidazol-3-ium) bromide (3): Bromoethane (0.5 mL) was added to a solution of 2BIm-NDI (50 mg, 0.08 mmol) in MeCN (1 mL). The resulting mixture was heated to reflux for 16 h to afford a yellow solid. The solvent was removed in vacuo and the residue was washed with diethyl ether to give **3** as a wheat-colored solid (65 mg, 98% yield). M. p.: 245-250 °C, ¹H NMR ((CD₃)₂SO, 400 MHz): δ (ppm) = 10.39 (s, 2H), 9.19 (s, 1H), 9.17 (s, 1H), 8.32 (d, *J* = 8 Hz, 2H), 7.84-7.80 (m, 2H), 7.75- 7.66 (m, 4H), 4.85-4.76 (m, 4H), 3.97-3.86 (m, 4H), 1.70 (t, *J* = 7.2, 6H), 1.55-1.48 (m, 4H), 1.31-1.25 (m, 4H), 0.844 (td, *J* = 7.2 Hz, 2Hz, 6H). ¹³C NMR ((CD₃)₂SO, 100 MHz): δ (ppm) = 161.1, 161.0, 160.23, 160.20, 143.0, 142.8, 134.7, 134.6, 132.16, 132.13, 130.69, 130.64, 128.4, 128.0, 127.5, 127.4, 126.9, 122.75, 122.71, 114.3, 113.7, 113.4, 42.8, 29.2, 19.6, 14.3, 14.2, 13.6. HRMS (ESI) *m/z*: [M-2Br]²⁺ calcd for C₄₀H₄₀N₆O₄²⁺ 334.1550, found 334.1546.

III. Single-crystal X-ray data of 2

Table S2. Crystallographic data and structure refinement details for 2.

Identification code	2
Empirical formula	C ₃₃ H ₃₄ N ₄ O ₅
Formula weight	566.64
Temperature/K	150.0
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	15.0103(4)
b/Å	12.9385(3)
c/Å	15.5389(5)
α/°	90
β/°	111.1040(10)
γ/°	90
Volume/Å ³	2815.41(14)
Z	4
ρ _{calc} /g/cm ³	1.337
μ/mm ⁻¹	0.091
F(000)	1200.0
Crystal size/mm ³	0.45 × 0.38 × 0.35
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.22 to 55.048
Index ranges	-19 ≤ h ≤ 19, -16 ≤ k ≤ 16, -20 ≤ l ≤ 20
Reflections collected	43768
Independent reflections	6472 [R _{int} = 0.0999, R _{sigma} = 0.0584]
Data/restraints/parameters	6472/26/408
Goodness-of-fit on F ²	1.040
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0512, wR ₂ = 0.1204
Final R indexes [all data]	R ₁ = 0.0911, wR ₂ = 0.1383
Largest diff. peak/hole / e Å ⁻³	0.63/-0.34

IV. Photophysical Study



Fig. S1 Photos of 1 under daylight and 365 nm irradiation (1 × 10⁻³ M) in water at rt.

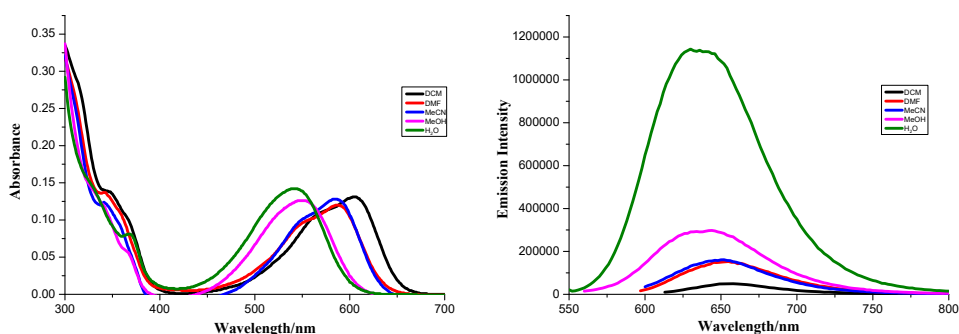


Fig. S2 UV-vis absorption and emission spectra of **1** in different solvents (1×10^{-5} M). Excited at the maximum absorption wavelengths in different solvents (see Table S3).

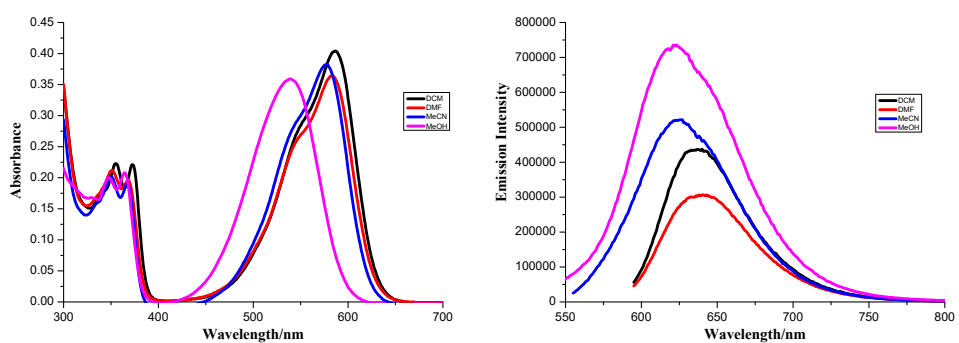


Fig. S3 UV-vis absorption and emission spectra of **2** in different solvents (1×10^{-5} M). Excited at the maximum absorption wavelengths in different solvents (see Table S3).

Table S3 Absorption maxima (λ_{abs}), absorption coefficients (ϵ), emission maxima (λ_{em}), and absolute fluorescence quantum yields (Φ_{F}) of **1-3** and **NDI** in different solvents (1×10^{-5} M).

Solvent	Compound	λ_{abs} (nm)	ϵ ($\text{M}^{-1} \cdot \text{cm}^{-1}$)	λ_{em} (nm)	Φ_{F} (%)
DCM	1	604	13000	658	0.23
	2	586	39800	637	3.45
DMF	1	587	12000	655	0.35
	2	583	36400	641	3.00
	NDI	380	13590	-	-
MeCN	1	584	12800	652	0.42
	2	577	29600	626	5.42
MeOH	1	550	12600	644	0.65
	2	539	35900	621	6.43
	3	375	9798	-	-
	NDI	378	12000	-	-
H ₂ O	1	541	14200	630	3.42

V. Cyclic Voltammetry Measurements

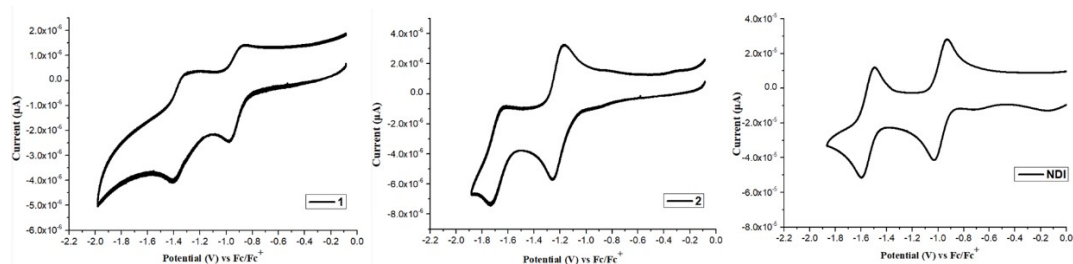


Fig. S4. Cyclic voltammetric curves of **1**, **2** and NDI in DMF.

Table S4. Electrochemical data of 1, 2 and NDI in DMF.

Compound	E_{red1} (V) ^a	E_{red2} (V) ^a	LUMO (eV) ^b	HOMO (eV) ^c	E_g (eV)
1	-0.91	-1.34	-3.89	-5.86	1.94
2	-1.20	-1.67	-3.60	-5.57	1.97
NDI	-0.97	-1.54	-3.83	-7.01	3.18

^aHalf-wave reduction potentials (vs Fc/Fc⁺) measured in 0.1 M solution of TBAPF₆ in DMF.

^bEstimated from $E_{LUMO} = -4.80 \text{ eV} - E_{red1}$. ^cEstimated from $E_{HOMO} = E_{LUMO} - E_g$.

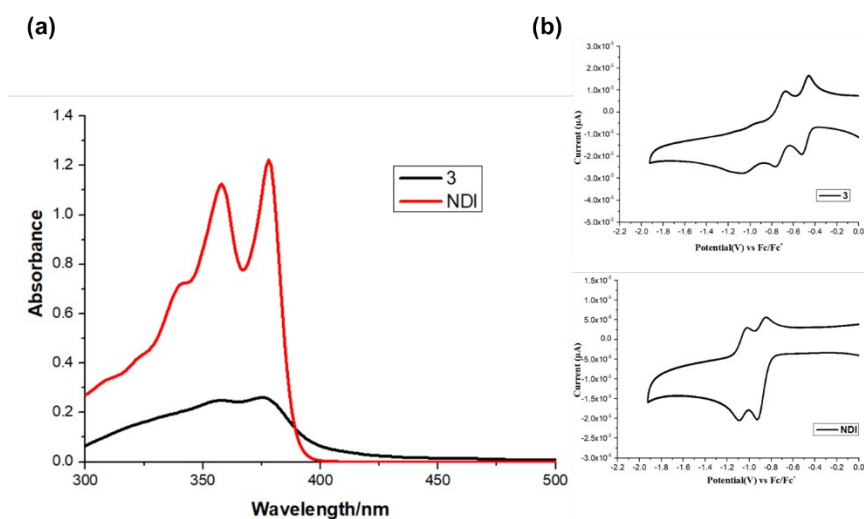


Fig. S5. (a) Absorption spectra of **3** and NDI in MeOH; (b) Cyclic voltammetric curves of **3** and NDI in MeOH.

Table S5. Electrochemical data of 3 and NDI in MeOH.

Compound	E_{red1} (V) ^a	E_{red2} (V) ^a	LUMO (eV) ^b	HOMO (eV) ^c	E_g (eV)
3	-0.47	-0.73	-4.33	-7.39	3.06
NDI	-0.88	-1.04	-3.92	-7.10	3.18

^aHalf-wave reduction potentials (vs Fc/Fc⁺) measured in 0.1 M solution of TBAPF₆ in MeOH.

^bEstimated from $E_{LUMO} = -4.80 \text{ eV} - E_{red1}$. ^cEstimated from $E_{HOMO} = E_{LUMO} - E_g$.

VI. DFT and TD-DFT Calculations.

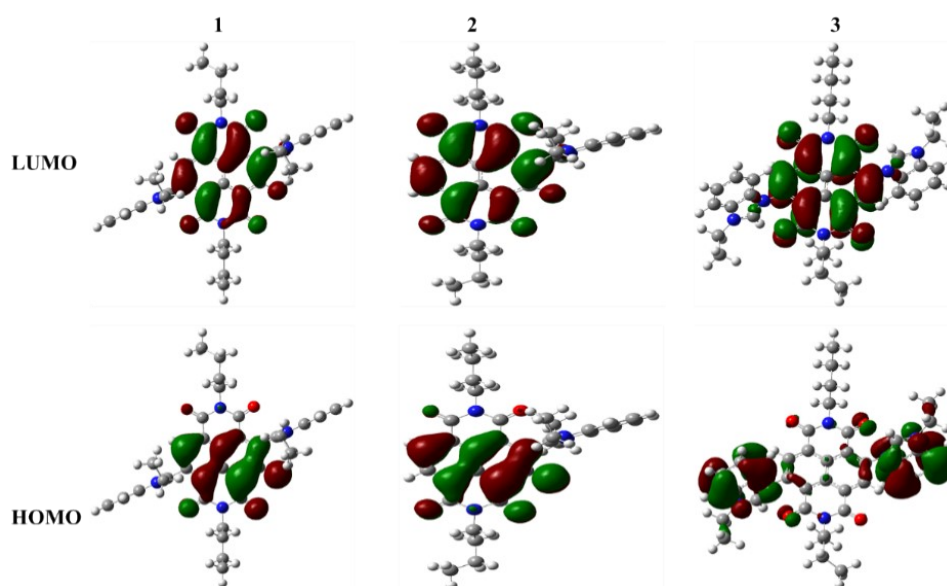


Fig. S6. Molecular orbitals of 1-3 according to DFT calculations at the B3LYP/6-31g(d,p) level.

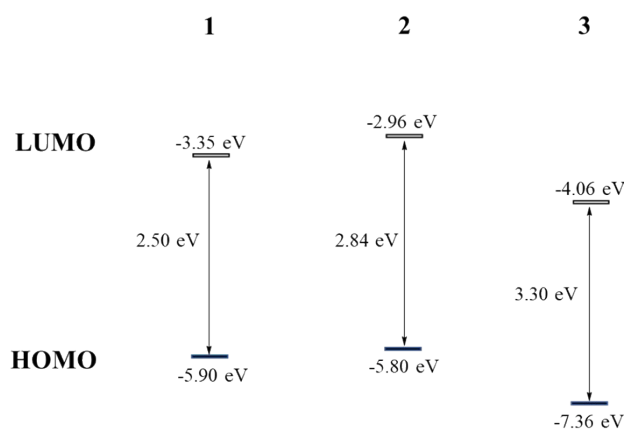


Fig. S7. Diagrams of the energy levels of 1-3 obtained by DFT calculations at the B3LYP/6-31g(d,p) level.

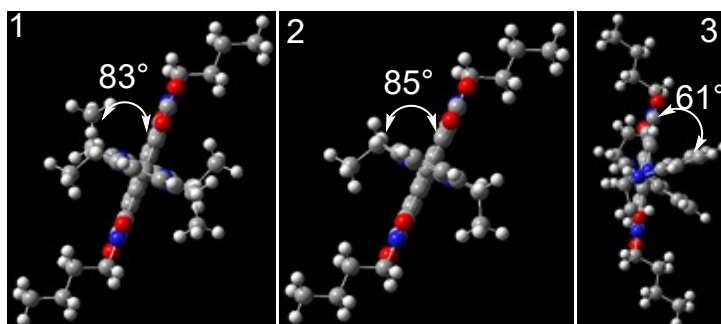


Fig. S8. DFT-optimized dihedral angles of 1-3.

Table S6 Calculated absorptions and oscillator strengths (*f*) of 1-3 obtained by TD-DFT calculations at the PBE1PBE/6-31g(d,p) level.

Compound	$\lambda_{\text{abs}}/\text{nm}$ (measured)	$\lambda_{\text{abs}}/\text{nm}$ (calculated)	Oscillator strengths (<i>f</i>)
1	587	558	0.2384
2	583	548	0.2277
3	375	368	0.2799

Table S7. Cartesian coordinates of optimized species.

1				2			
Symbolic	Z-matrix:			Symbolic	Z-matrix:		
Charge=1	Multiplicity=1			Charge=0	Multiplicity=1		
C	-3.82642	2.31815	0.15325	C	-3.42771	4.00172	0.47521
C	-2.48973	2.23488	0.00415	C	-2.19831	3.73822	0.03077
C	-2.00551	0.96908	-0.05681	C	-1.89275	2.49818	-0.38019
C	-2.80151	-0.12207	-0.05082	C	-2.82996	1.52856	-0.35926
C	-4.14264	0.0218	0.0923	C	-4.08128	1.7762	0.1125
C	-4.64915	1.25966	0.2142	C	-4.35631	3.03216	0.52161
C	-2.30332	-1.36866	-0.21167	C	-2.51486	0.29648	-0.80183
C	-3.19808	-2.35583	-0.14736	C	-3.43305	-0.64695	-0.57827
C	-4.49798	-2.28959	0.1125	C	-4.67772	-0.46132	-0.11682
C	-4.96721	-1.04522	0.13783	C	-5.02245	0.79948	0.17245
C	-6.30102	-0.9575	0.30755	C	-6.31752	1.06902	0.48515
C	-5.98851	1.46491	0.33987	C	-5.57565	3.36079	1.01483
C	-0.66483	0.74736	-0.01685	C	-0.61733	2.25317	-0.78182
N	-0.20036	-0.51959	-0.30648	N	-0.34989	0.95798	-1.16628
C	-0.988	-1.66119	-0.45592	C	-1.30576	-0.03454	-1.35036
O	-6.50009	2.55527	0.47177	O	-5.84394	4.45268	1.4688
O	-7.0608	-1.89154	0.39233	O	-7.32087	0.39347	0.41172
O	0.09056	1.64317	0.28321	O	0.24241	3.10715	-0.80948
O	-0.34986	-2.66792	-0.70792	O	-0.9431	-1.01375	-1.97555
N	-6.78699	0.3353	0.31896	N	-6.53354	2.37511	0.92979
C	-1.88968	3.43816	-0.21278	C	-5.22908	-1.67439	0.11126
C	-5.1704	-3.46232	0.17284	N	-5.02851	-2.6648	-0.74032
N	-0.93559	3.74846	-1.07616	C	-5.55671	-3.72802	-0.19238
C	-0.78544	5.04978	-1.03441	C	-6.10553	-3.39074	0.9814
C	-1.5708	5.55333	-0.07714	N	-5.91978	-2.13855	1.08291
N	-2.17471	4.53876	0.37915	C	-5.61061	-4.99219	-0.63742
N	-6.23516	-3.78957	-0.52039	C	-6.19342	-5.92676	0.13051
C	-6.54191	-5.0194	-0.18673	C	-6.70128	-5.59828	1.32961
C	-5.67937	-5.45189	0.7417	C	-6.65533	-4.3287	1.76654
N	-4.89465	-4.47258	0.90579	C	-6.22119	-1.45063	2.36425
C	-0.04128	5.88694	-1.77391	C	-4.67051	-2.63746	-2.24742
C	-0.0578	7.2027	-1.50203	C	-7.69248	-1.37053	2.80971
C	-0.81807	7.68735	-0.50662	C	-5.94097	-2.81449	-3.09843
C	-1.59129	6.86102	0.21581	O	-3.06281	-1.92661	-0.62184

C	-7.4881	-5.85763	-0.63472	C	-9.69427	2.4938	4.82849
C	-7.58041	-7.09038	-0.10748	C	-9.51899	2.78221	3.33168
C	-6.72849	-7.49535	0.84923	C	-8.08494	2.49501	2.86196
C	-5.75754	-6.67506	1.28207	C	-7.90054	2.75395	1.35882
C	-0.32106	2.91061	-2.19533	C	3.06619	0.98982	-4.86909
C	-2.97662	4.69792	1.62807	C	2.78399	0.65751	-3.39784
C	-3.82466	-4.51487	1.93329	C	1.33217	0.97729	-3.00787
C	-6.76883	-3.10961	-1.79635	C	1.04701	0.64726	-1.53266
C	1.2139	2.82185	-2.24543	H	-3.61522	5.03731	0.80504
C	-2.07841	5.00948	2.84093	H	-1.47617	4.57149	0.03865
C	-4.41974	-4.33522	3.33945	H	-5.16621	-5.28494	-1.6012
C	-8.28487	-2.92928	-1.98254	H	-6.2329	-6.9739	-0.21397
O	-2.90753	-3.57596	-0.52759	H	-7.15447	-6.37985	1.96283
C	-10.7325	0.69963	3.40811	H	-7.0648	-4.10195	2.76005
C	-10.2548	0.69568	1.95	H	-5.66277	-1.98476	3.17195
C	-8.73099	0.52521	1.84923	H	-5.77219	-0.43419	2.39576
C	-8.24851	0.51813	0.38988	H	-4.25856	-1.65985	-2.59227
C	3.55511	-0.72525	-3.64335	H	-3.92614	-3.43124	-2.49214
C	3.17871	-0.65683	-2.15741	H	-7.78124	-0.79749	3.7613
C	1.65976	-0.76174	-1.94947	H	-8.35311	-0.88325	2.06407
C	1.26613	-0.68091	-0.46288	H	-8.1544	-2.35841	3.01003
H	-4.30256	3.30921	0.08601	H	-5.70529	-2.75868	-4.18645
H	0.58099	5.53422	-2.6079	H	-6.44406	-3.79075	-2.92635
H	0.5544	7.89405	-2.10578	H	-6.68142	-2.01316	-2.87006
H	-0.82651	8.77052	-0.2986	H	-10.7379	2.70552	5.15679
H	-2.23861	7.2762	1.00314	H	-9.47626	1.42587	5.05947
H	-8.19711	-5.56617	-1.41988	H	-9.0112	3.12479	5.44184
H	-8.36271	-7.78058	-0.46661	H	-9.77213	3.85002	3.12768
H	-6.81569	-8.51182	1.26845	H	-10.2353	2.15147	2.75246
H	-5.04728	-7.02167	2.04813	H	-7.83346	1.43326	3.08393
H	-0.76795	1.8938	-2.23421	H	-7.37032	3.1255	3.44192
H	-0.65401	3.36877	-3.15869	H	-8.12651	3.82009	1.12986
H	-3.76186	5.47779	1.49407	H	-8.69982	2.25033	0.77234
H	-3.50074	3.77386	1.95784	H	4.12169	0.75309	-5.13702
H	-3.25722	-5.47202	1.86482	H	2.40494	0.4036	-5.54741
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H	-6.2537	-2.1379	-1.97143	H	3.48204	1.23964	-2.74974
H	-6.40782	-3.72646	-2.65567	H	2.98853	-0.42548	-3.22034
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H	1.65166	2.2932	-1.37466	H	1.76297	1.19297	-0.87593
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H	-1.33325	4.19496	2.99667				
H	-1.50882	5.95776	2.73772				

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H	-10.557	1.6529	1.46163
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H	3.22518	-1.68721	-4.09798
H	3.08251	0.10587	-4.21534
H	3.55111	0.30659	-1.73373
H	3.68736	-1.48385	-1.6067
H	1.30023	-1.7148	-2.40146
H	1.15241	0.05711	-2.5083
H	1.84825	0.14033	0.0073
H	1.64648	-1.56307	0.10144

3

Symbolic Z-matrix:

Charge=2 Multiplicity=1

C	-3.47436	2.36505	0.02642
C	-2.16316	2.28015	-0.24718
C	-1.6285	1.04077	-0.10507
C	-2.4017	-0.06402	0.00483
C	-3.74462	0.04261	0.15536
C	-4.2586	1.28957	0.22814
C	-1.85715	-1.29687	0.0156
C	-2.67199	-2.36677	0.03095
C	-4.01933	-2.31269	0.09288
C	-4.51995	-1.06275	0.29283
C	-0.27372	0.92193	0.05353
N	0.26022	-0.3476	0.00449
C	-0.50936	-1.49377	-0.08747
C	-5.8044	-0.88603	0.73508
N	-6.34711	0.38022	0.6252
C	-5.59042	1.50933	0.41358

O	-6.07663	2.62071	0.43009
O	-6.4666	-1.76587	1.24587
O	0.40363	1.90664	0.26412
O	0.02491	-2.57742	-0.2045
N	-1.50478	3.34105	-0.55608
N	-4.67423	-3.41742	-0.04364
C	-5.85705	-3.63485	-0.4983
C	-6.15472	-4.94342	-0.41805
N	-5.11636	-5.55929	0.06104
C	-4.24733	-4.60025	0.20771
C	-0.50595	3.46842	-1.35318
C	0.00511	4.70368	-1.2517
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C	-1.6944	4.52251	-0.10828
C	0.05283	2.61969	-2.23512
C	1.12322	3.0073	-2.94953
C	1.64325	4.23635	-2.79802
C	1.0791	5.1045	-1.9438
C	-6.7664	-2.84214	-1.09621
C	-7.95635	-3.33201	-1.48335
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C	-7.33223	-5.4576	-0.79691
C	-0.57074	6.76613	0.09425
C	0.48843	6.84332	1.19919
C	-4.92225	-7.0269	0.34186
C	-5.53771	-7.40155	1.69437
C	-9.85541	1.28501	4.11256
C	-9.57484	0.99763	2.63163
C	-8.07158	0.83711	2.35564
C	-7.78831	0.54693	0.87258
C	4.42206	-0.47371	-2.78808
C	3.84649	-0.56041	-1.36827
C	2.31557	-0.43337	-1.36881
C	1.72582	-0.48709	0.04864
H	-3.92918	3.36531	-0.02219
H	-2.18366	-3.34004	-0.10724
H	-3.26168	-4.835	0.62656
H	-2.47785	4.78547	0.61355
H	-0.35808	1.61207	-2.40735
H	1.57868	2.31028	-3.67344
H	2.52306	4.53965	-3.38975
H	1.48868	6.12011	-1.82902
H	-6.56219	-1.78545	-1.3252
H	-8.69149	-2.66598	-1.96654

H	-9.22521	-5.02578	-1.65136
H	-7.54503	-6.53399	-0.70362
H	-0.29201	7.42912	-0.7574
H	-1.54723	7.13946	0.48315
H	0.60318	7.88708	1.57193
H	0.20652	6.19942	2.06373
H	1.48244	6.50287	0.82949
H	-5.37917	-7.63284	-0.47455
H	-3.83334	-7.26856	0.34547
H	-5.39097	-8.48382	1.91514
H	-5.06861	-6.81695	2.51878
H	-6.63239	-7.1965	1.71006
H	-10.9485	1.39899	4.29745
H	-9.48707	0.45619	4.75944
H	-9.35634	2.22528	4.44094
H	-9.98152	1.83221	2.01176
H	-10.1114	0.06612	2.33053
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H	-7.53973	1.76839	2.66312
H	-8.20933	1.35858	0.23585
H	-8.35767	-0.35133	0.53929
H	5.53251	-0.56641	-2.77571
H	4.02096	-1.28765	-3.43431
H	4.16836	0.50063	-3.26531
H	4.289	0.25225	-0.74374
H	4.14072	-1.53394	-0.90825
H	1.87514	-1.25001	-1.98845
H	2.03312	0.53334	-1.84615
H	2.19266	0.2997	0.68326
H	2.03477	-1.42704	0.55959

VII. Cell Imaging Experiments and Cytotoxicity Assays

1) Cell culture A549 cells were hatched in RPMI Medium 1640 basic (1X) supplemented with 10% (v/v) FBS (fetal bovine serum), 100 kU/L of penicillin, and 100 mg/L of streptomycin at 37 °C in a humidified atmosphere containing 5% CO₂.

2) A549 cells were cultivated in the presence of **1** in the phosphate buffered solution (PBS) for 15 min at 37 °C and **2** in PBS containing 1% DMSO for 15 min at 37 °C after being cultured in the RPMI Medium 1640 basic (1X) (containing 10% of fetal bovine serum (FBS), 100.0 kU/L of penicillin, and 100.0 mg/L of streptomycin in a 5% CO₂ atmosphere).

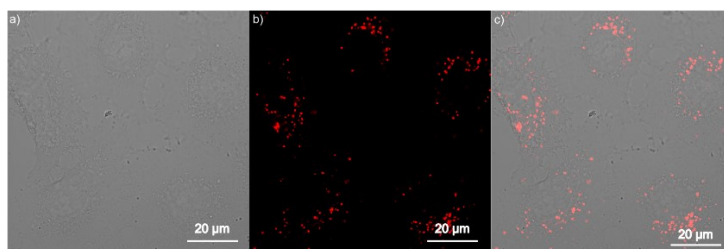


Fig. S9 a) Bright-field image; and b) fluorescent image of A549 cells stained with **1** ($1.0 \mu\text{M}$, $\lambda_{\text{ex}} = 543 \text{ nm}$, $\lambda_{\text{em}} = 600\text{--}700 \text{ nm}$); c) merged image of a) and b).

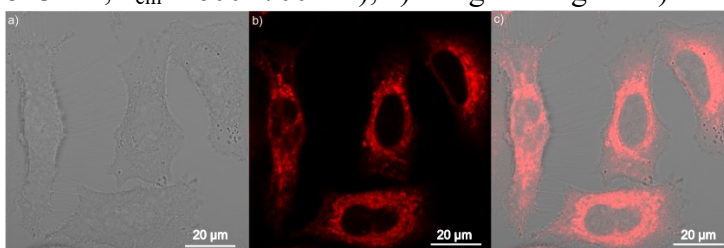


Fig. S10 a) Bright-field image; and b) fluorescent image of A549 cells stained with **2** ($1.0 \mu\text{M}$, $\lambda_{\text{ex}} = 543 \text{ nm}$, $\lambda_{\text{em}} = 600\text{--}700 \text{ nm}$); c) merged image of a) and b).

3) Confocal imaging experiment data

Table S8 Manders' coefficients and Pearson's coefficient in confocal imaging experiments

Entry	concentration	λ_{em} (nm)	Manders' coefficients	Pearson's coefficient
1	$1.0 \mu\text{M}$	600-700	$m_1 = 0.88$, $m_2 = 0.98$	0.93
2	$1.0 \mu\text{M}$	600-700	$m_1 = 0.93$, $m_2 = 0.99$	0.91

Manders' coefficients and Pearson's coefficient are calculated by Image Pro Plus software.

4) Cytotoxicity assays

The cytotoxicity studies of **1** and **2** were examined by CellTiter 96® Aqueous One Solution Cell Proliferation Assay. A549 cells were seeded at 1×10^4 cells/well in 96-well culture plates for a stationary culture. After being incubated for 12 h, the medium was replaced with fresh complete medium, and the sample was then added to achieve final concentrations at 0, 0.0625, 0.125, 0.25, 0.5, 1.0, 2.0 and 4.0 μM . After 12 hours of incubation, 20.0 μL of CellTiter 96® Aqueous One Solution in PBS was added to each well and the plates were incubated for an additional 1 hour. Then, the absorbance of each sample was measured on the microplate reader (model 550, BioRad, USA) at a wavelength of 490 nm. The cell viability was calculated by the following formula: (mean optical density (OD) in treated wells/mean OD in control wells) \times 100%.

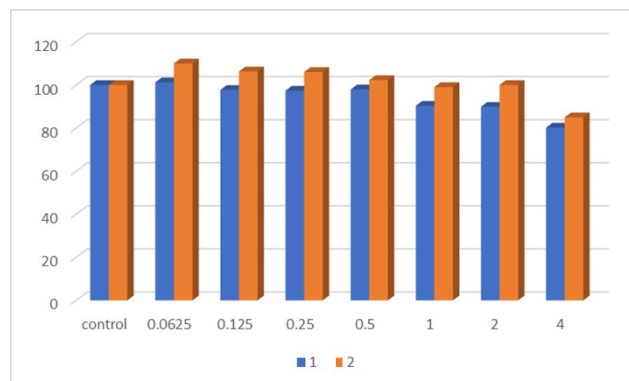


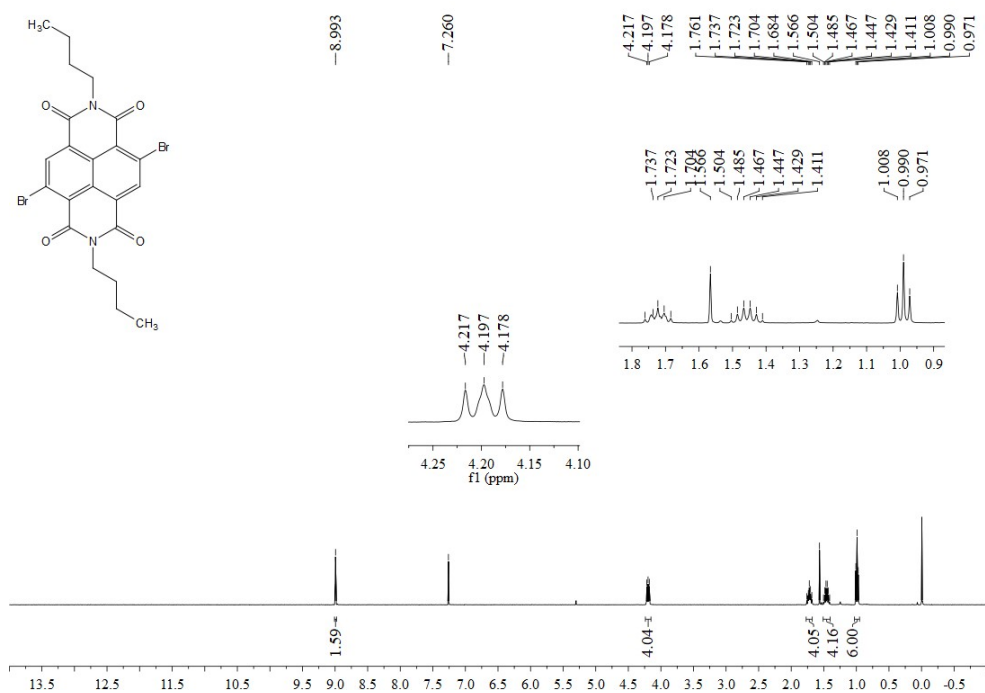
Fig. 11. Cell viability values (%) estimated by MTS using A549 cells, cultured in the presence of 0 μ M – 4.0 μ M of **1** and **2** for 12 h at 37 $^{\circ}$ C, respectively.

VIII. References

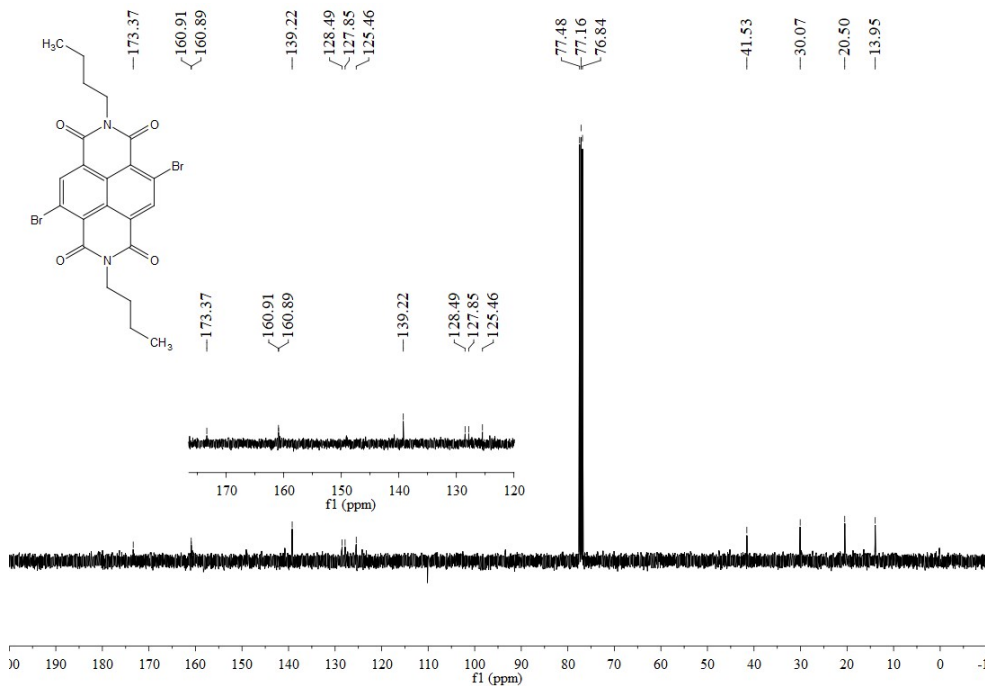
- [1] J. A. V. Er, A. G. Tennyson, J. W. Kamplain, V. M. Lynch and C. W. Bielawski, *Eur. J. Inorg. Chem.*, 2009, **13**, 1729.
- [2] A. Sarkar, S. Dhiman, A. Chalishazar and S. J. George, *Angew. Chem., Int. Ed.*, 2017, **56**, 13767.
- [3] S. Li, J. Tang, Y. Zhao, R. Jiang, T. Wang, G. Gao and J. You, *Chem. Commun.*, 2017, **53**, 3489.
- [4] S. Fuertes, H. Garca, M. Peralvarez, W. Hertog, J. Carreras and V. Sicilia, *Chem. Eur. J.* 2015, **21**, 1620.

IX. Copies of ^1H and ^{13}C NMR Spectra

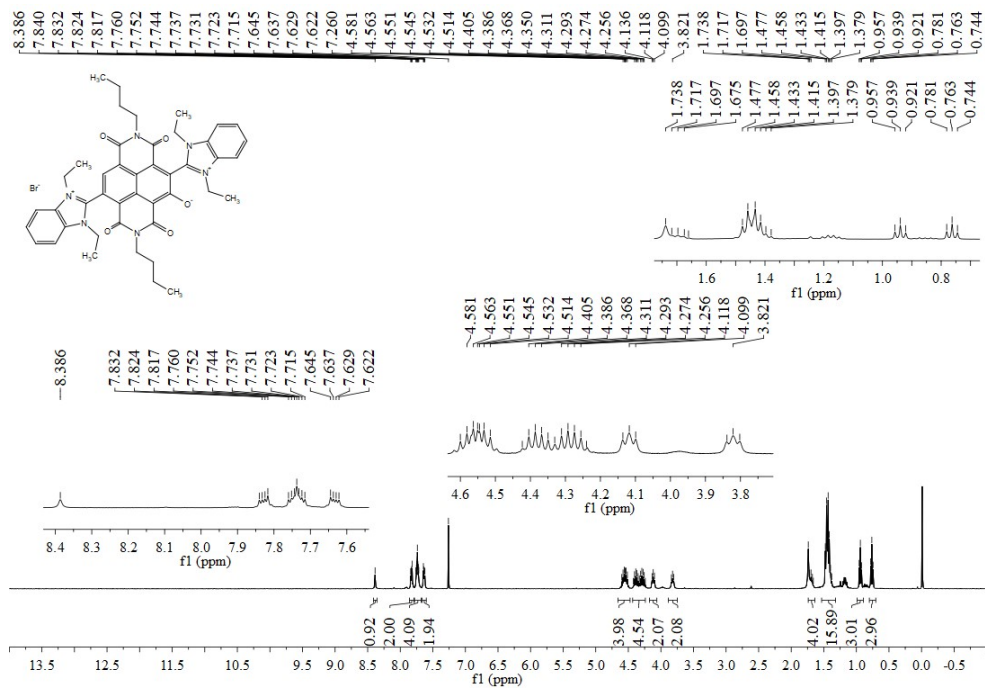
^1H NMR spectra of **2Br-NDI** (CDCl_3)



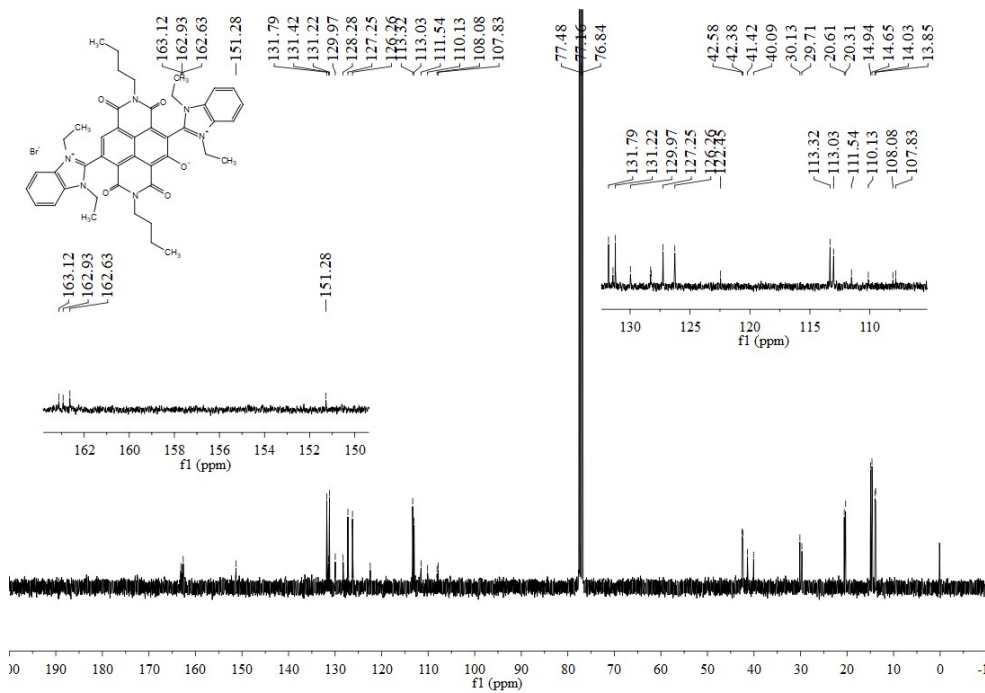
^{13}C NMR spectra of **2Br-NDI** (CDCl_3)



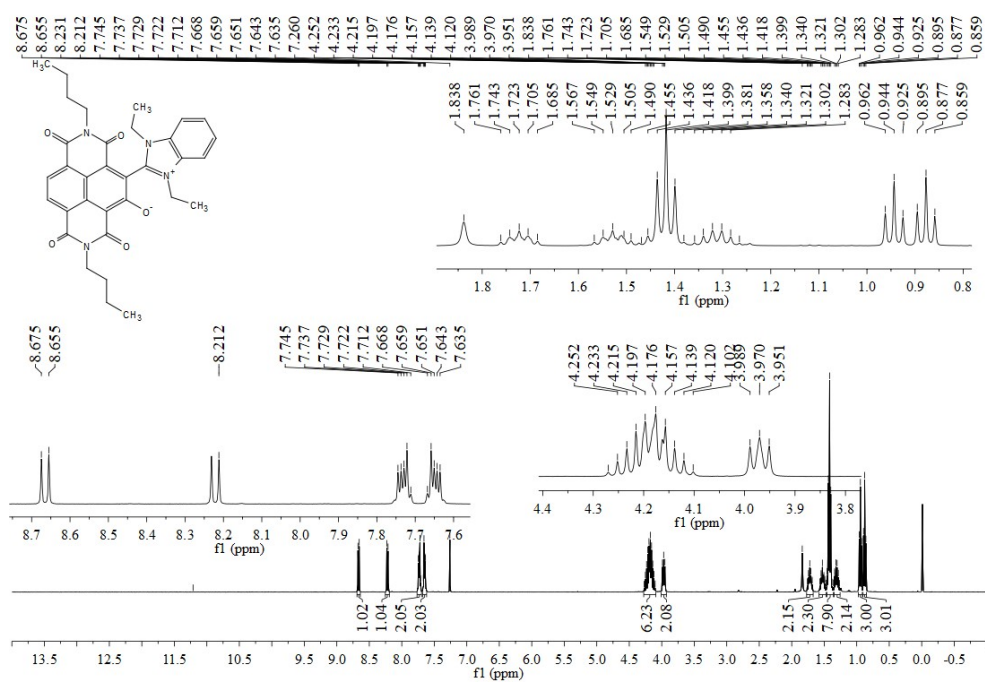
¹H NMR spectra of **1** (CDCl₃)



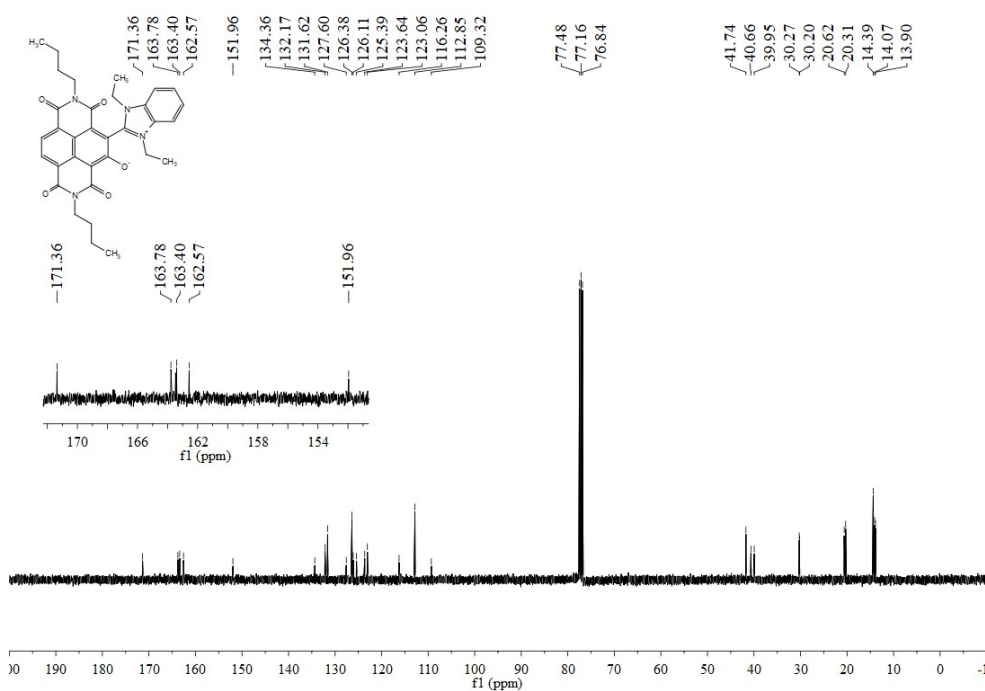
¹³C NMR spectra of **1** (CDCl₃)



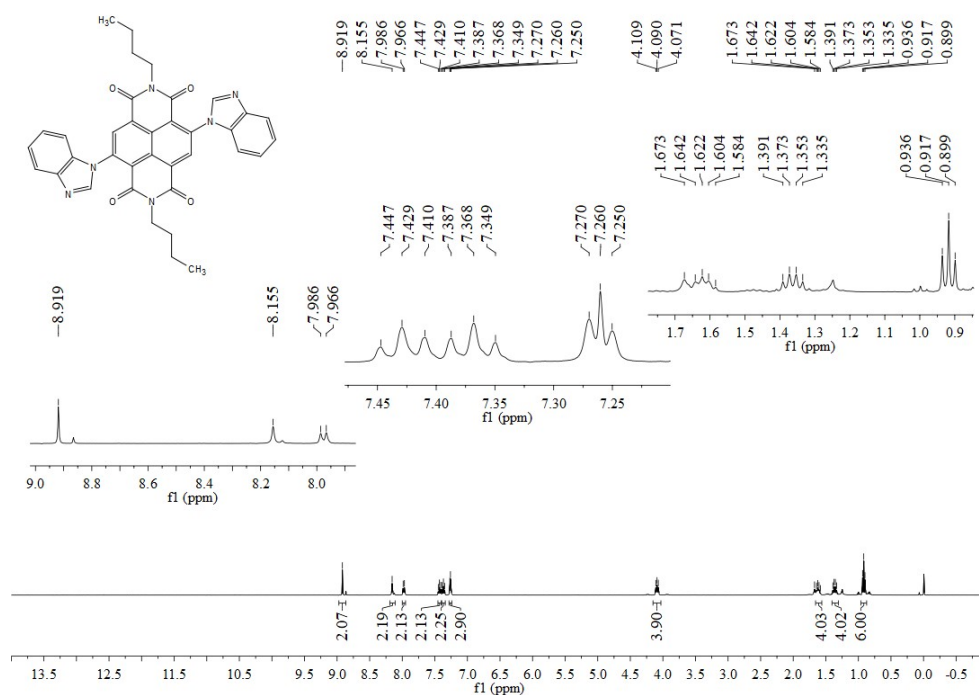
¹H NMR spectra of **2** (CDCl₃)



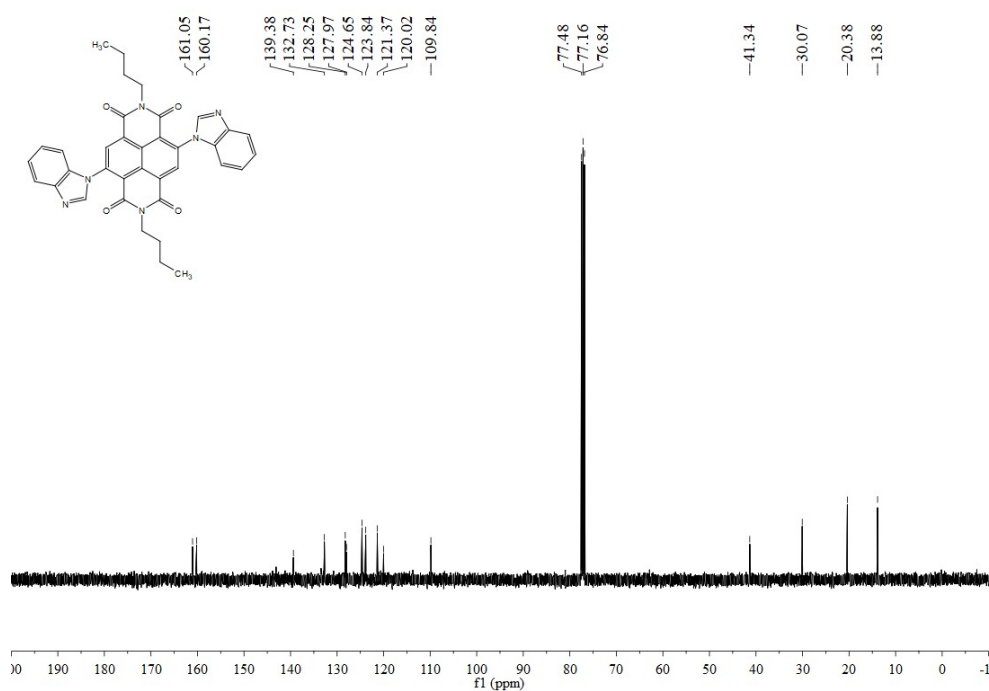
¹³C NMR spectra of **2** (CDCl₃)



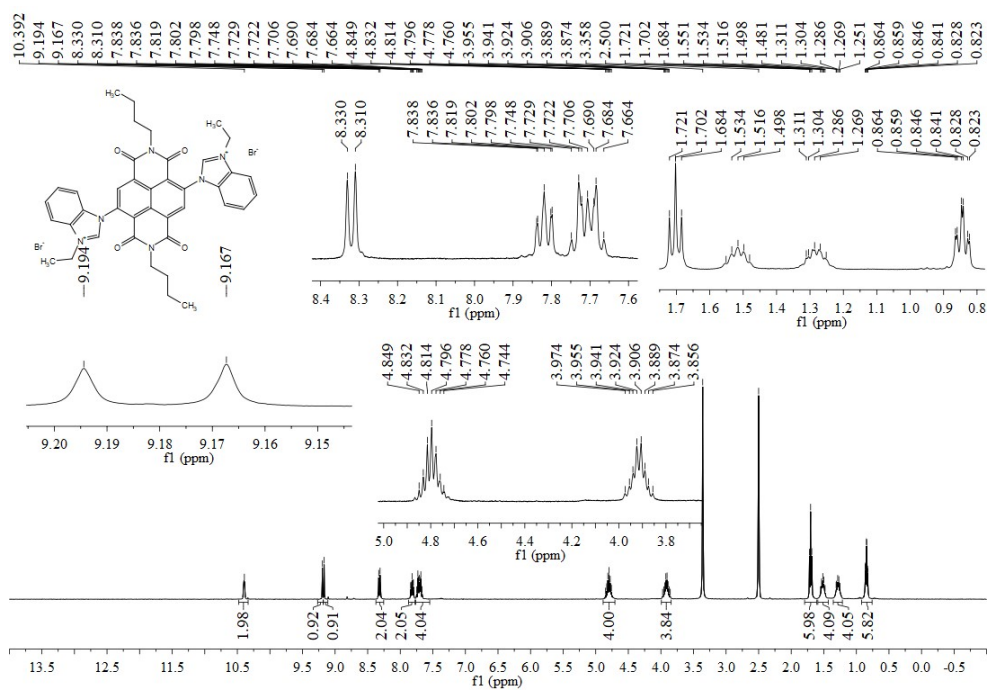
¹H NMR spectra of **2BBZM-NDI** (CDCl₃)



¹³C NMR spectra of **2BBZM-NDI** (CDCl₃)



^1H NMR spectra of **3** ($(\text{CD}_3)_2\text{SO}$)



^{13}C NMR spectra of **3** ($(\text{CD}_3)_2\text{SO}$)

