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Electronic Supplementary Information

Polymorphism and mechanochromism of *N*-alkylated 1,4-dihydropyridine derivatives containing different electron-withdrawing end groups

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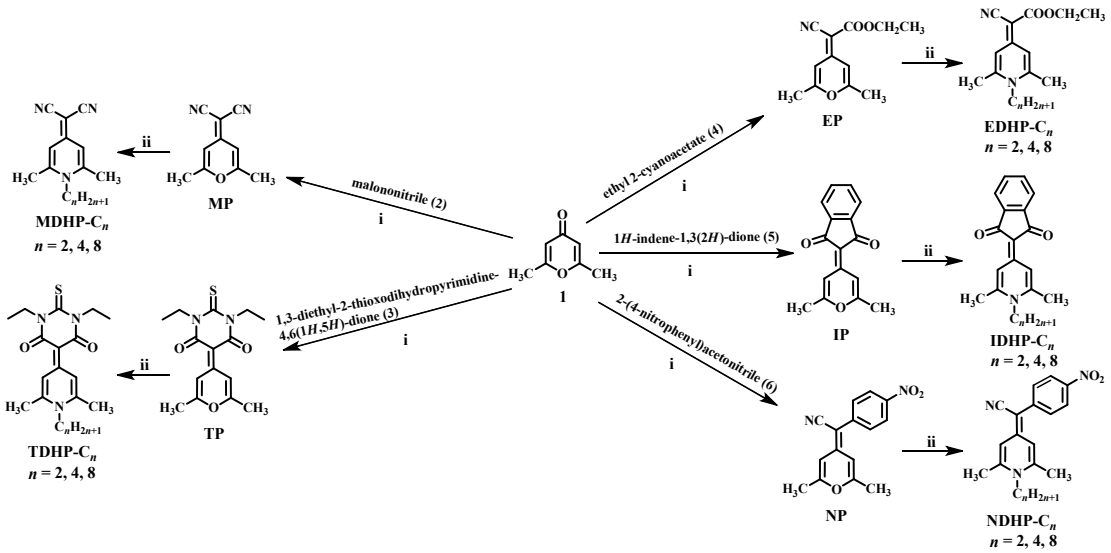


Scheme S1. Synthetic routes to various 4*H*-pyran and DHP derivatives. Reagents and conditions: (i) Ac_2O, reflux; (ii) $C_2H_5NH_2$, *n*-$C_4H_9NH_2$, or *n*-$C_8H_{17}NH_2$, CH_3CN.

Measurements and materials

NMR spectra were recorded on a Bruker DRX 500 NMR spectrometer. Electrospray ionization-mass spectrometry (ESI-MS) spectra were performed with a Finnigan DECAX-30000 LCQ Deca mass spectrometer. The elemental analysis was conducted on an Elementar Vario MICRO analyzer. Emission spectra were performed with a HITACHI F-7000 fluorometer. X-ray diffraction (XRD)

patterns were measured on a Bruker D8 Advance X-ray diffractometer. Differential scanning calorimetry (DSC) experiments were performed with a TA-DSC Q2000 at a heating rate of 10 °C/min. Absolute emission quantum yields (Φ_F) in solid state and time-resolved emission decay parameters were performed with a FluoroMax-4 (Horiba Jobin Yvon) fluorometer. Single-crystal X-ray diffraction measurements were conducted on a Bruker-Nonius Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. 2,6-Dimethyl-4-pyrone (**1**), malononitrile (**2**), 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)- dione (**3**), ethyl 2-cyanoacetate (**4**), 1*H*-indene-1,3(2*H*)-dione (**5**), 2-(4-nitrophenyl)acetonitrile (**6**), ethylamine, *n*-butylamine, and *n*-octylamine were purchased from commercial suppliers and used directly. 2-(2,6-Dimethyl-4*H*-pyran-4-ylidene)malononitrile (**MP**),[1] 2-(1-ethyl-2,6-dimethyl-pyridin- 4(1*H*)-ylidene)malononitrile (**MDHP-C*2***),[1] 2-(1-butyl-2,6-dimethylpyridin-4(1*H*)-ylidene)- malononitrile (**MDHP-C*4***),[2] 2-(2,6-dimethyl-1-octylpyridin-4(1*H*)-ylidene)malononitrile (**MDHP-C*8***),[2,3] ethyl 2-cyano-2-(2,6-dimethyl-4*H*-pyran-4-ylidene)acetate (**EP**),[4] ethyl 2-cyano-2-(2,6-dimethyl-1-octylpyridin-4(1*H*)-ylidene)acetate (**EDHP-C*8***),[4] 2-(2,6-dimethyl- 4*H*-pyran-4-ylidene)-1*H*-indene-1,3(2*H*)-dione (**IP**),[5] 2-(1-ethyl-2,6-dimethylpyridin-4(1*H*)- ylidene)-1*H*-indene-1,3(2*H*)-dione (**IDHP-C*2***),[6] 2-(1-butyl-2,6-dimethylpyridin-4(1*H*)-ylidene)- 1*H*-indene-1,3(2*H*)-dione (**IDHP-C*4***),[6] and 2-(2,6-dimethyl-1-octylpyridin-4(1*H*)-ylidene)-1*H*- indene-1,3(2*H*)-dione (**IDHP-C*8***)[6] were synthesized according to the literatures.

General procedure for TP and NP

A mixture of compound **1** (8.0 mmol, 0.99 g), compound **3**/**6** (24.0 mmol), and acetic anhydride (15 mL) was refluxed for 4 h. The reaction mixture was cooled to room temperature and then K_2CO_3 was added to adjust the pH value to neutral. The mixture was extracted with ethyl acetate (2 × 80 mL). The combined organic layers were washed with water and brine, and then dried by the addition of anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified with column chromatography (petroleum ether/ethyl acetate) (10:1, v/v) to afford pure 4*H*-pyran derivatives **TP** and **NP**, respectively.

5-(2,6-Dimethyl-4*H*-pyran-4-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (TP). Orange solids (2.08 g), 85% yield.^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.79 (s, 2H), 4.54 (q, J = 7.0 Hz, 4H), 2.44 (s, 6H), 1.27 (t, J = 6.5 Hz, 6H).^{13}C NMR ($CDCl_3$, 125 MHz): δ 177.73, 165.62, 161.74, 158.23, 111.63, 96.58, 43.23, 20.64, 12.43. MS (ESI, *m*/*z*): 307.10 (M^++H).

2-(2,6-Dimethyl-4*H*-pyran-4-ylidene)-2-(4-nitrophenyl)acetonitrile (NP). Orange-yellow solids (1.61 g), 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.20-8.22 (m, 4H), 7.52-7.55 (m, 2H), 6.44 (d, J = 1.0 Hz, 1H), 6.29 (d, J = 1.0 Hz, 1H), 2.20 (s, 3H), 2.12 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.19, 159.11, 146.02, 144.88, 141.57, 128.79, 124.06, 120.16, 107.51, 103.41, 86.95, 19.80, 19.55. MS (ESI, *m*/*z*): 269.10 (M^++H).

General procedure for TDHP-C*n*, EDHP-C*n*, and NDHP-C*n*

A mixture of **TP**/**EP**/**NP** (5 mmol), various aliphatic amine (25 mmol), and acetonitrile (15 mL) was heated under nitrogen at 80 °C for 24 h. The reaction mixture was cooled to room temperature and then poured into methanol, a large amount of solids were precipitated in the mixture. After filtration, the precipitate was washed with methanol three times, and then dried to afford various pure DHP derivatives.

1,3-Diethyl-5-(1-ethyl-2,6-dimethylpyridin-4(1*H*)-ylidene)-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (TDHP-C_2). Pale yellow solids (1.33 g), 80% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.93 (s, 2H), 4.60 (q, J = 7.0 Hz, 4H), 4.19 (q, J = 7.0 Hz, 2H), 2.62 (s, 6H), 1.42 (t, J = 7.0 Hz, 3H), 1.31 (t, J = 7.0 Hz, 6H).^{13}C NMR ($CDCl_3$, 125 MHz): δ 177.00, 161.89, 155.42, 147.83, 122.83, 91.68, 44.98, 43.00, 20.73, 14.39, 12.60. MS (ESI, *m*/*z*): 334.15 (M^++H). Anal. Calcd for $C_{17}H_{23}N_3O_2S$: C, 61.23; H, 6.95; N, 12.60. Found: C, 61.55; H, 6.90; N, 12.52.

5-(1-Butyl-2,6-dimethylpyridin-4(1*H*)-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (TDHP-C_4). Light green solids (1.36 g), 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.92 (s, 2H), 4.60 (q, J = 7.0 Hz, 4H), 4.06 (t, J = 8.0 Hz, 2H), 2.60 (s, 6H), 1.66-1.73 (m, 2H), 1.43-1.50 (m, 2H), 1.30 (t, J = 7.0 Hz, 6H), 1.00 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 176.98, 161.88, 155.29, 147.92, 122.72, 91.63, 49.80, 42.98, 31.31, 20.89, 19.94, 13.40, 12.60. MS (ESI, *m*/*z*): 362.15 (M^++H). Anal. Calcd for $C_{19}H_{27}N_3O_2S$: C, 63.13; H, 7.53; N, 11.62. Found: C, 63.47; H, 7.60; N, 11.54.

5-(2,6-Dimethyl-1-octylpyridin-4(1*H*)-ylidene)-1,3-diethyl-2-thioxodihydropyrimidine-4,6(1*H*,5*H*)-dione (TDHP-C_8). Green solids (1.61 g), 77% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.94 (s, 2H), 4.61 (q, J = 7.0 Hz, 4H), 4.05 (t, J = 8.0 Hz, 2H), 2.60 (s, 6H), 1.68-1.74 (m, 2H), 1.27-1.47 (m, 16H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 177.03, 161.93, 155.35, 147.89, 122.76, 91.69, 50.07, 43.02, 31.55, 29.45, 28.97, 28.90, 26.69, 22.47, 20.93, 13.94, 12.62. MS (ESI, *m*/*z*): 418.25 (M^++H). Anal. Calcd for $C_{23}H_{35}N_3O_2S$: C, 66.15; H, 8.45; N, 10.06. Found: C, 65.88; H, 8.39; N, 10.14.

Ethyl 2-cyano-2-(1-ethyl-2,6-dimethylpyridin-4(1*H*)-ylidene)acetate (EDHP-C_2). White solids (0.84 g), 68% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.12 (s, 1H), 6.72(s, 1H), 4.15 (q, J = 7.0 Hz, 2H), 4.00 (q, J = 7.0 Hz, 2H), 2.43 (s, 3H), 2.41(s, 3H), 1.33 (t, J = 7.0 Hz, 3H), 1.27 (q, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.44, 154.41, 146.58, 146.41, 122.11, 115.89, 114.84, 67.54, 59.06, 43.60, 20.48, 20.11, 14.71, 14.65. MS (ESI, *m*/*z*): 247.10 (M^++H). Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.69; H, 7.30; N, 11.27.

Ethyl 2-(1-butyl-2,6-dimethylpyridin-4(1*H*)-ylidene)-2-cyanoacetate (EDHP-C_4). White solids (1.04 g), 76% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 (s,1H), 6.72 (s, 1H), 4.15 (q, J = 7.0 Hz, 2H), 3.87 (t, J = 8.5 Hz, 2H), 2.42 (s, 3H), 2.40 (s, 3H), 1.59-1.65 (m, 2H), 1.39-1.44 (m, 2H), 1.28 (t, J = 7.0 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H).^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.46, 154.34, 146.69, 146.52, 122.09, 115.86, 114.79, 67.53, 59.06, 48.52, 31.65, 20.64, 20.26, 19.86, 14.64, 13.43. MS (ESI, *m*/*z*): 275.15 (M^++H). Anal. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.41; H, 8.13; N, 10.13.

2-(1-Ethyl-2,6-dimethylpyridin-4(1*H*)-ylidene)-2-(4-nitrophenyl)acetonitrile (NDHP-C_2). Red solids (1.11 g), 75% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.07-8.10 (m, 2H), 7.47-7.50 (m, 2H), 6.80 (d, J = 1.0 Hz, 1H), 6.66 (d, J = 1.0 Hz, 1H), 3.89 (q, J = 7.0 Hz, 2H), 2.36 (s, 3H), 2.31 (s, 3H), 1.33 (t, J = 7.5Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.78, 145.31, 145.15, 145.07, 143.09, 125.80, 124.08, 123.51, 115.65, 110.40, 75.91, 42.79, 20.50, 20.09, 15.05. MS (ESI, *m*/*z*): 296.10 (M^++H). Anal. Calcd for $C_{17}H_{17}N_3O_2$: C, 69.14; H, 5.80; N, 14.23. Found: C, 68.77; H, 5.84; N, 14.35.

2-(1-Butyl-2,6-dimethylpyridin-4(1*H*)-ylidene)-2-(4-nitrophenyl)acetonitrile (NDHP-C_4). Black solids (1.13 g), 70% yield. ^{1}H NMR ($CDCl_3$, 500MHz): δ 8.07-8.10 (m, 2H), 7.47-7.50 (m, 2H), 6.79 (d, J = 2.0 Hz, 1H), 6.65 (d, J = 2.0 Hz, 1H), 3.77 (t, J = 8.5 Hz, 2H), 2.35 (s, 3H), 2.30 (s, 3H), 1.60-1.66 (m, 2H), 1.39-1.44 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.74, 145.43, 145.27, 145.08, 143.07, 125.78, 124.07, 123.51, 115.62, 110.36, 75.88, 47.80, 32.06, 20.66, 20.24, 19.87, 13.54. MS (ESI, *m*/*z*): 324.10 (M^++H). Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 70.57; H, 6.55; N, 12.99. Found: C, 70.98; H, 6.59; N, 13.10.

2-(2,6-Dimethyl-1-octylpyridin-4(1*H*)-ylidene)-2-(4-nitrophenyl)acetonitrile (NDHP-C_8). Deep red solids (1.54 g), 81% yield. ^{1}H NMR ($CDCl_3$, 500MHz): δ 8.06-8.09 (m, 2H), 7.47-7.50 (m, 2H), 6.79 (d, J = 2.5 Hz, 1H), 6.65 (d, J = 2.0 Hz, 1H), 3.75 (t, J = 8.5 Hz, 2H), 2.35 (s, 3H), 2.30 (s, 3H), 1.60-1.67 (m, 2H), 1.27-1.37 (m, 10H), 0.87 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.74, 145.41, 145.26, 145.09, 143.04, 125.76, 124.06, 123.51, 115.62, 110.36, 75.86, 48.06, 31.59, 30.08, 29.02, 28.99, 26.59, 22.50, 20.66, 20.25, 13.97. MS (ESI, *m*/*z*): 380.20 (M^++H). Anal. Calcd for $C_{23}H_{29}N_3O_2$: C, 72.79; H, 7.70; N, 11.07. Found: C, 72.40; H, 7.64; N, 11.16.

References

1 (a) L. L. Woods. *J. Am. Chem. Soc.*, 1958, **80**, 1440−1442; (b) H. Li, Y. Guo, G. Li, H. Xiao, Y. Lei, X. Huang, J. Chen, H.Wu, J. Ding and Y. Cheng, *J. Phys. Chem. C*, 2015, **119**, 6737–6748.

2. R. Boonsin, G. Chadeyron, J. P. Roblin, D. Boyer and R. Mahiou, *J. Mater. Chem. C*, 2015, **3**, 9580–9587.

3. Y. Lei, D. Yang, H. Hua, C. Dai, L. Wang, M. Liu, X. Huang, Y. Guo, Y. Cheng and H. Wu, *Dyes Pigm.*, 2016, **133**, 261–272.

4. G. Kwak, S. Wang, M. S. Choi, H. Kim, K. H. Choi, Y. S. Han, Y. Hur and S. H. Kim, *Dyes Pigm.*, 2008, **78**, 25–33.

5. Y. Liu, Y. Lei, F. Li, J. Chen, M. Liu, X. Huang, W. Gao, H. Wu, J. Ding and Y. Cheng, *J. Mater. Chem. C*, 2016, **4**, 2862–2870.

6. Y. Liu, Y. Lei, M. Liu, F. Li, H. Xiao, J. Chen, X. Huang, W. Gao, H. Wu and Y. Cheng, *J. Mater. Chem. C*, 2016, **4**, 5970–5980.

2. Photophysical properties and XRD curves of various compounds in solid state

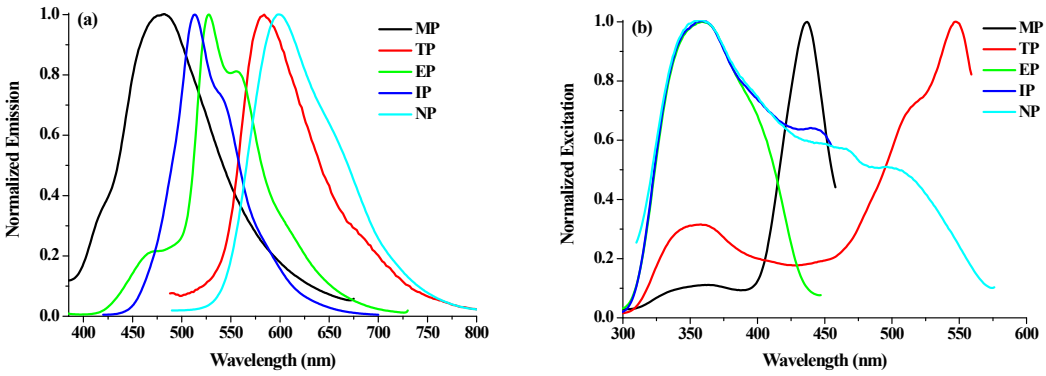
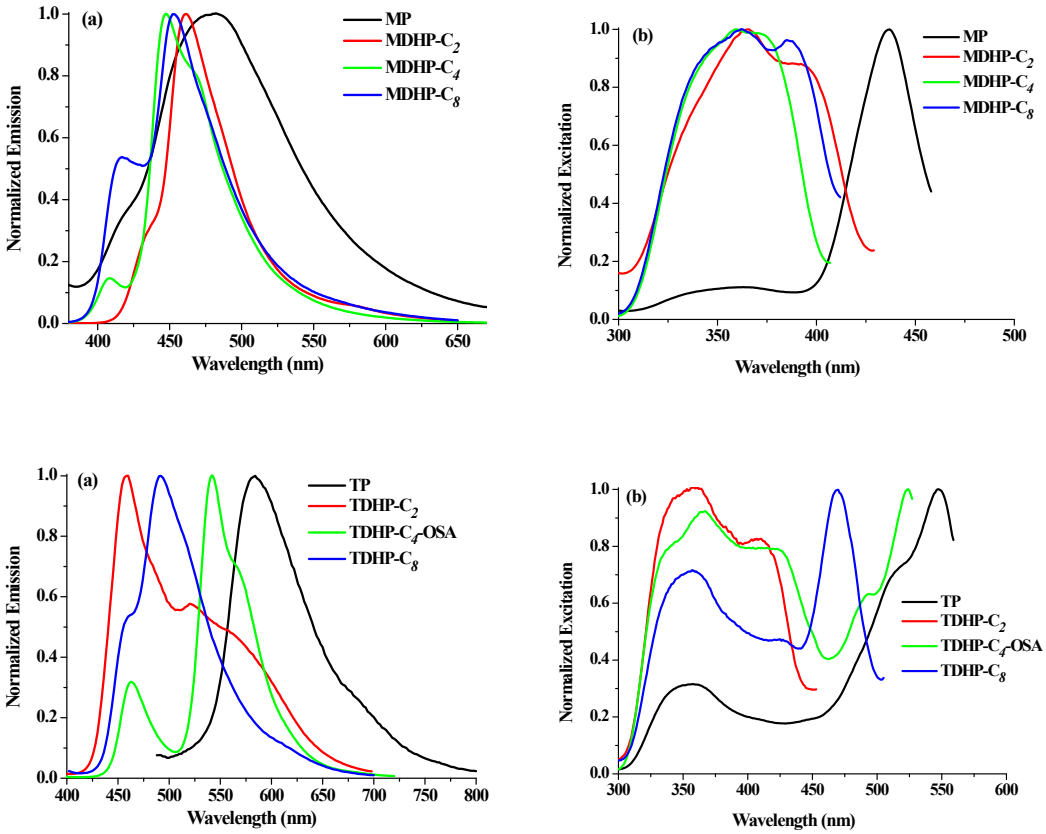


Fig. S1 Normalized fluorescence spectra (a) and excitation spectra (b) of the as-synthesized solids of various 4*H*-pyran derivatives.



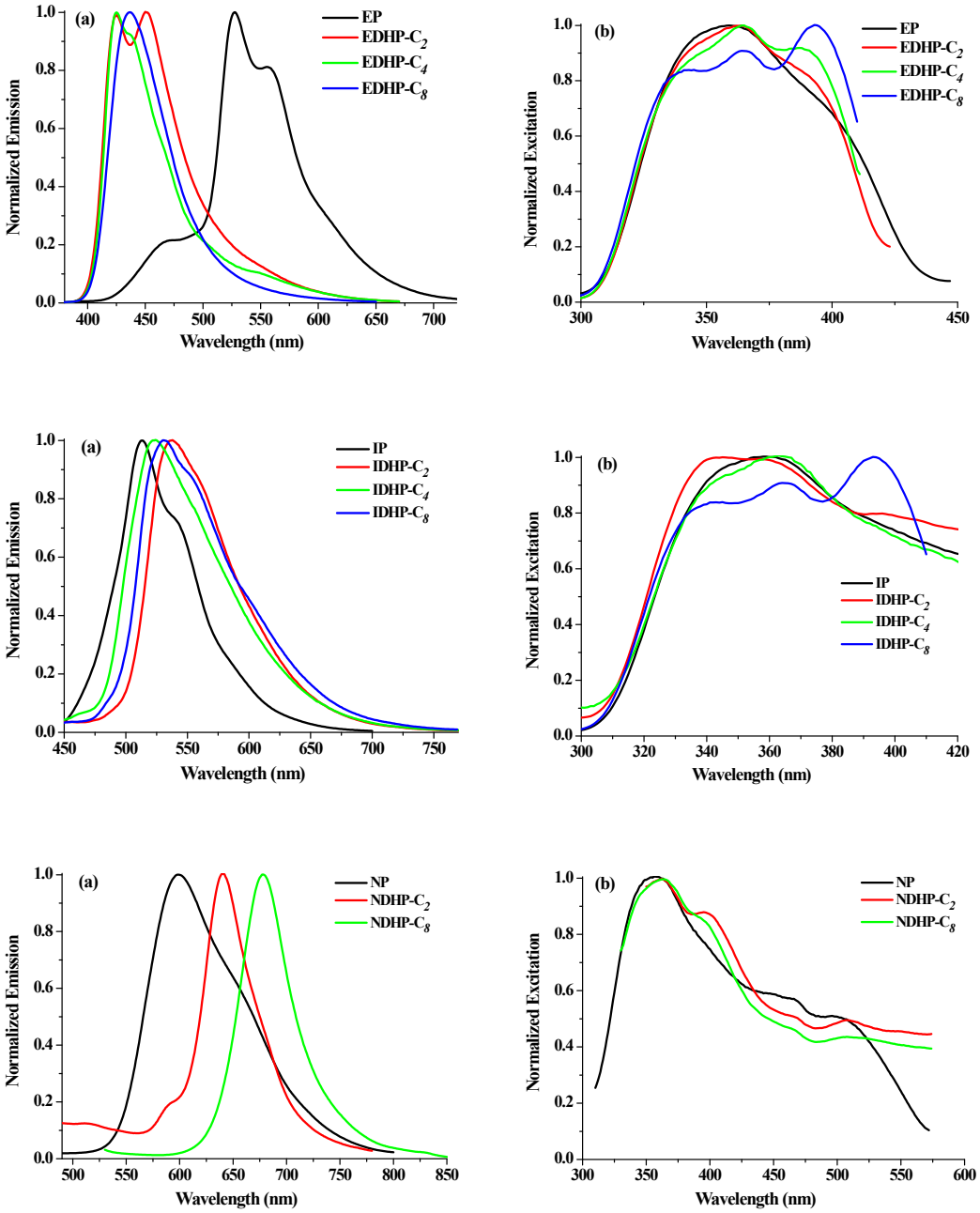


Fig. S2 Comparison of fluorescence spectra (a) and excitation spectra (b) of various 4*H*-pyran (as-synthesized) and DHP (original) derivatives solids.

Table S1 Emission wavelengths, excitation wavelengths, and fluorescence quantum yields of **MP**, **MDHP-C*n***, **TP**, and **TDHP-C*n*** solids under different conditions

Sample	Type	λ_{em} (nm)	λ_{ex} (nm)	Φ_F (%)	$\Delta\lambda_{MC}$ (nm)[a]
MP	As-synthesized	481	365	0.6	
MDHP-C*2*	Original	461	360	48.8	41
	MDHP-C*2*-*l*	489	361	57.2	-30[b], 13[c]
	MDHP-C*2*-*c*	470	362	79.7	-11[b], 32[c]
	Gently ground	459	361	51.3	
	Strongly ground	502	363	40.3	
	Fumed	462	364	47.5	
MDHP-C*4*	Original	408, 447	364	30.1	0
	MDHP-C*4*-*lc*	421, 466	363	18.1	-19
	MDHP-C*4*-*sb*	408, 456	362	38.9	-9
	Ground	408 (s)[d], 447	362	33.9	
MDHP-C*8*	Original	416, 453	361	25.5	
	MDHP-C*8*-*c*	466	363	23.0	-12
	Ground	419, 454	362	27.1	
TP	As-synthesized	584	490	2.0	
TDHP-C*2*	Original	458, 522, 570 (s)	362	7.5	-14
	TDHP-C*2*-*o*	456, 597	364	12.2	41
	TDHP-C*2*-*ly*	458, 596 (s)	344	10.7	40
	Ground	460, 556 (s)	362	7.0	
TDHP-C*4*	**TDHP-C*4*-OSA**	463, 542	366	14.7	-4
	TDHP-C*4*-OSB	456, 533	366	10.9	5
	TDHP-C*4*-*o*	543, 581	380	20.1	-43
	TDHP-C*4*-*g*	508	367	15.9	30
	Ground	467, 538	340	11.2	
TDHP-C*8*	Original	455 (s), 492	362	9.7	-3
	Ground	489	358	8.6	

[a] $\Delta\lambda_{MC} = \lambda_{Ground}-\lambda_{Original}$. [b] $\Delta\lambda_{MC} = \lambda_{Gently\ ground}-\lambda_{Original}$. [c] $\Delta\lambda_{MC} = \lambda_{Strongly\ ground}-\lambda_{Original}$. [d] s = shoulder peak.

Table S2 Emission wavelengths, excitation wavelengths, and fluorescence quantum yields of **EP**, **EDHP-C*n***, **IP**, **IDHP-C*n***, **NP**, and **NDHP-C*n*** solids under different conditions

Sample	Type	λ_{em} (nm)	λ_{ex} (nm)	Φ_F (%)	$\Delta\lambda_{MC}$ (nm)[a]
EP	As-synthesized	471, 527, 556	359	31.4	
EDHP-C*2*	Original	424, 451	350	35.7	4
	Ground	424, 455	350	30.8	
	Fumed	425, 445	350	32.8	
EDHP-C*4*	Original	424, 438 (s)[b]	340	37.1	5
	Ground	423, 443	340	31.2	
	Fumed	425	340	36.4	
EDHP-C*8*	Original	437	330	26.3	17
	Ground	454	330	18.0	
	Fumed	440	330	24.9	
IP	As-synthesized	513, 546 (s)	358	20.4	
IDHP-C*2*	Original	537	400	3.0	3
	Ground	534	400	-[c]	
IDHP-C*4*	Original	523	380	2.8	5
	Ground	518	380	-	
IDHP-C*8*	Original	532	400	0.8	2
	Ground	530	400	-	
NP	As-synthesized	599	480	4.0	
NDHP-C*2*	Original	640	480	1.8	0
	Ground	640	480	-	
NDHP-C*8*	Original	678	500	1.4	0
	Ground	678	500	-	

[a] $\Delta\lambda_{MC} = \lambda_{Ground}-\lambda_{Original}$. [b] s = shoulder peak. [c] No detection.

Table S3 Fluorescence decay parameters[a] of TDHP derivatives

Compound	Φ_F (%)	λ_{em}^{max} (nm)	τ_1 (ns)	τ_2 (ns)	A_1	A_2	$\langle\tau\rangle$ (ns)	k_f (s^{-1})	k_{nr} (s^{-1})
TDHP-C*2*-*o*	12.2	597	1.77	7.71	0.36	0.64	5.57	2.2×10^7	1.6×10^8
TDHP-C*2*-*ly*	10.7	596	1.21	7.27	0.32	0.68	5.33	2.0×10^7	1.7×10^8
TDHP-C*4*-*o*	20.1	581	0.75	7.44	0.30	0.70	5.43	3.7×10^7	1.5×10^8
TDHP-C*4*-*g*	15.9	508	0.95	5.82	0.59	0.41	2.95	5.4×10^7	2.9×10^8
TDHP-C*4*-OSA	14.7	542	2.38	8.76	0.54	0.46	5.31	2.8×10^7	1.6×10^8
TDHP-C*4*-OSB	10.9	533	1.51	10.89	0.69	0.31	4.41	2.5×10^7	2.0×10^8

[a] Determined from $I = A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)$, where τ_1 and τ_2 are the lifetimes of the shorter- and longer-lived species, and A_1 and A_2 are their respective amplitudes, respectively. The weighted mean lifetime $\langle\tau\rangle$ was calculated by the following equation: $\langle\tau\rangle = (A_1\tau_1+A_2\tau_2)/(A_1+A_2)$. The radiative rate constant k_f was calculated by the equation: $k_f = \Phi_F/\langle\tau\rangle$. The non-radiative rate constant k_{nr} was calculated by the equation: $k_{nr} = (1-\Phi_F)/\langle\tau\rangle$.

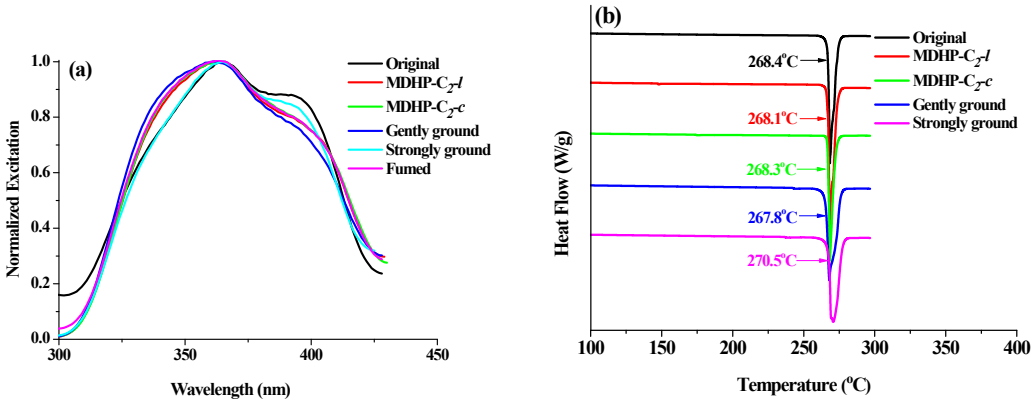


Fig. S3 Normalized excitation spectra (a) and DSC curves (b) of **MDHP-C$_2$** solid samples under various conditions.

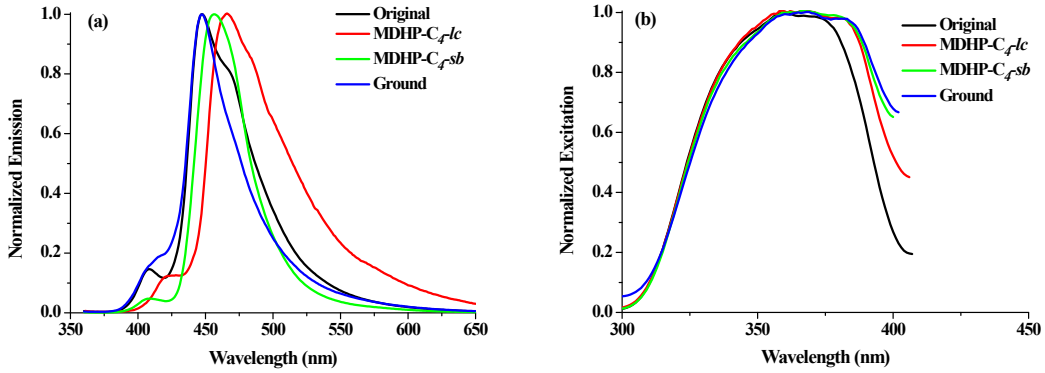


Fig. S4 Normalized fluorescence spectra (a) and excitation spectra (b) of **MDHP-C$_4$** solid samples under various conditions.

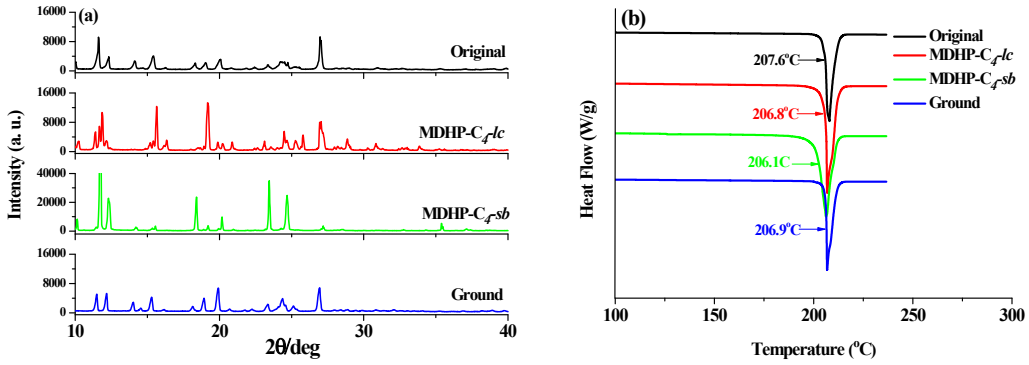


Fig. S5 XRD (a) and DSC curves (b) of **MDHP-C$_4$** solid samples under various conditions.

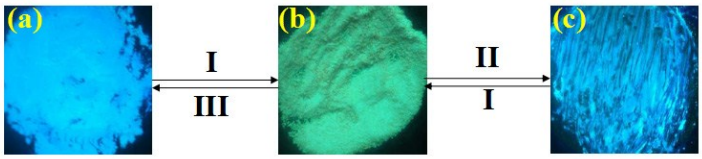


Fig. S6 Fluorescence images of **MDHP-C$_8$** solid samples taken under UV irradiation at 365 nm: (a) original sample; (b) **MDHP-C$_8$-*c*** sample; (c) ground sample. Conditions: (I) a recrystallization process using CH_3CN as a solvent; (II) grinding; (III) a recrystallization process using a *n*-hexane/$CHCl_3$ (30:1, v:v).

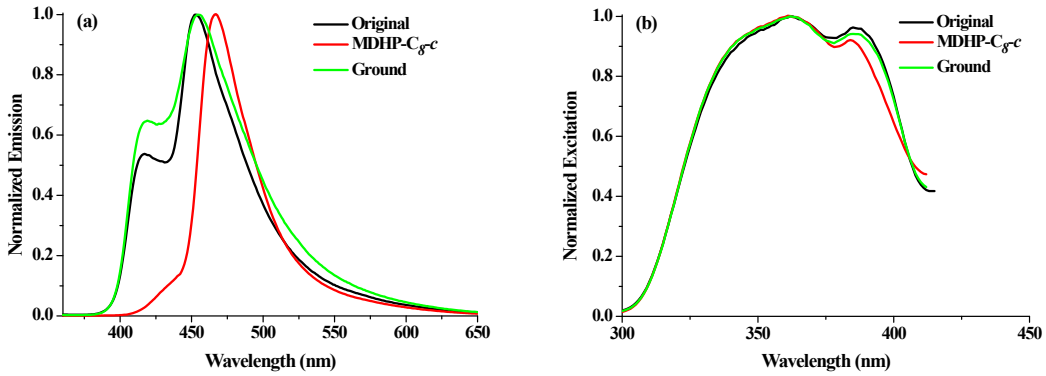


Fig. S7 Normalized fluorescence spectra (a) and excitation spectra (b) of **MDHP-C$_8$** solid samples under various conditions.

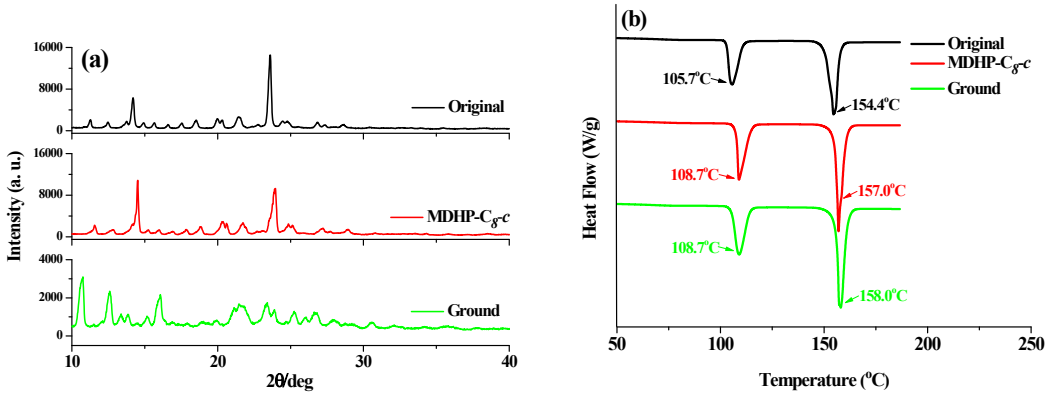


Fig. S8 XRD (a) and DSC curves (b) of **MDHP-C$_8$** solid samples under various conditions.

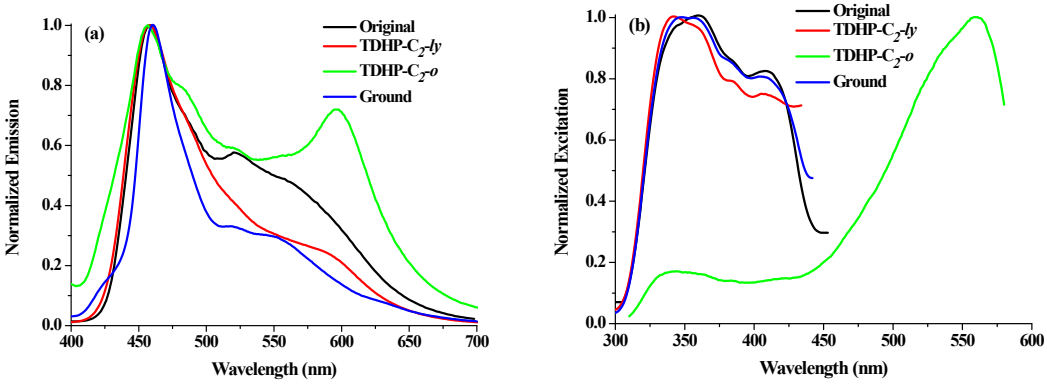


Fig. S9 Normalized fluorescence spectra (a) and excitation spectra (b) of **TDHP-C*2*** solid samples under various conditions.

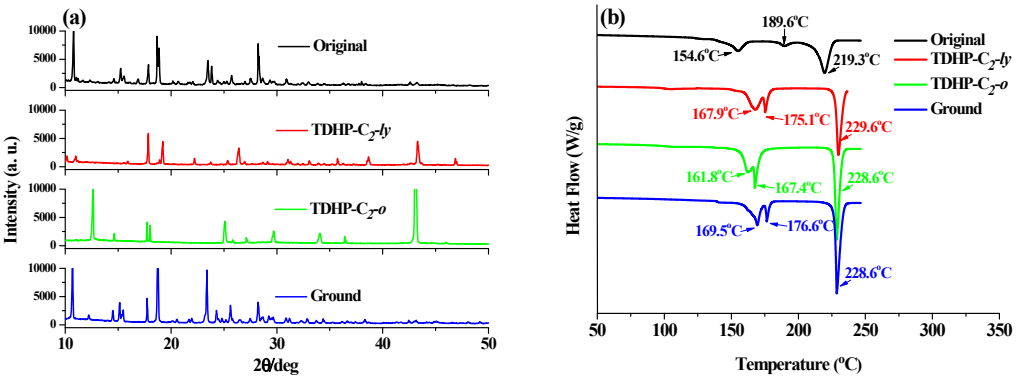


Fig. S10 XRD (a) and DSC curves (b) of **TDHP-C*2*** solid samples under different conditions.

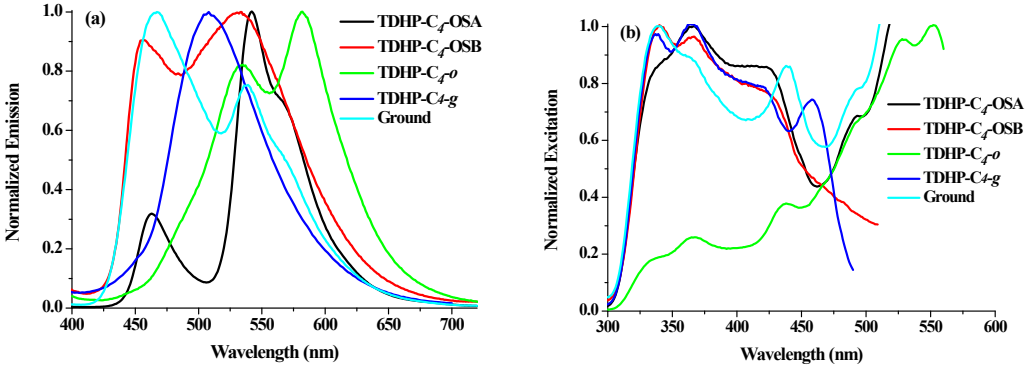


Fig. S11 Normalized fluorescence spectra (a) and excitation spectra (b) of **TDHP-C*4*** solid samples under various conditions.

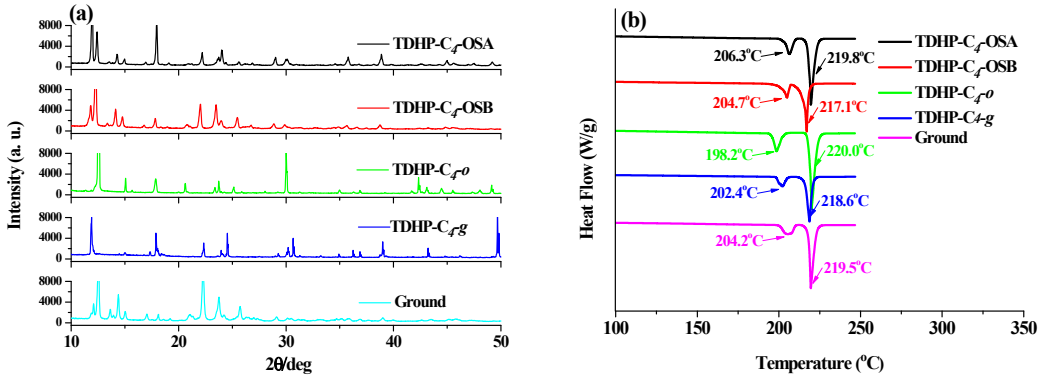


Fig. S12 XRD (a) and DSC curves (b) of **TDHP-C_4** solid samples under various conditions.

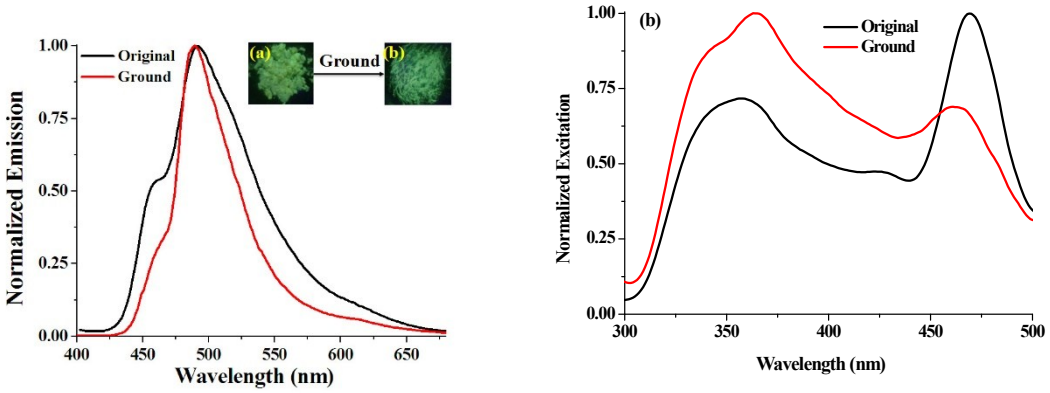


Fig. S13 (Left) Normalized fluorescence spectra of **TDHP-C_8** solid samples before and after grinding. Inset: fluorescence images of **TDHP-C_8** solid samples taken under a 365 nm UV lamp: (a) original sample; (b) ground sample. (Right) Normalized excitation spectra spectra of **TDHP-C_8** solid samples before and after grinding.

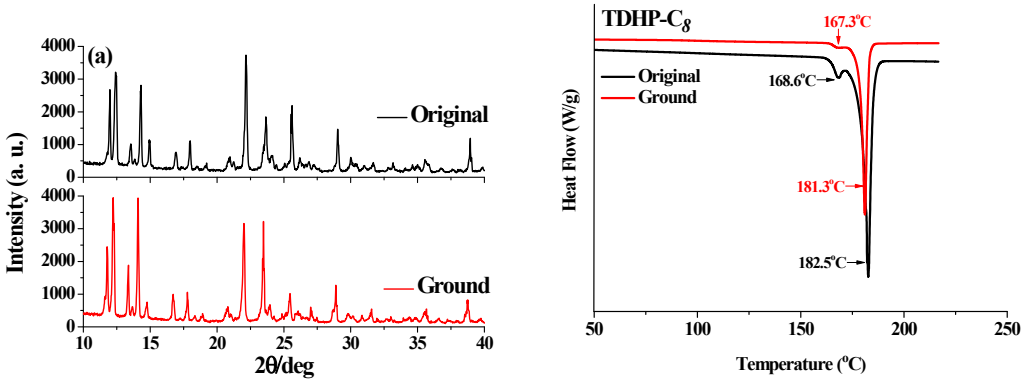


Fig. S14 XRD (a) and DSC curves (b) of **TDHP-C_8** solid samples before and after grinding.

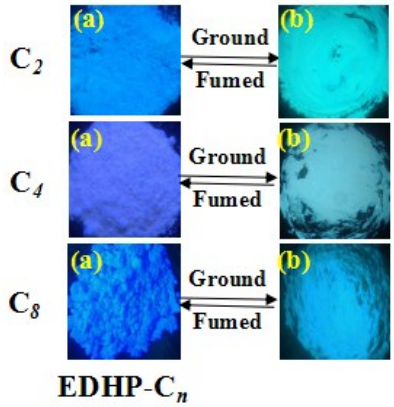


Fig. S15 Fluorescence images of **EDHP-C$_n$** solid samples taken under irradiation at 365 nm with a UV lamp: (a) original sample (fumed sample using EA vapor); (b) ground sample.

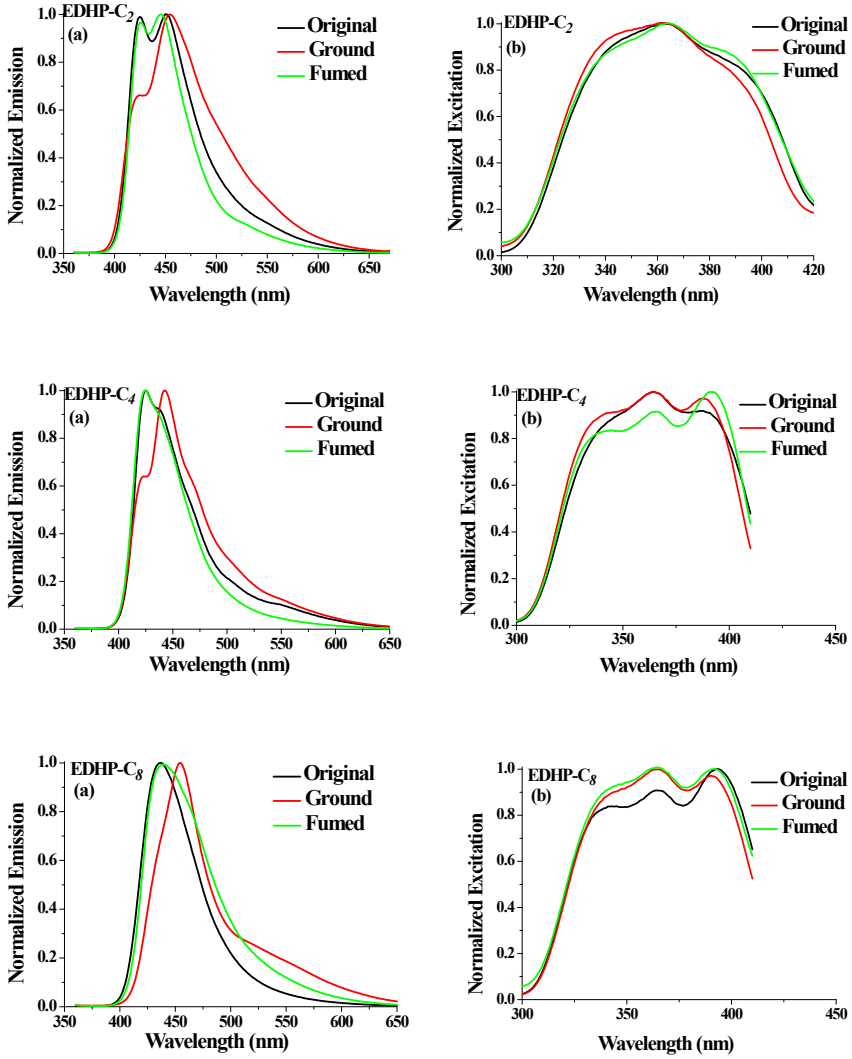


Fig. S16 Normalized fluorescence spectra (a) and excitation spectra (b) of **EDHP-C$_n$** solid samples under different conditions.

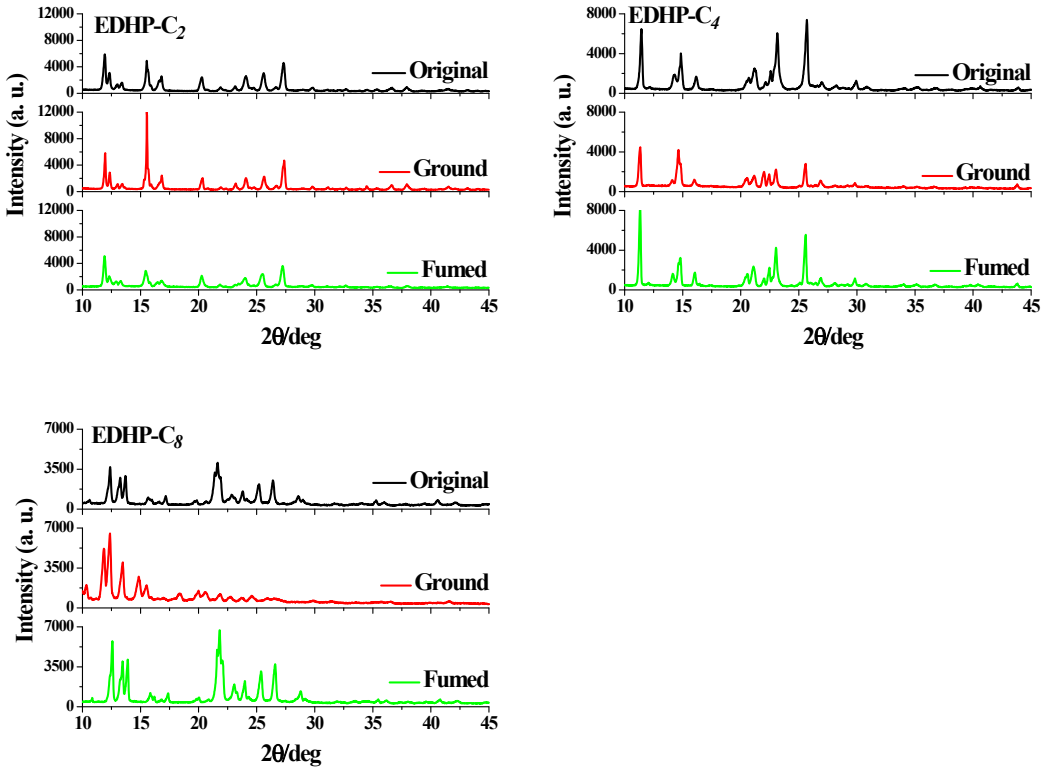


Fig. S17 XRD curves of the solid samples of **EDHP-C$_n$** under various conditions.

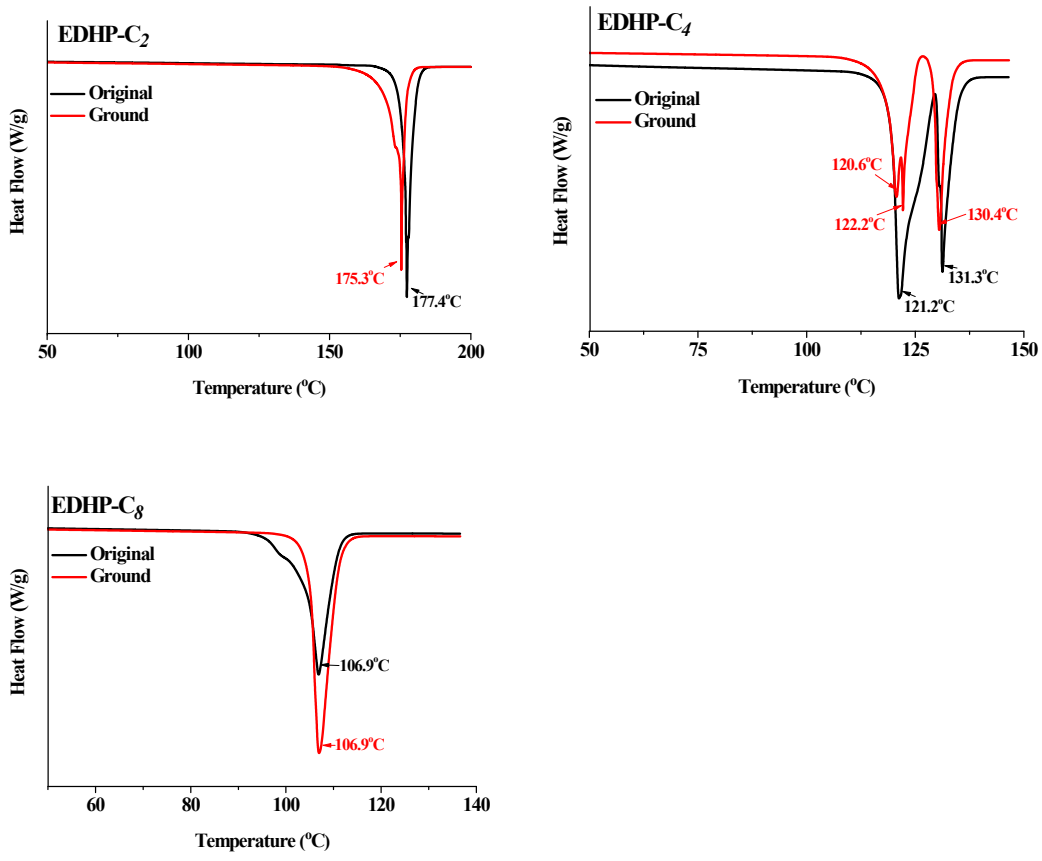


Fig. S18 DSC curves of the solid samples of **EDHP-C$_n$** under various conditions.

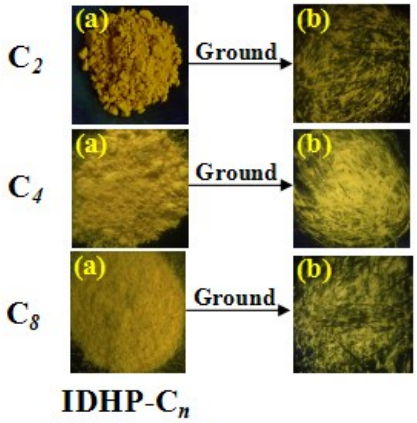


Fig. S19 Fluorescence images of **IDHP-C$_n$** solid samples taken under irradiation at 365 nm with a UV lamp: (a) original sample; (b) ground sample.

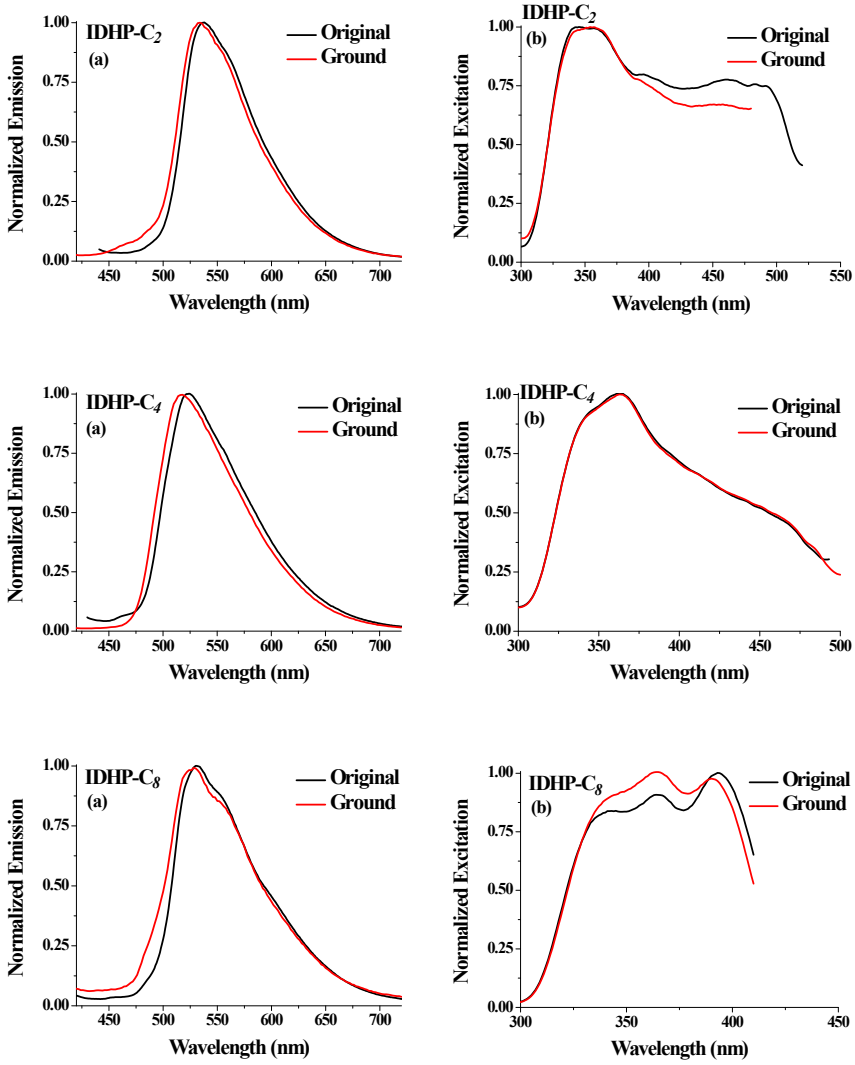


Fig. S20 Normalized fluorescence spectra (a) and excitation spectra (b) of **IDHP-C$_n$** solid samples before and after grinding.

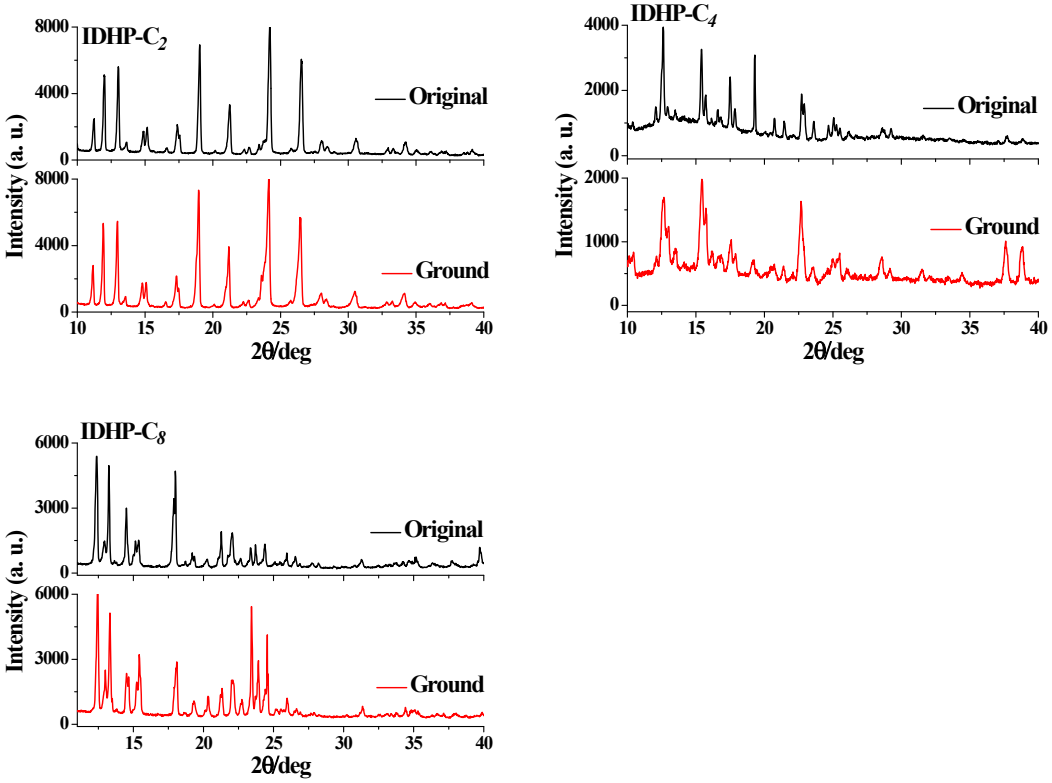


Fig. S21 XRD curves of the solid samples of **IDHP-C$_n$** before and after grinding.

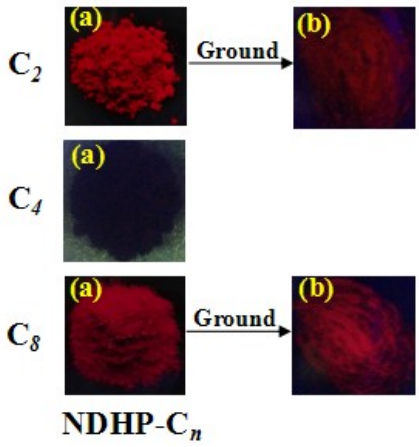


Fig. S22 Fluorescence images of **NDHP-C$_n$** solid samples taken under irradiation at 365 nm with a UV lamp: (a) original sample; (b) ground sample.

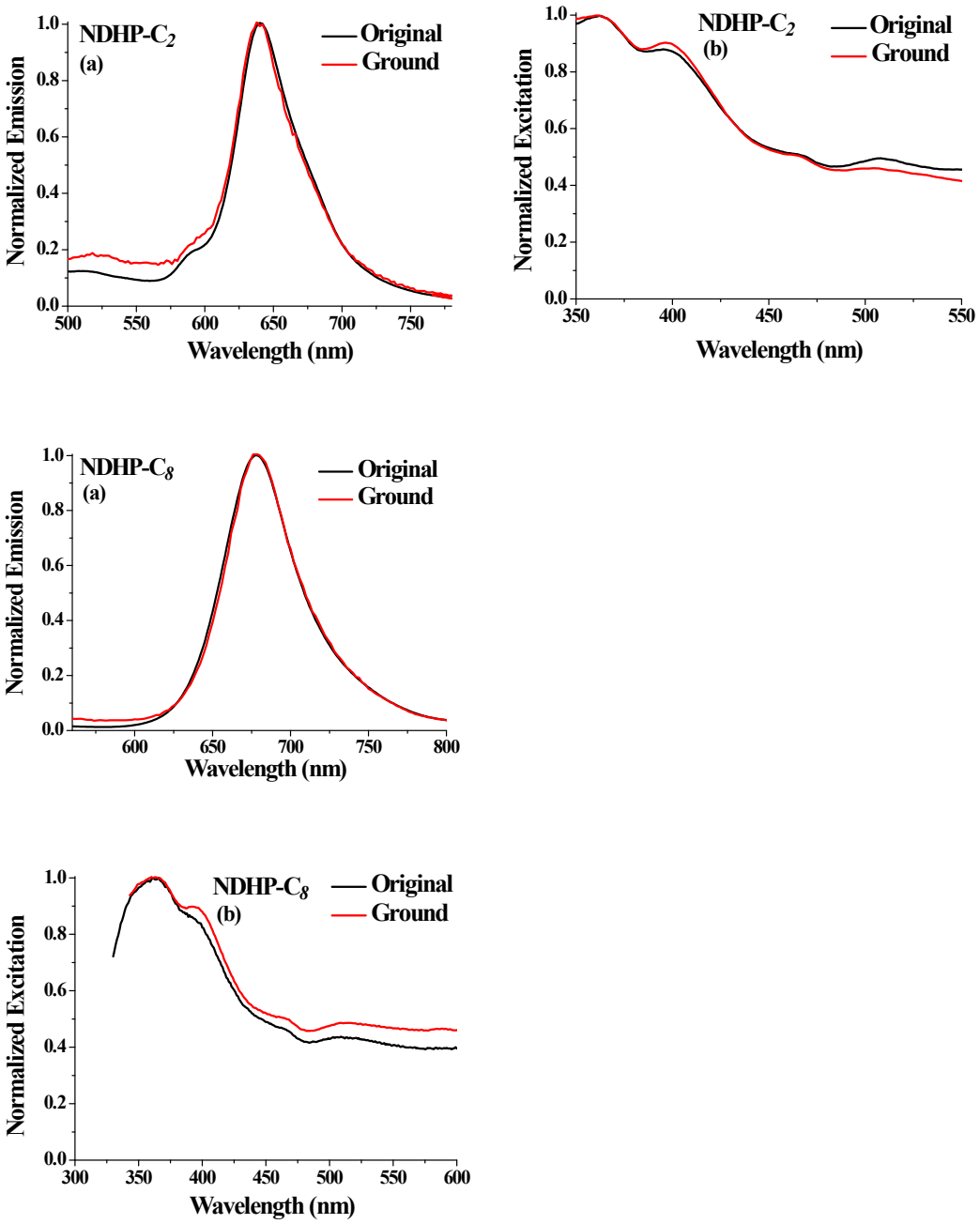


Fig. S23 Normalized fluorescence spectra (a) and excitation spectra (b) of **NDHP-C$_n$** solid samples before and after grinding.

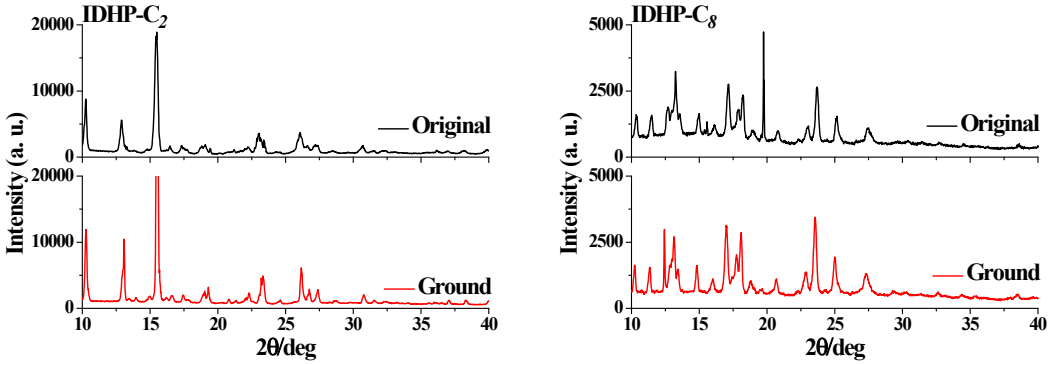


Fig. S24 XRD curves of the solid samples of **NDHP-C*n*** before and after grinding.

3. Culture methods, crystal data, intermolecular interactions, and packing motifs of various single crystals

CCDC 1498114-1498127 contains supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Single crystals of **MP** (No. 1498114), **TP** (No. 1498119), and **IP** (No. 1498124) were obtained from a $CHCl_3/CH_3OH$ solution, respectively. Single crystals of **MDHP-C*2*-*c*** (No. 1498115), **MDHP-C*4*-*sb*** (No. 1498117), **TDHP-C*2*-*ly*** (No. 1498121), **TDHP-C*4*-*g*** (No. 1498122), **TDHP-C*8*** (No. 1498123), **IDHP-C*2*** (No. 1498125), **EDHP-C*4*** (No. 1498126), and **NDHP-C*2*** (No. 1498127) were cultured from a slow diffusion of an *n*-hexane/$CHCl_3$ mixture (6:1, v:v) , respectively. Single crystals of **MDHP-C*2*-*l*** (No. 1498116), **MDHP-C*4*-*lc***, and **MDHP-C*8*-*c*** (No. 1498118) were cultured from a recrystallization process using acetonitrile as a solvent, respectively. Single crystals of **TDHP-C*2*-*o*** (No. 1498120) and **TDHP-C*4*-*o*** was obtained from a slow evaporation of $CHCl_3$/EA (1:6 = v:v) mixed solvent, respectively.

Table S4 Crystal data and details of collection and refinement for **MP** and **MDHP-C*n***

	MP	**MDHP-C*2*-*c***	**MDHP-C*2*-*l***	**MDHP-C*4*-*sb***	**MDHP-C*4*-*lc***	**MDHP-C*8*-*c***
Empirical formula	$C_{10}H_8N_2O$	$C_{12}H_{13}N_3$	$C_{12}H_{13}N_3$	$C_{14}H_{17}N_3$	$C_{14}H_{17}N_3$	$C_{18}H_{25}N_3$
Formula weight	172.18	199.25	199.25	227.31	227.30	283.41
Temperature (K)	133(2) K	298(2)	293(2)	298(2)	293(2)	298(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	P c
Z	2	2	2	2	2	4
D_{calcd} [Mg/m^3]	1.306	1.271	1.230	1.152	1.109	1.131
F (000)	180	212	212	244	244	616

θ range [°]	2.42-26.00	2.00-25.99	1.99-25.50	2.10-25.49	2.09-25.50	1.45-25.99
R_1 [I>2σ(I)]	0.0320	0.0374	0.0481	0.0345	0.0484	0.0371
wR_2 [I>2σ(I)]	0.0850	0.1256	0.1216	0.1041	0.1255	0.1018
a [Å]	7.1417(9)	6.9599(7)	7.084(3)	7.6023(8)	7.7496(18)	9.3267(14)
b [Å]	7.8540(10)	7.5636(8)	7.646(3)	9.0012(10)	9.118(2)	14.003(2)
c [Å]	8.9569(11)	10.3122(10)	10.376(5)	9.9056(11)	9.953(2)	14.7925(18)
α [deg]	72.724(2)	98.430(2)	98.929(9)	79.040(2)	79.121(5)	90.00
β [deg]	74.137(2)	92.196(2)	91.731(9)	84.018(2)	83.706(5)	120.492(7)
γ [deg]	68.176(2)	103.452(2)	103.705(9)	80.824(2)	81.650(5)	90.00
V [Å^3]	437.76(10)	520.77(9)	538.1(4)	655.05(12)	680.9(3)	1664.7(4)
GOF	1.036	1.065	1.072	1.067	1.049	1.079
R(int)	0.0164	0.0182	0.0179	0.0217	0.0212	0.0345
No. of reflcns collected	3198	5014	3089	9125	3927	12263
No. of unique reflcns	1713	2018	1996	2417	2534	5351
R_1 (all data)	0.0362	0.0404	0.0599	0.0369	0.0721	0.0409
wR_2 (all data)	0.0888	0.1281	0.1319	0.1070	0.1404	0.1046

Table S5 Crystal data and details of collection and refinement for **TP** and **TDHP-C*n***

	TP	**TDHP-C*2*-*ly***	**TDHP-C*2*-*o***	**TDHP-C*4*-*g***	**TDHP-C*4*-*o***	**TDHP-C*8***
Empirical formula	$C_{15}H_{18}N_2O_3S$	$C_{17}H_{25}N_3O_3S$	$C_{17}H_{25}N_3O_3S$	$C_{19}H_{27}N_3O_2S$	$C_{19}H_{27}N_3O_2S$	$C_{23}H_{35}N_3O_2S$
Formula weight	306.37	351.46	351.46	361.50	361.50	417.60
Temperature (K)	133(2)	293(2)	298(2)	298(2)	298(2)	133(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*P* 2(1)/c	*P* 2(1)/n	*P* 2(1)/c	*P*$\bar{1}$	*P*$\bar{1}$	*P* 2(1)/n
Z	4	4	4	2	2	4
D_{calcd} [Mg/m^3]	1.389	1.329	1.320	1.283	1.275	1.224
F (000)	648	752	752	388	388	904
θ range [°]	2.32-25.50	2.07-25.50	2.30-26.00	1.38-26.00	2.71-26.00	1.92-26.00
R_1 [I>2σ(I)]	0.0393	0.0516	0.0444	0.0443	0.0399	0.0390
wR_2 [I>2σ(I)]	0.0961	0.1440	0.1379	0.1278	0.1171	0.0961
a [Å]	16.414(4)	10.9669(13)	10.9827(13)	8.252(6)	8.2620(8)	9.2082(16)
b [Å]	5.0946(12)	14.1993(16)	14.2402(17)	8.626(6)	8.6448(9)	12.659(2)
c [Å]	17.538(4)	12.5425(15)	12.5749(11)	15.276(10)	15.313(2)	19.962(3)
α [deg]	90	90	90	96.785(14)	96.778(2)	90
β [deg]	92.146(4)	115.925(2)	115.917(8)	98.511(13)	98.531(2)	103.023(3)
γ [deg]	90	90	90	117.108(13)	117.060(2)	90
V [Å^3]	1465.6(6)	1756.6(4)	1768.9(3)	935.7(11)	941.60(18)	2267.0(7)
GOF	0.980	1.023	1.072	1.052	1.069	1.008
R(int)	0.0399	0.0289	0.0211	0.0276	0.0212	0.0325
No. of reflcns collected	9465	9920	14001	9128	14096	11879
No. of unique reflcns	2710	3252	3481	3655	3677	4365
R_1 (all data)	0.0551	0.0619	0.0508	0.0678	0.0451	0.0579
wR_2 (all data)	0.1076	0.1532	0.1436	0.1399	0.1207	0.1075

Table S6 Crystal data and details of collection and refinement for **IP**, **IDHP-C$_2$**, **EDHP-C$_4$**, and **NDHP-C$_2$**

	IP	**IDHP-C$_2$**	**EDHP-C$_4$**	**NDHP-C$_2$**
Empirical formula	$C_{16}H_{14}O_4$	$C_{18}H_{17}NO_2$	$C_{16}H_{22}N_2O_2$	$C_{17}H_{17}N_3O_2$
Formula weight	270.27	279.32	274.36	295.34
Temperature (K)	293(2)	293(2)	100(2)	298(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*$\bar{1}$	*P* 2(1)/n	*P*$\bar{1}$	*P* 2(1)/c
Z	2	4	2	4
D_{calcd} [Mg/m^3]	1.367	1.324	1.194	1.281
F (000)	284	592	296	624
θ range [°]	2.25-25.50	2.31-26.00	2.61-25.50	1.20-26.00
R_1 [I>2σ(I)]	0.0544	0.0465	0.0645	0.0488
wR_2 [I>2σ(I)]	0.1350	0.1067	0.1804	0.1384
a [Å]	5.0293(11)	8.914(2)	7.932(4)	17.031(3)
b [Å]	9.305(2)	13.304(3)	8.098(5)	11.1503(19)
c [Å]	14.420(3)	12.052(3)	12.503(7)	8.1223(13)
α [deg]	78.510(5)	90	100.451(11)	90
β [deg]	87.882(5)	101.441(4)	99.409(11)	96.862(3)
γ [deg]	83.349(4)	90	99.622(12)	90
V [Å^3]	656.8(2)	1400.8(5)	763.0(7)	1531.4(4)
GOF	1.088	1.031	1.107	1.093
R(int)	0.0262	0.0436	0.0303	0.0271
No. of reflcns collected	3806	8183	9304	11832
No. of unique reflcns	2432	2750	2764	2985
R_1 (all data)	0.0679	0.0725	0.1044	0.0590
wR_2 (all data)	0.1447	0.1174	0.2331	0.1461

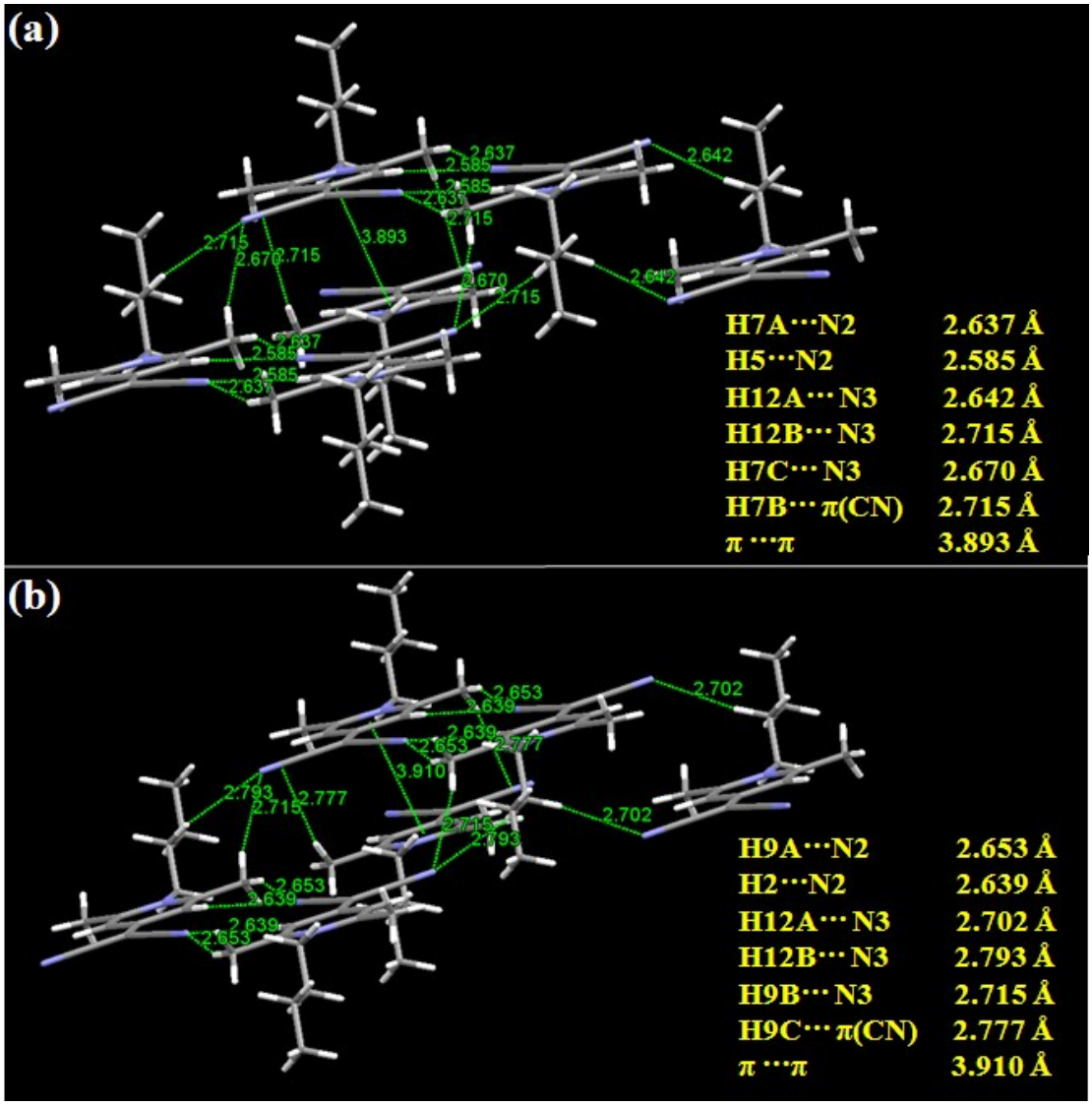


Fig. S25 The schematic intermolecular interactions in the crystals of **MDHP-C$_4$-*sb*** (a) and **MDHP-C$_4$-*lc*** (b).

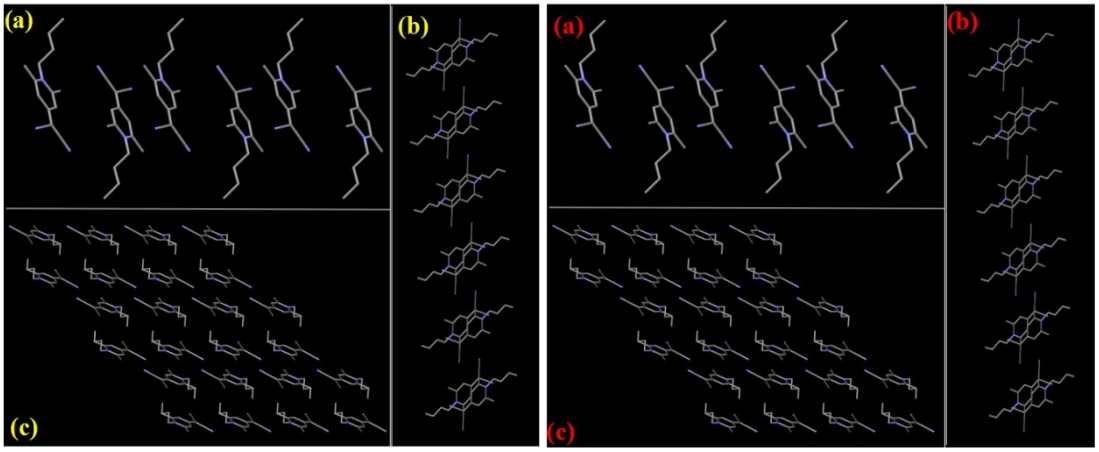


Fig. S26 The packing motif in the crystal of **MDHP-C$_4$-*sb*** (left) and **MDHP-C$_4$-*lc*** (right): (a) viewed along the *a*-axis; (b) viewed along the *b*-axis; (c) viewed along the *c*-axis. The hydrogen atoms have been omitted for clarity.

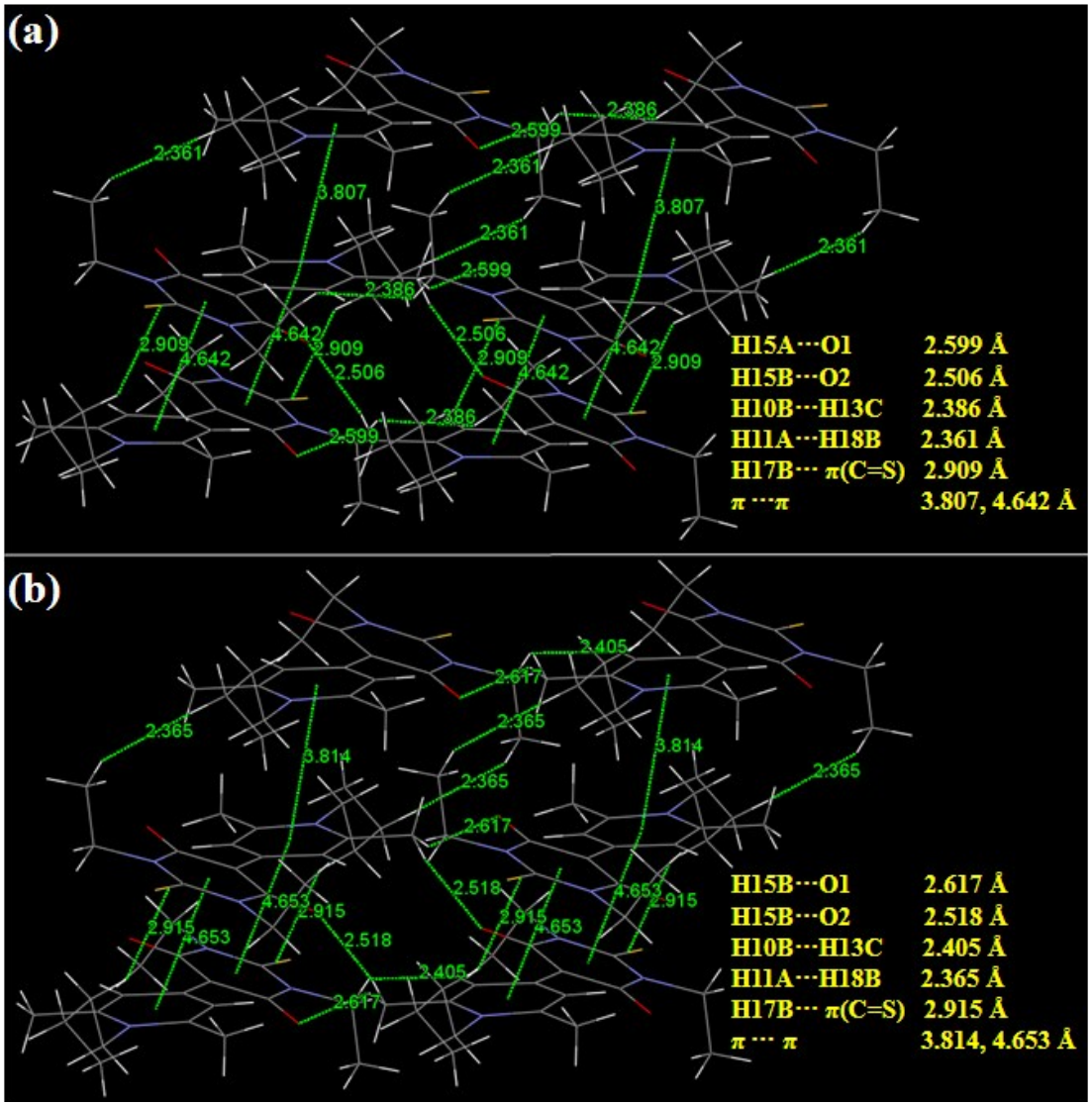


Fig. S27 The schematic intermolecular interactions in the crystals of **TDHP-C$_4$-*g*** (a) and **TDHP-C$_4$-*o*** (b).

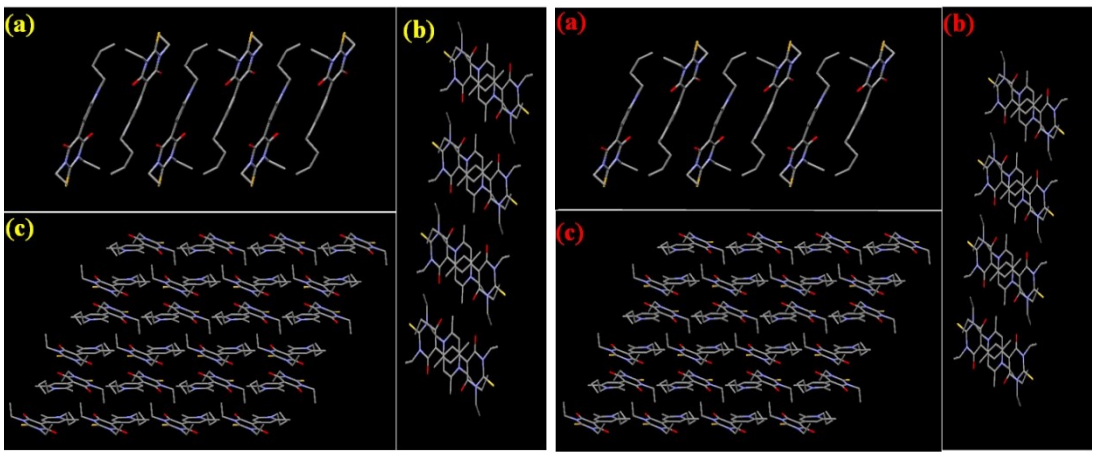


Fig. S28 The packing motif in the crystal of **TDHP-C$_4$-*g*** (left) and **TDHP-C$_4$-*o*** (right): (a) viewed along the *a*-axis; (b) viewed along the *b*-axis; (c) viewed along the *c*-axis. The hydrogen atoms have been omitted for clarity.

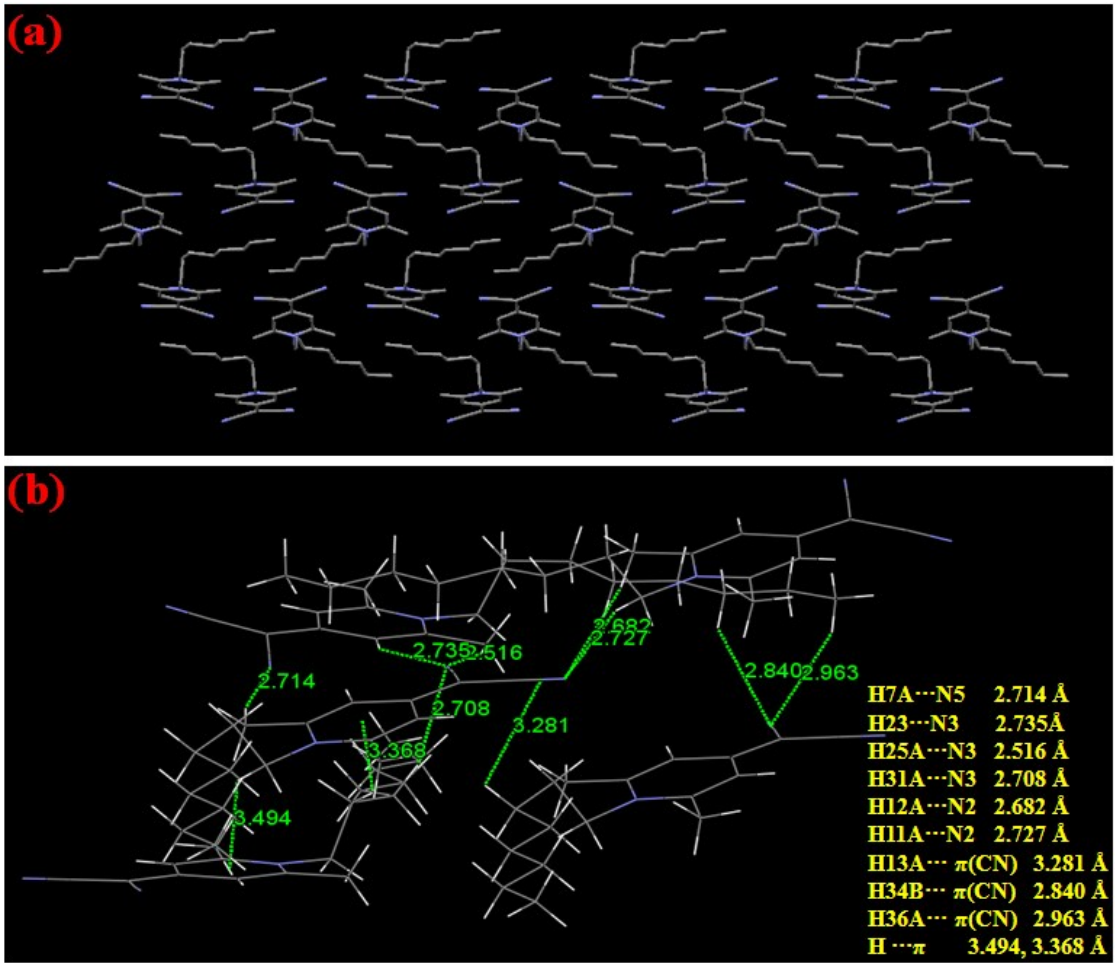


Fig. S29 (a) The packing motif in the crystal of **MDHP-*C*$_8$-*c***. The hydrogen atoms have been omitted for clarity. (b) The schematic intermolecular interactions in the crystal of **MDHP-*C*$_8$-*c***.

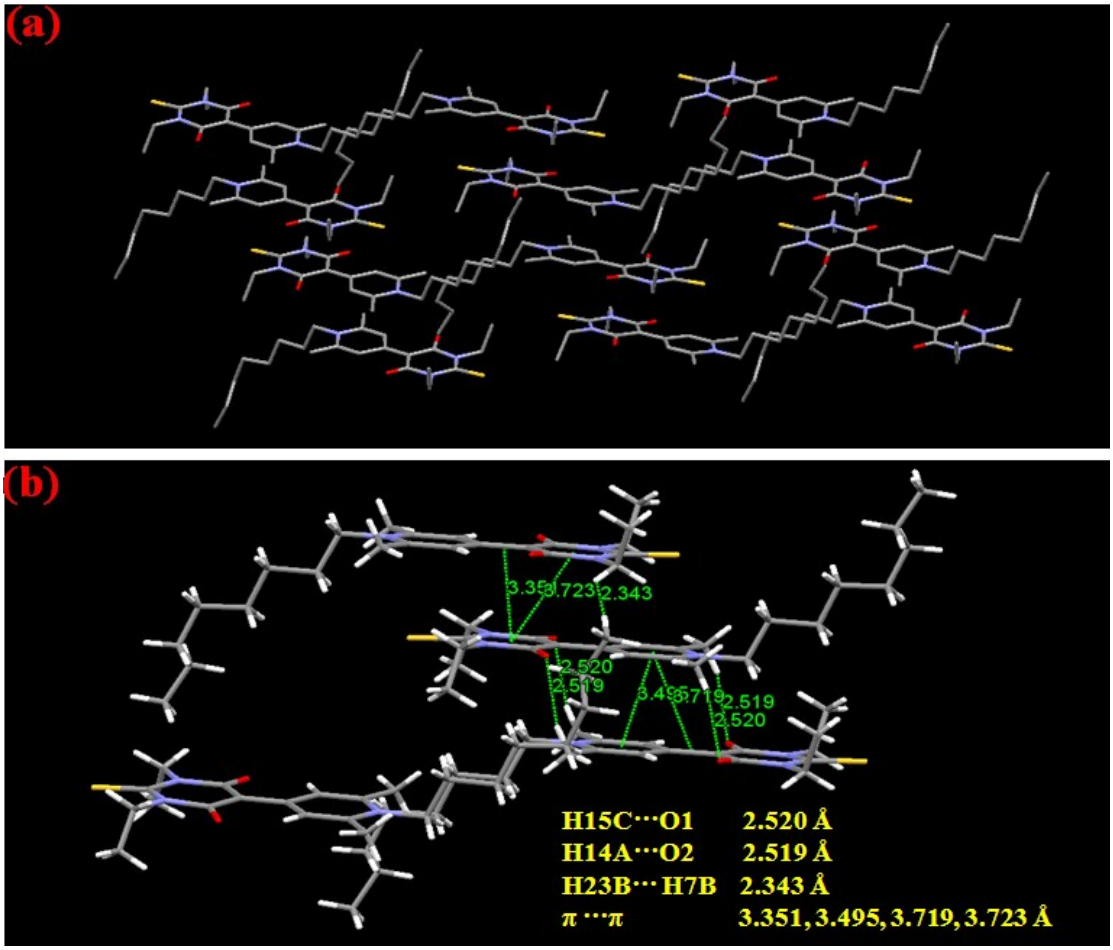


Fig. S30 (a) The packing motif in the crystal of **TDHP-C_8**. The hydrogen atoms have been omitted for clarity. (b) The schematic intermolecular interactions in the crystal of **TDHP-C_8**.

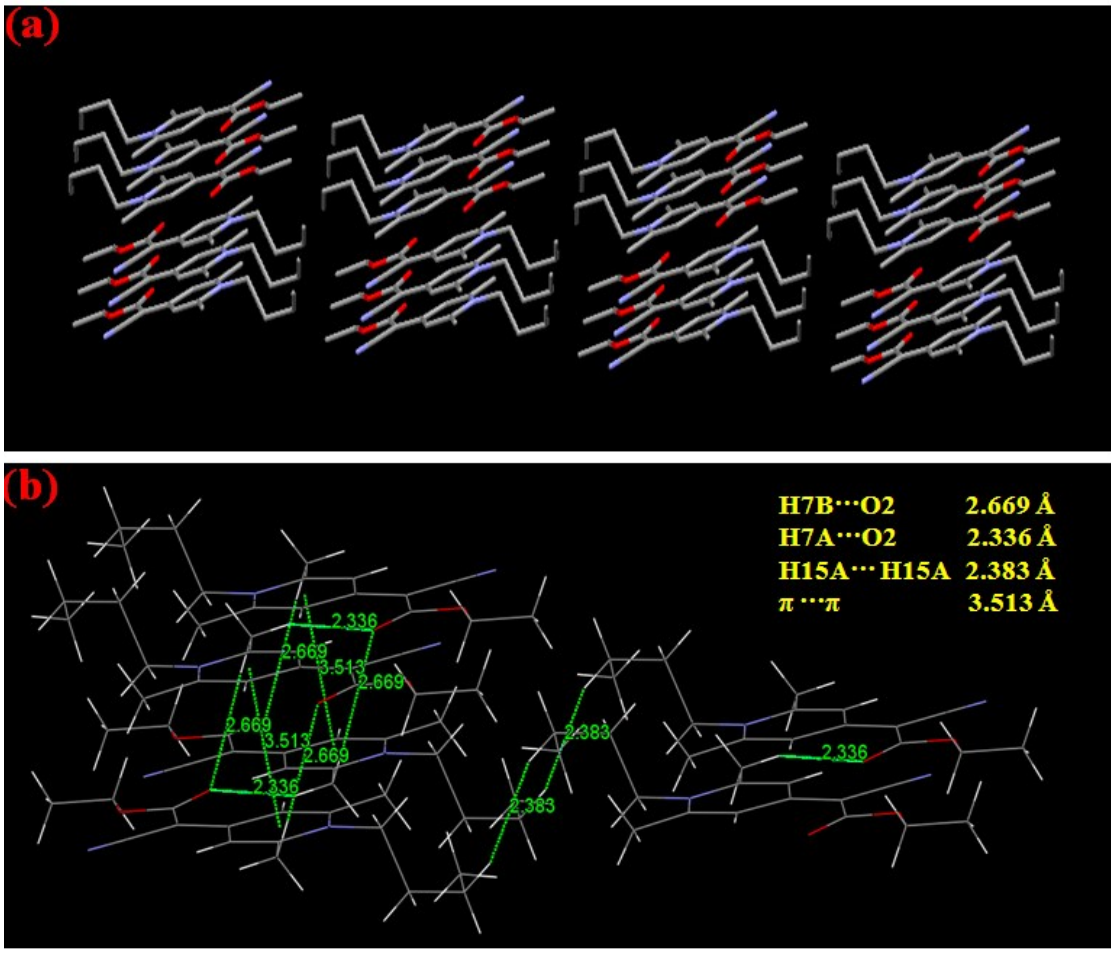


Fig. S31 (a) The packing motif in the crystal of **EDHP-C_4**. The hydrogen atoms have been omitted for clarity. (b) The schematic intermolecular interactions in the crystal of **EDHP-C_4**.

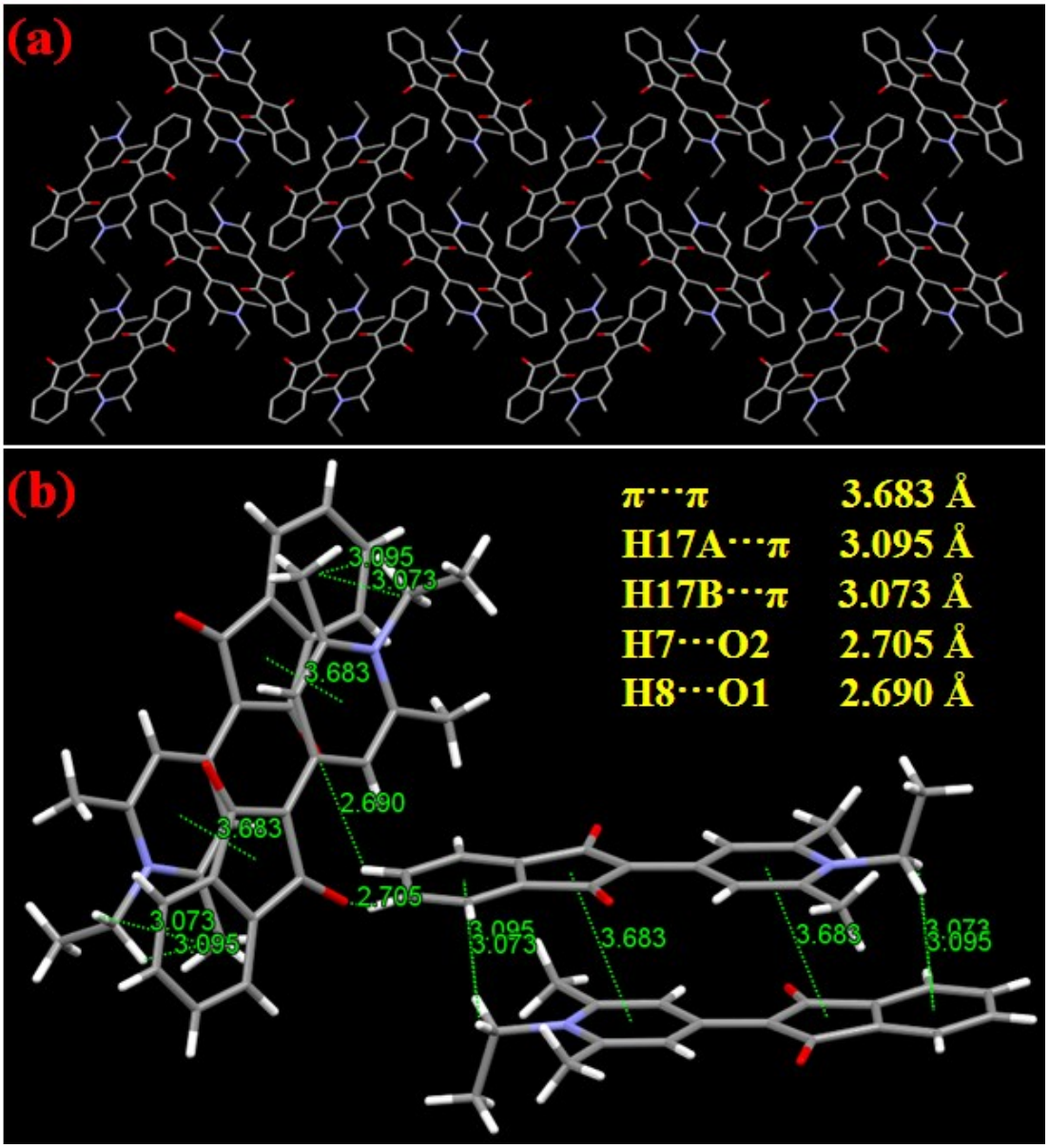


Fig. S32 (a) The packing motif in the crystal of **IDHP-C$_2$** viewed along the *a*-axis. The hydrogen atoms have been omitted for clarity. (b) The schematic intermolecular interactions in the crystal of **IDHP-C$_2$**.

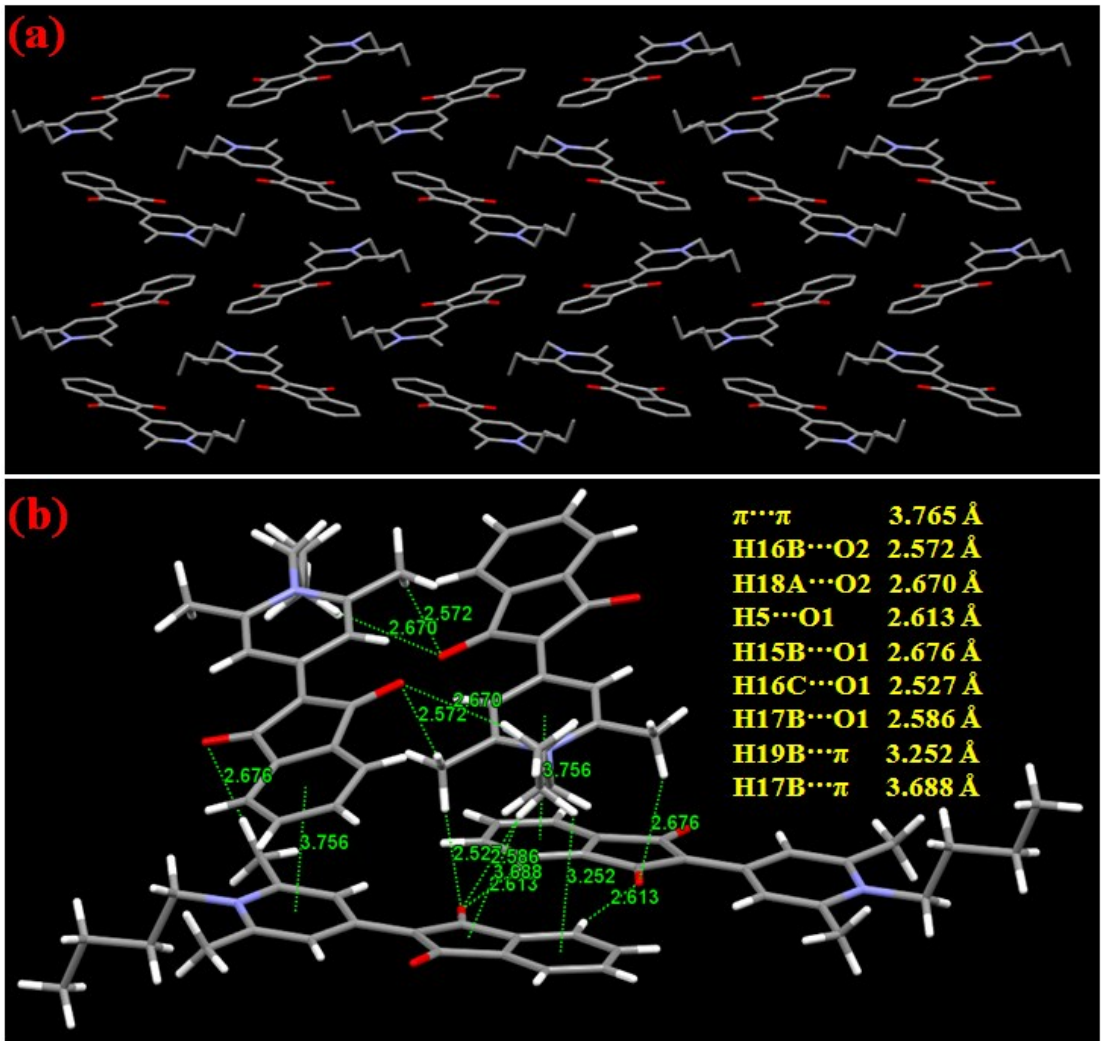


Fig. S33 (a) The packing motif in the crystal of **IDHP-C$_4$** viewed along the *a*-axis. The hydrogen atoms have been omitted for clarity. (b) The schematic intermolecular interactions in the crystal of **IDHP-C$_4$**.

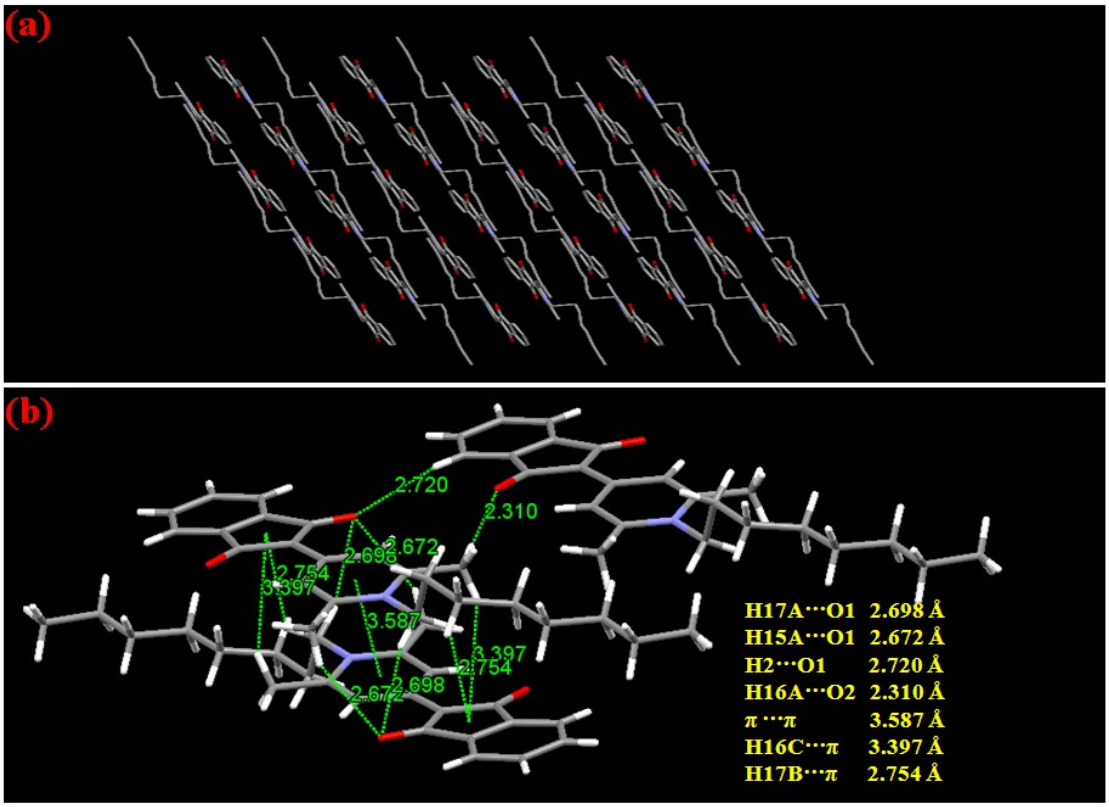


Fig. S34 (a) The packing motif in the crystal of **IDHP-C*8*** viewed along the *c*-axis. The hydrogen atoms have been omitted for clarity. (b) The schematic intermolecular interactions in the crystal of **IDHP-C*8***.

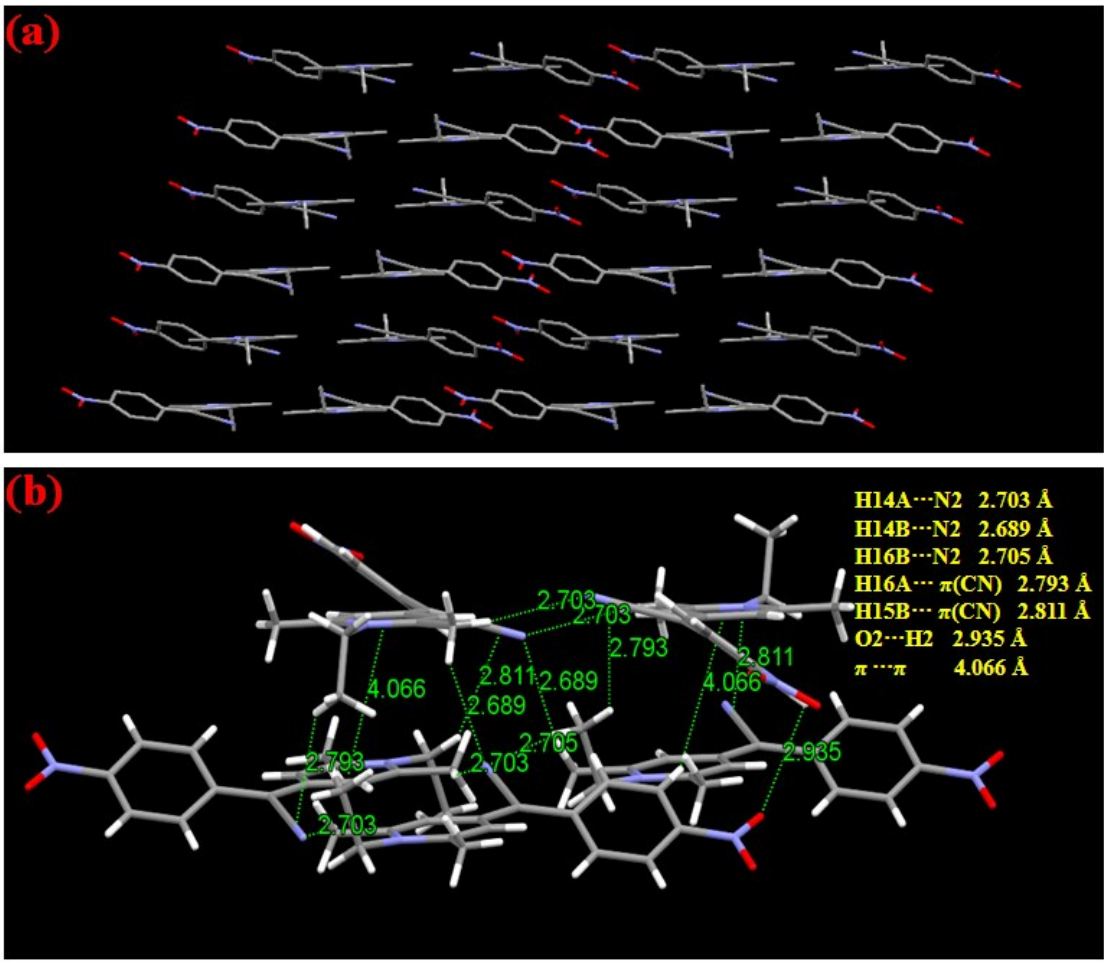


Fig. S35 (a) The packing motif in the crystal of **NDHP-C_2**. The hydrogen atoms have been omitted for clarity. (b) The schematic intermolecular interactions in the crystal of **NDHP-C_2**.

4. NMR of various compounds

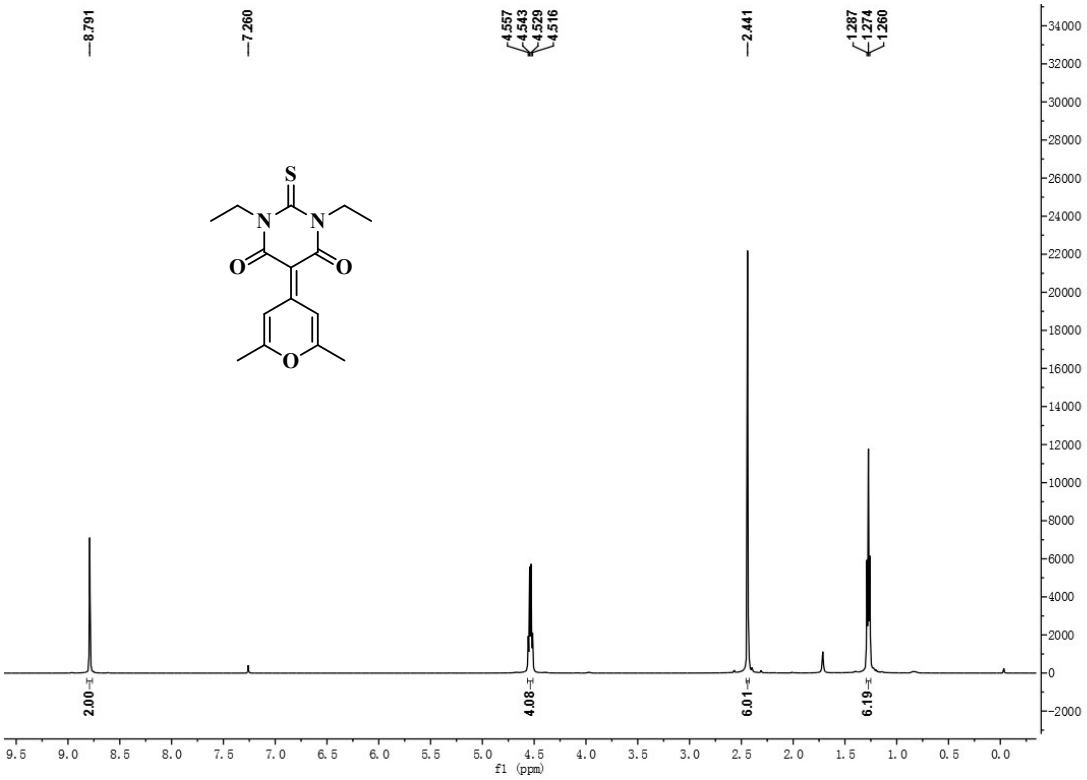


Fig. S36 ^{1}H NMR of **TP** ($CDCl_3$, 500 MHz).

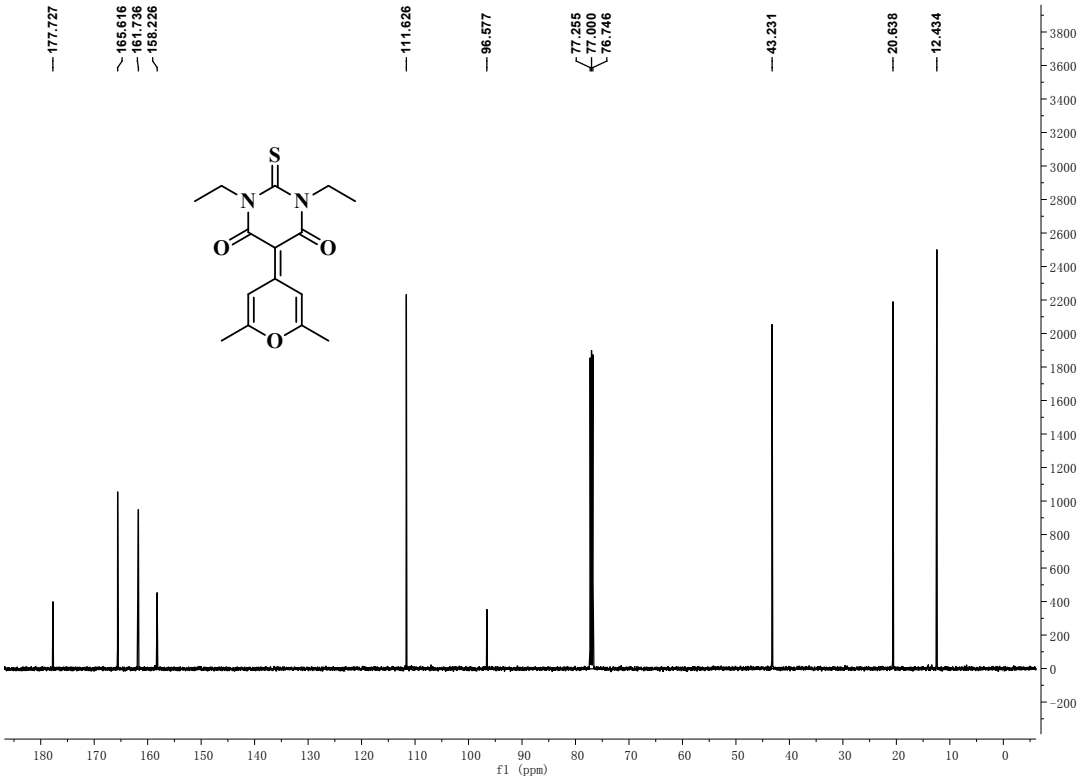


Fig. S37 ^{13}C NMR of **TP** ($CDCl_3$, 125 MHz).

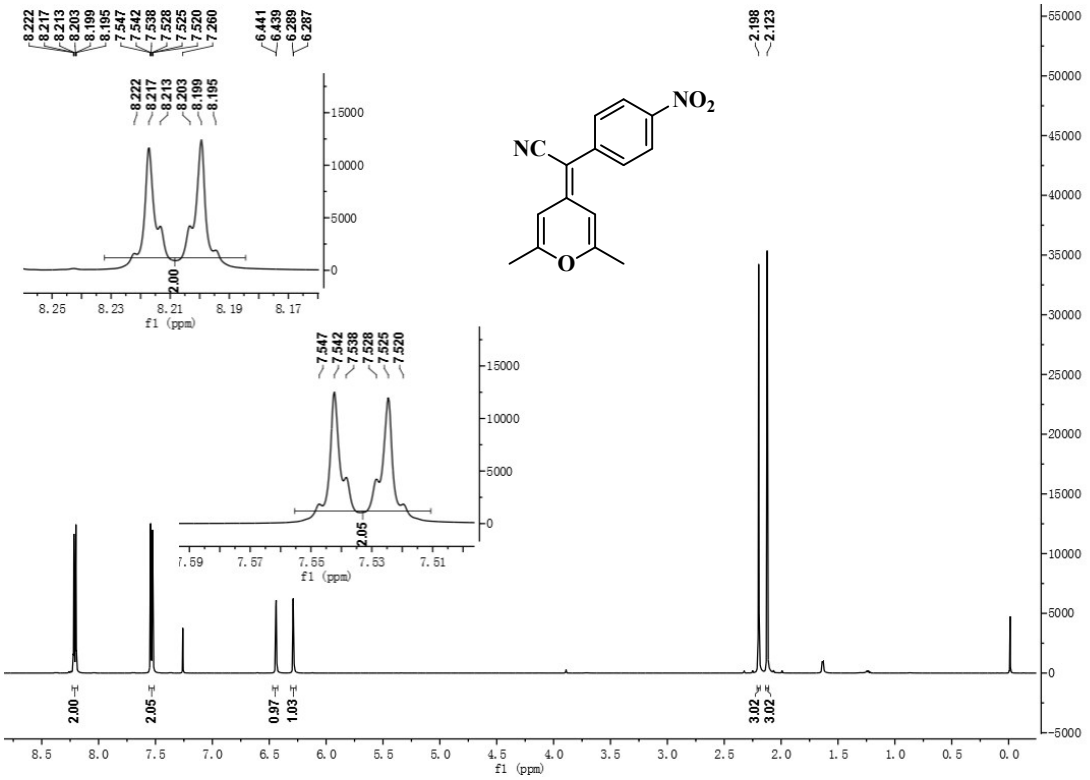


Fig. S38 ^{1}H NMR of **NP** ($CDCl_3$, 500 MHz).

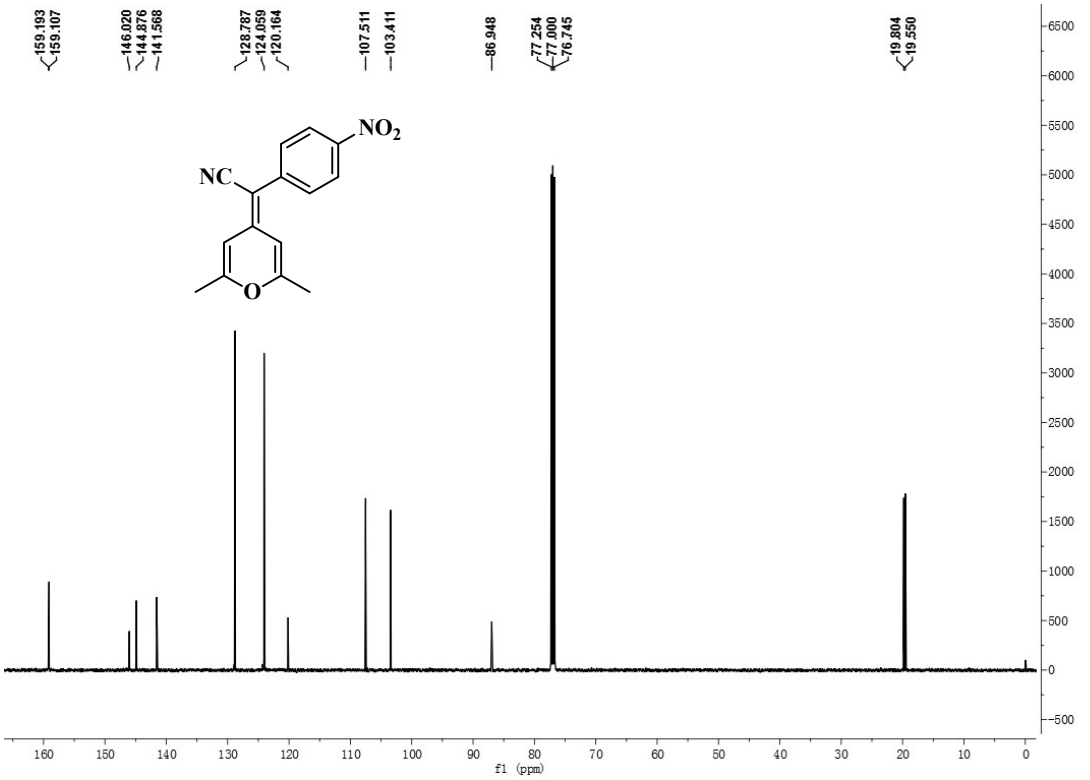


Fig. S39 ^{13}C NMR of **NP** ($CDCl_3$, 125 MHz).

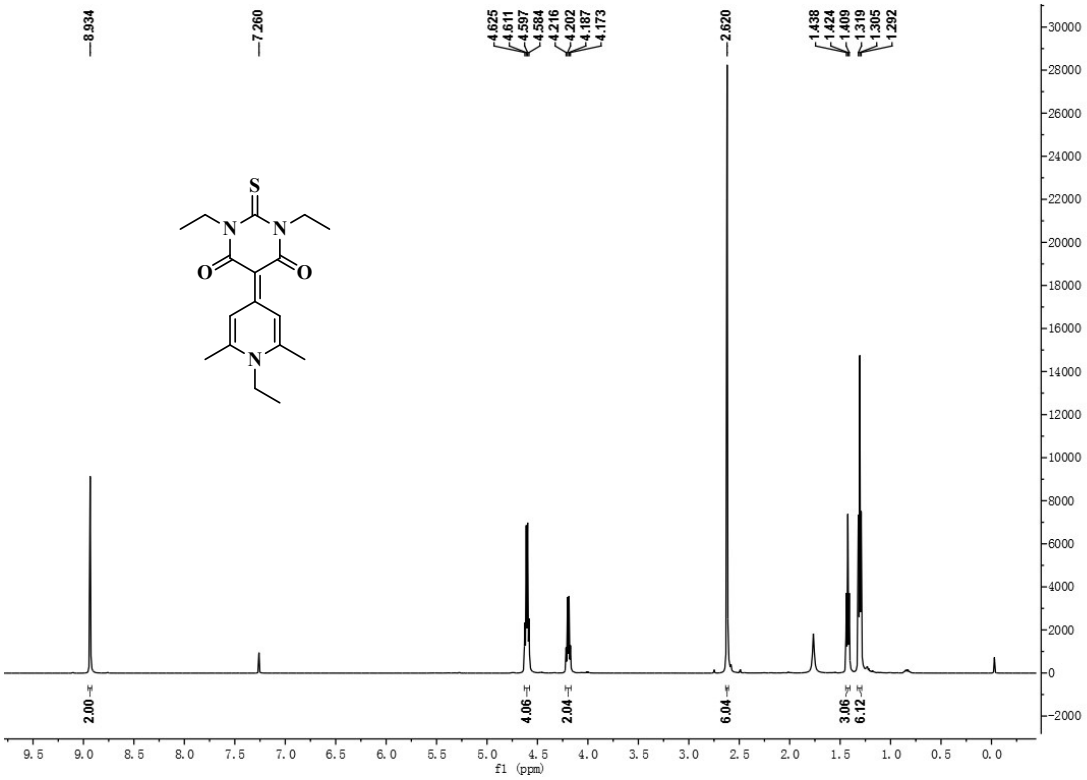


Fig. S40 ^{1}H NMR of **TDHP-C$_2$** ($CDCl_3$, 500 MHz).

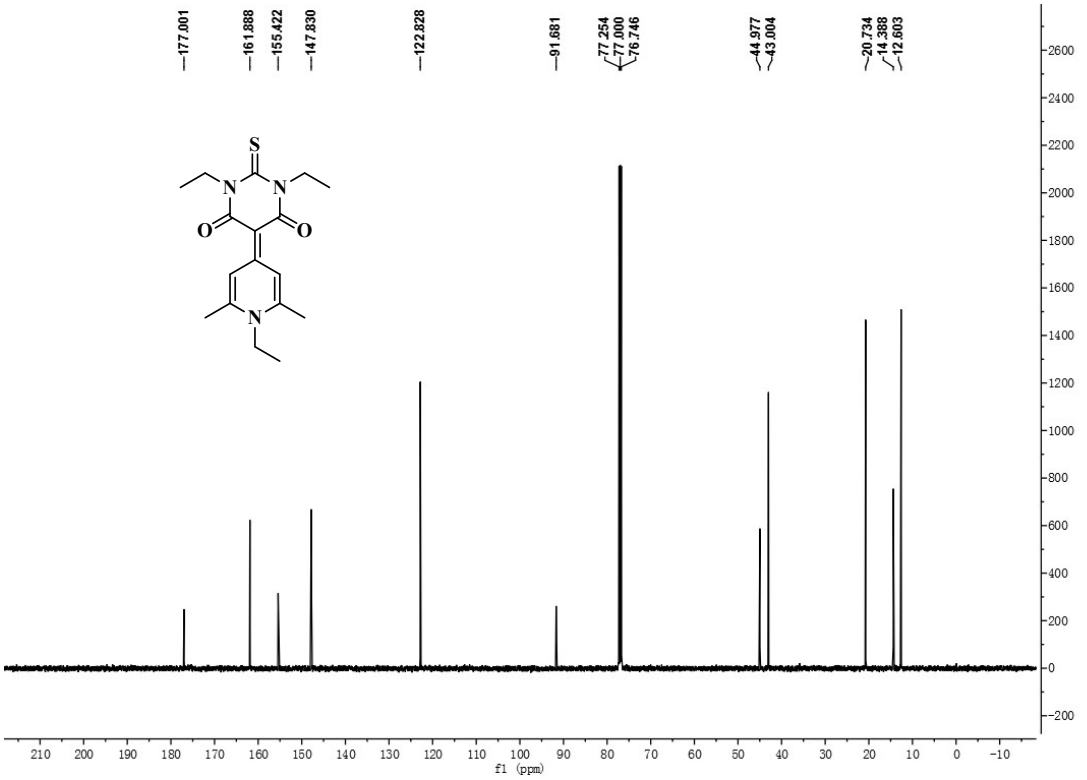


Fig. S41 ^{13}C NMR of **TDHP-C$_2$** ($CDCl_3$, 125 MHz).

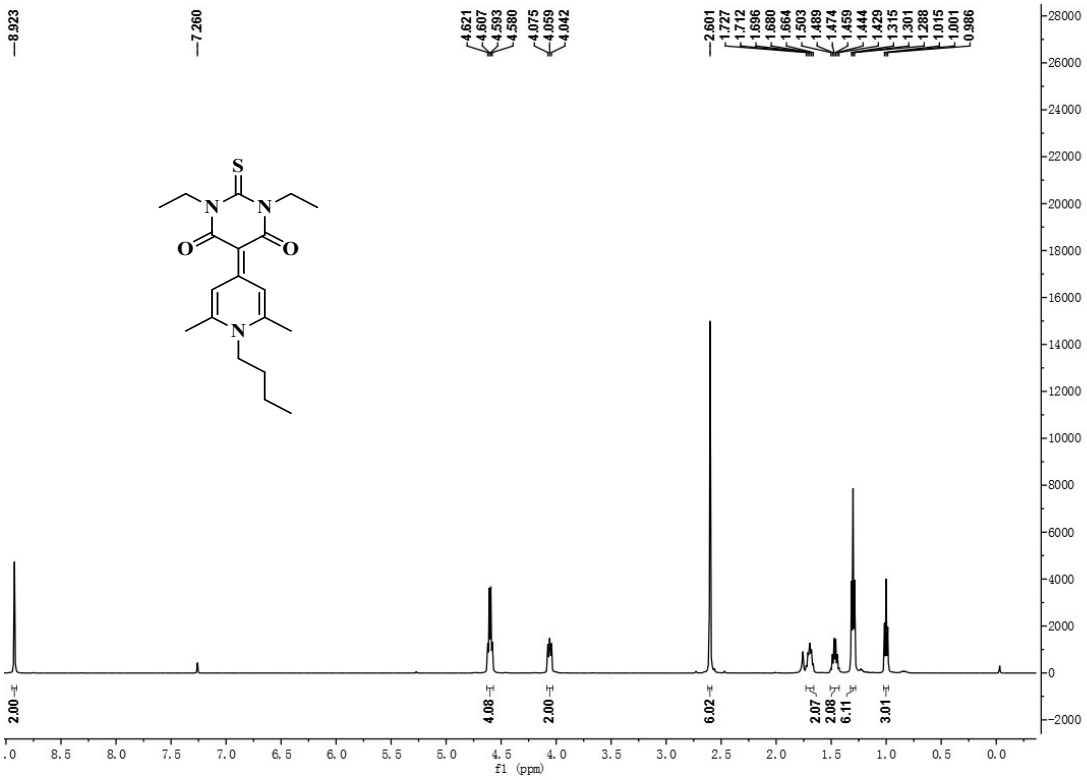


Fig. S42 ^{1}H NMR of **TDHP-C*4*** ($CDCl_3$, 500 MHz).

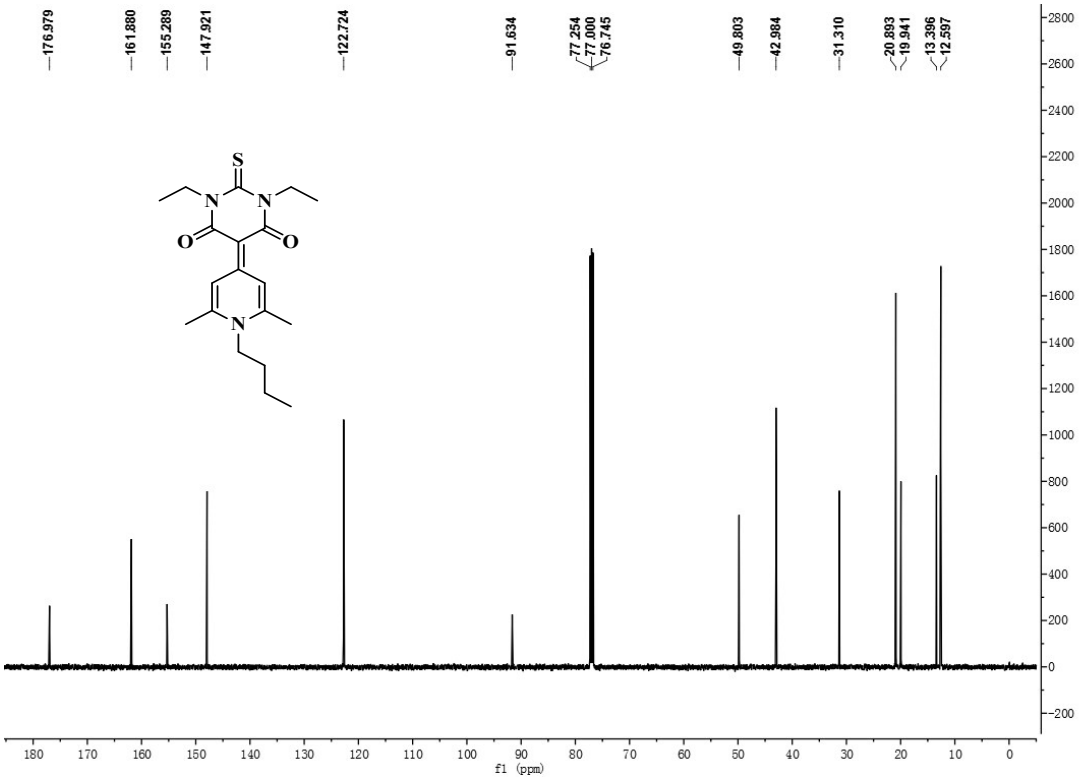


Fig. S43 ^{13}C NMR of **TDHP-C*4*** ($CDCl_3$, 125 MHz).

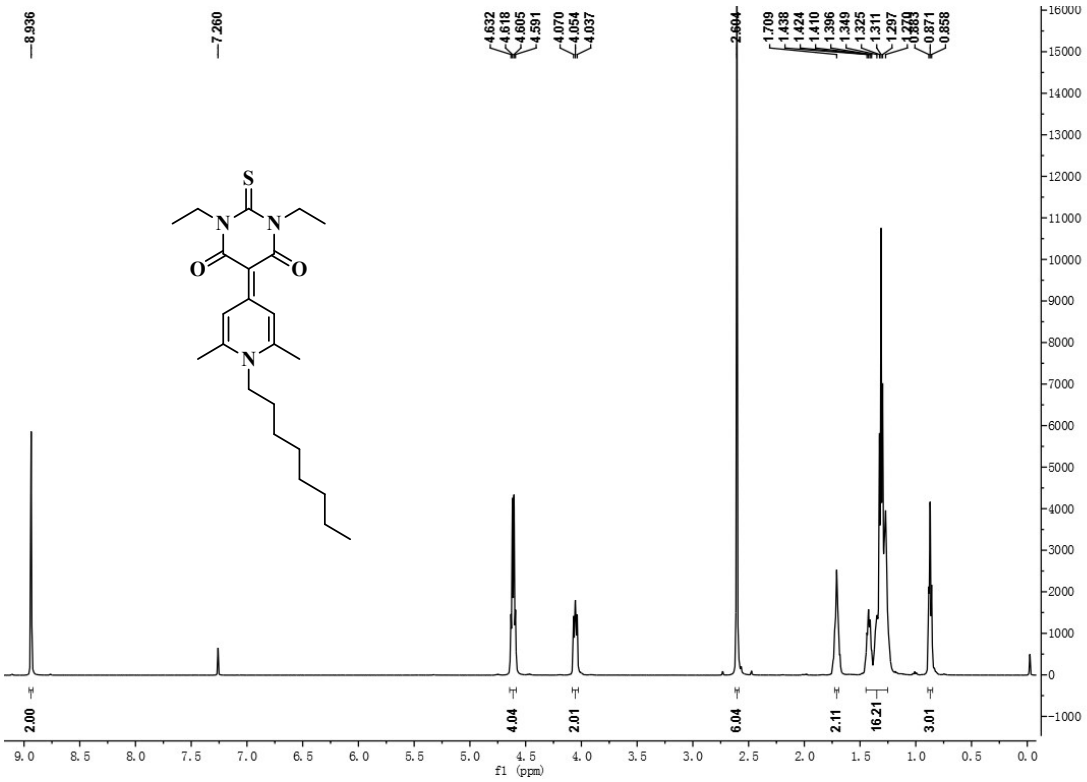


Fig. S44 ^{1}H NMR of **TDHP-C*8*** ($CDCl_3$, 500 MHz).

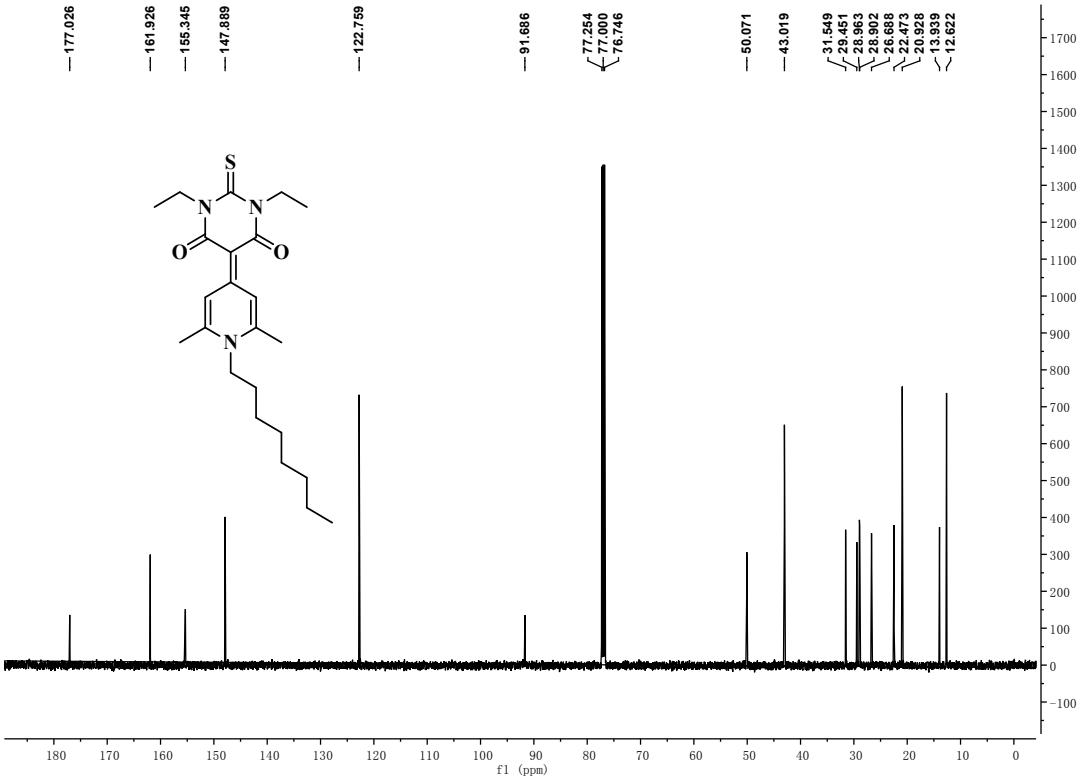


Fig. S45 ^{13}C NMR of **TDHP-C*8*** ($CDCl_3$, 125 MHz).

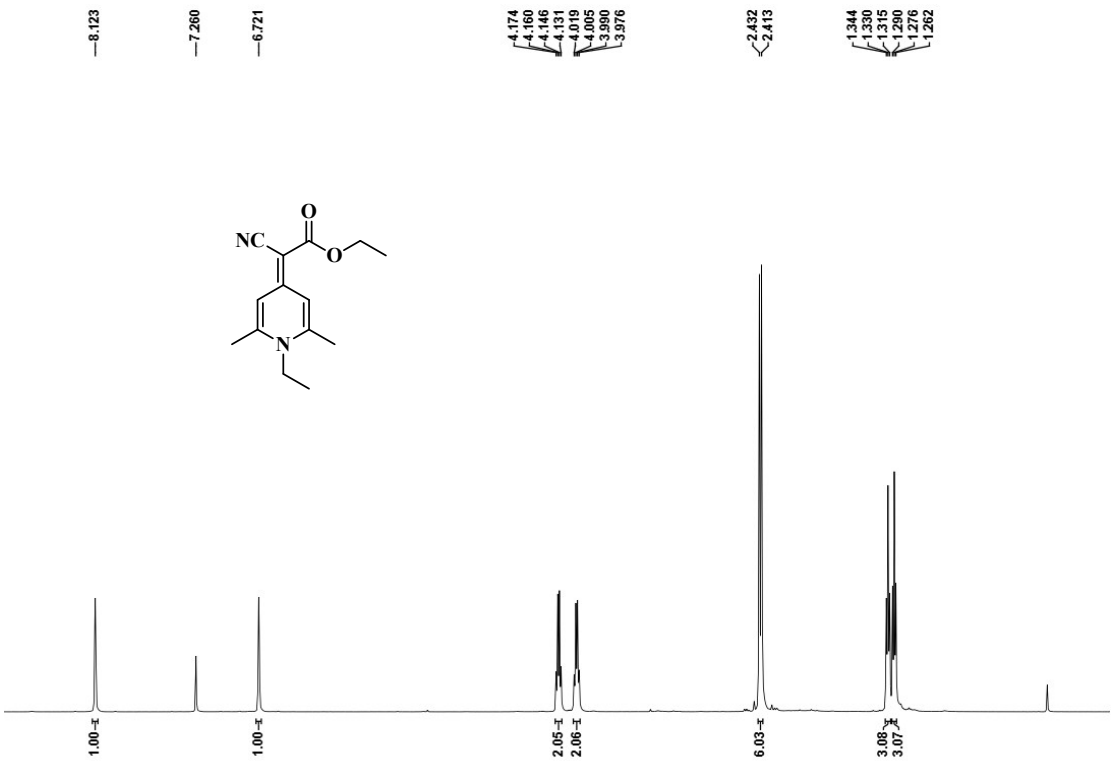


Fig. S46 ^{1}H NMR of **EDHP-C*2*** ($CDCl_3$, 500 MHz).

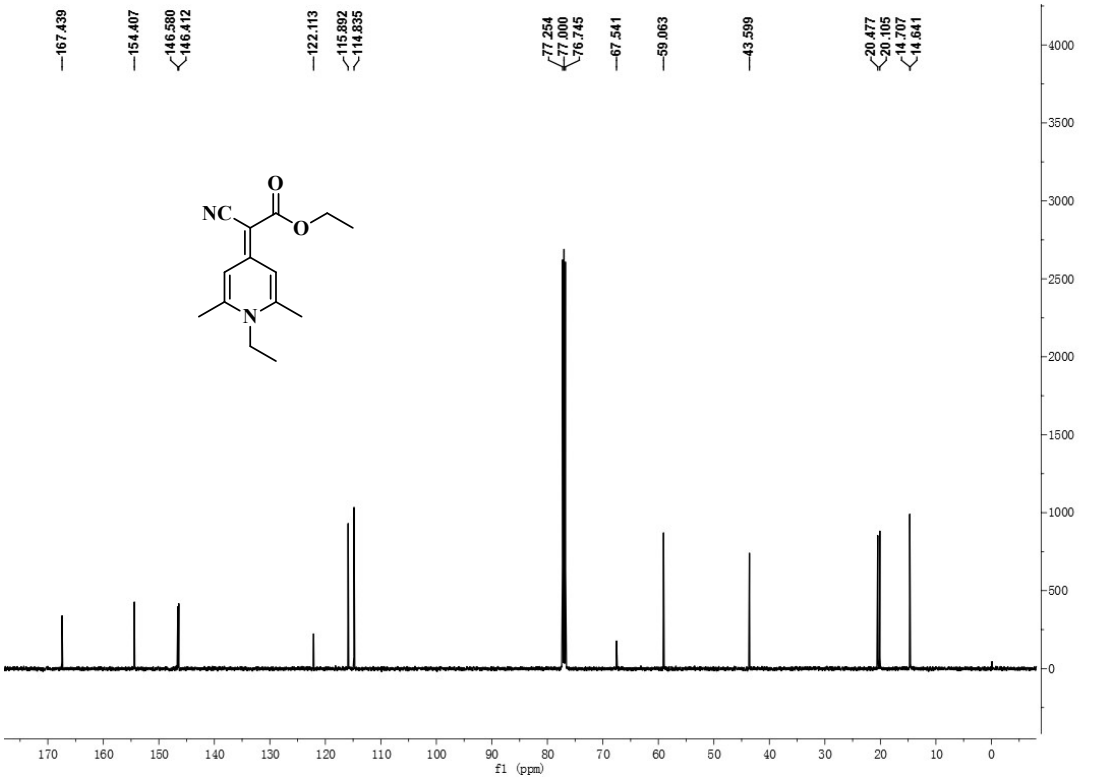


Fig. S47 ^{13}C NMR of **EDHP-C*2*** ($CDCl_3$, 125 MHz).

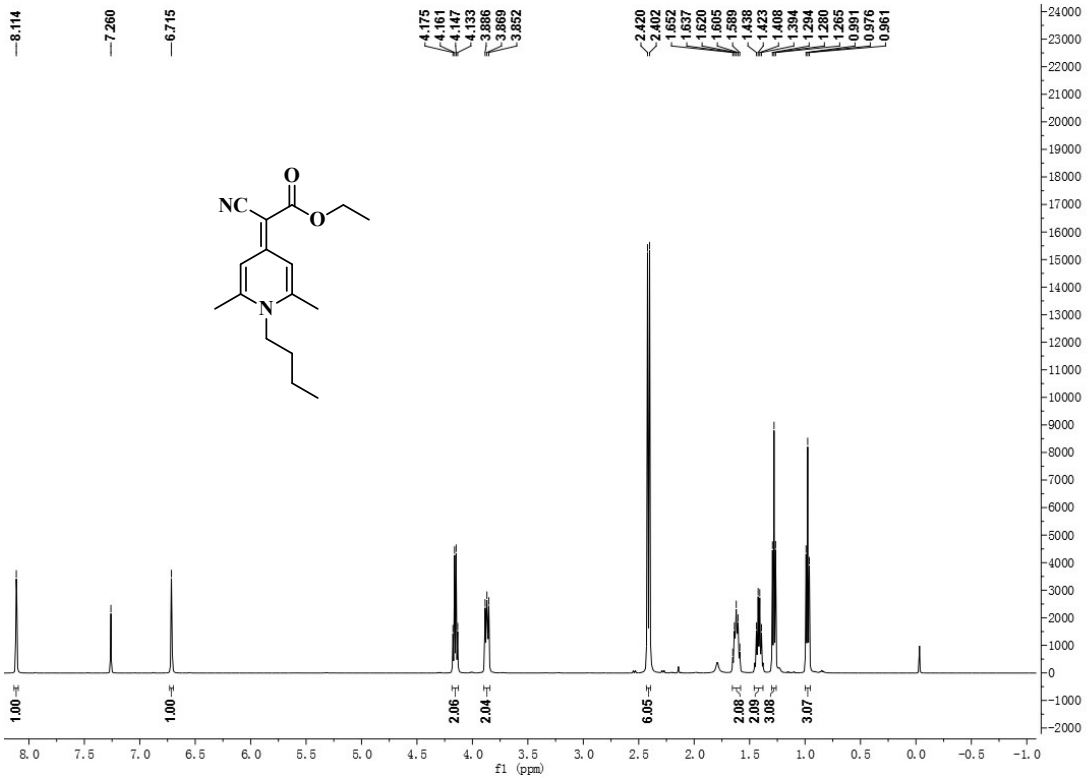


Fig. S48 ^{1}H NMR of **EDHP-C*4*** ($CDCl_3$, 500 MHz).

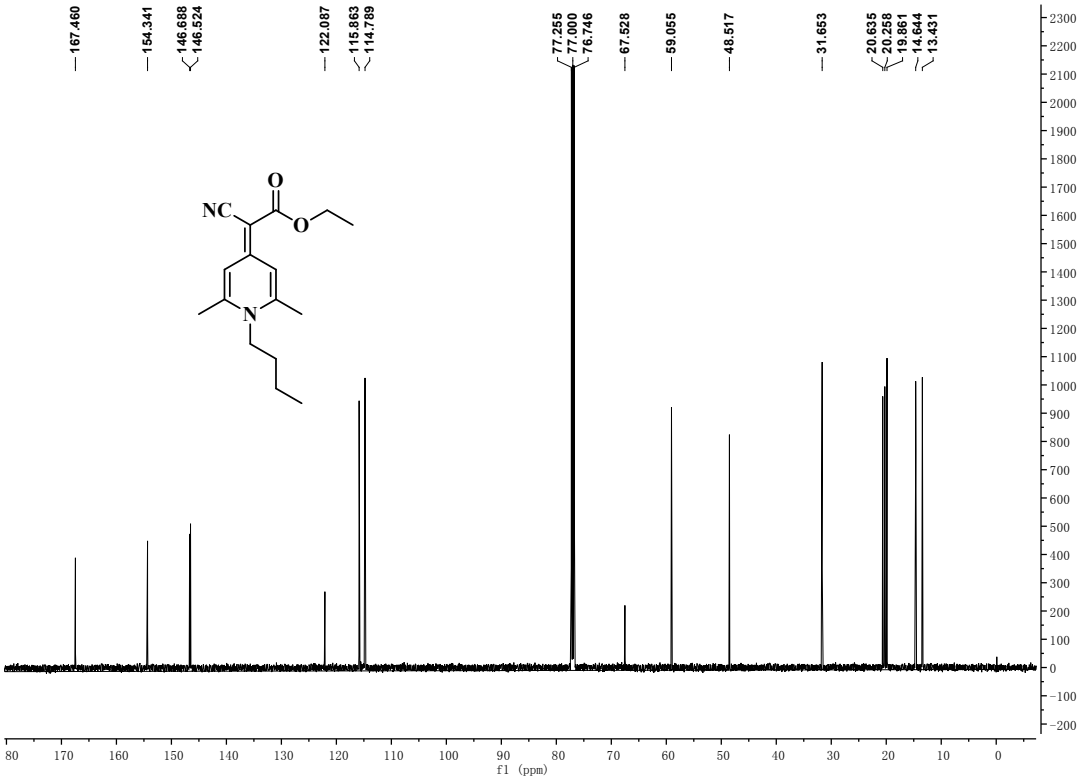


Fig. S49 ^{13}C NMR of **EDHP-C*4*** ($CDCl_3$, 125 MHz).

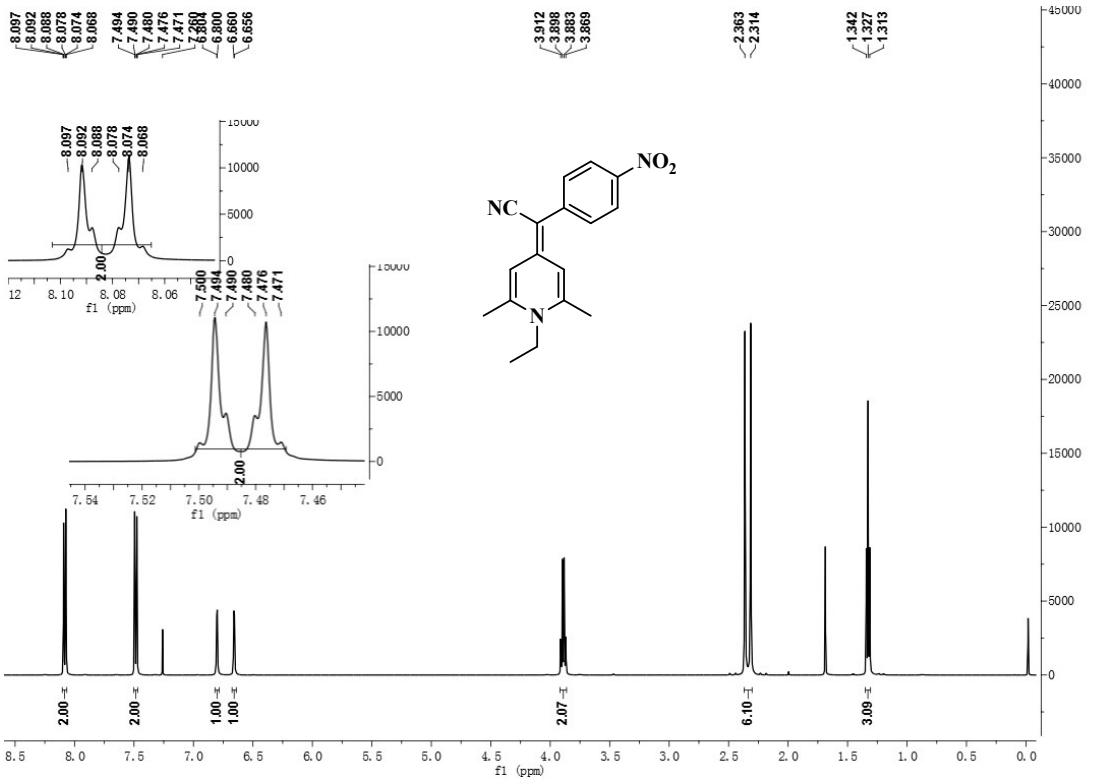


Fig. S50 ^{1}H NMR of **NDHP-C*2*** ($CDCl_3$, 500 MHz).

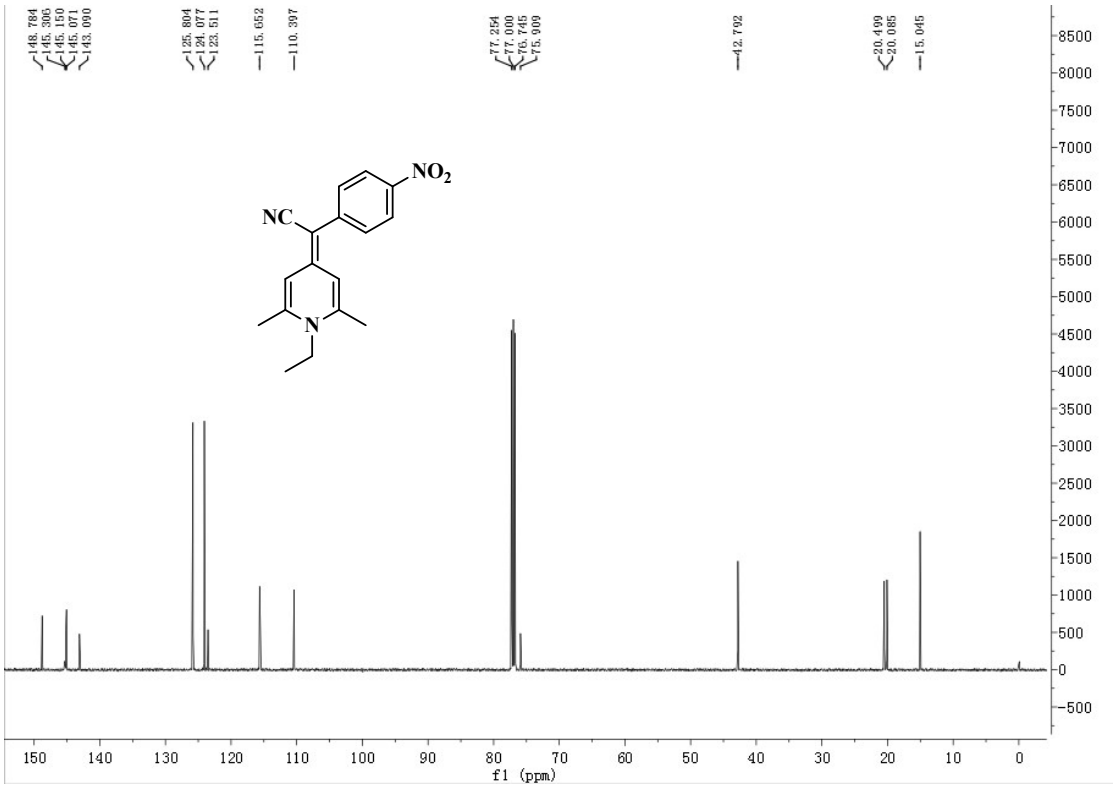


Fig. S51 ^{13}C NMR of **NDHP-C*2*** ($CDCl_3$, 125 MHz).

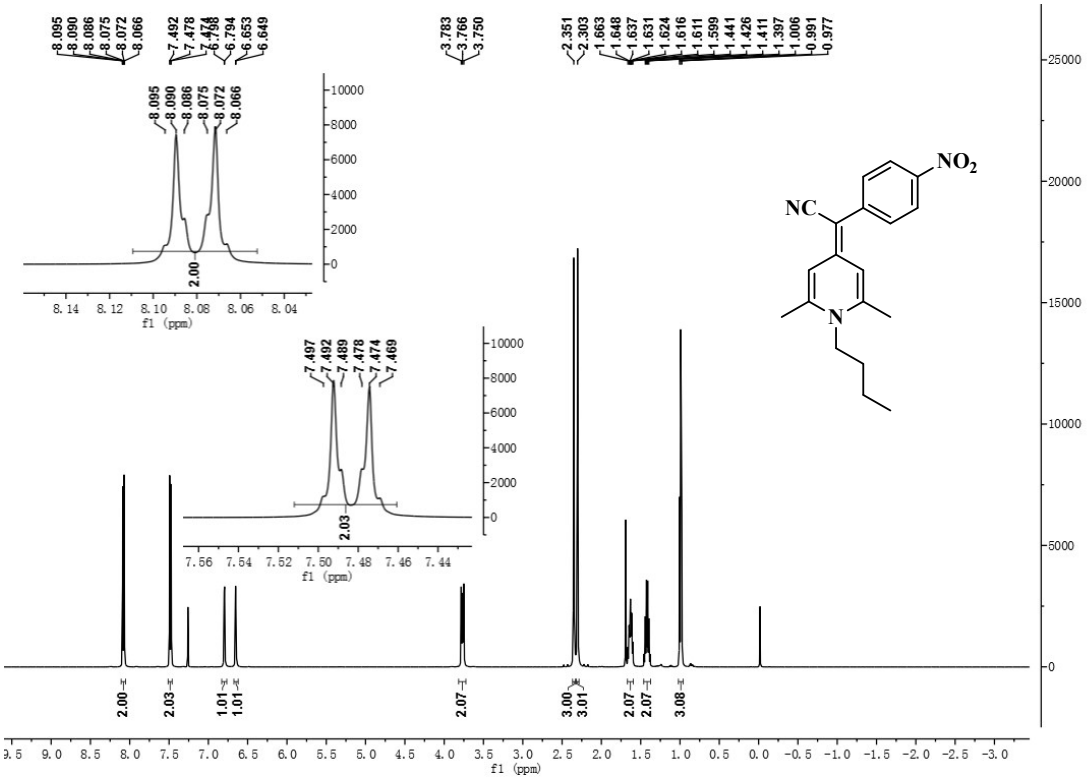


Fig. S52 ^{1}H NMR of **NDHP-C*4*** ($CDCl_3$, 500 MHz).

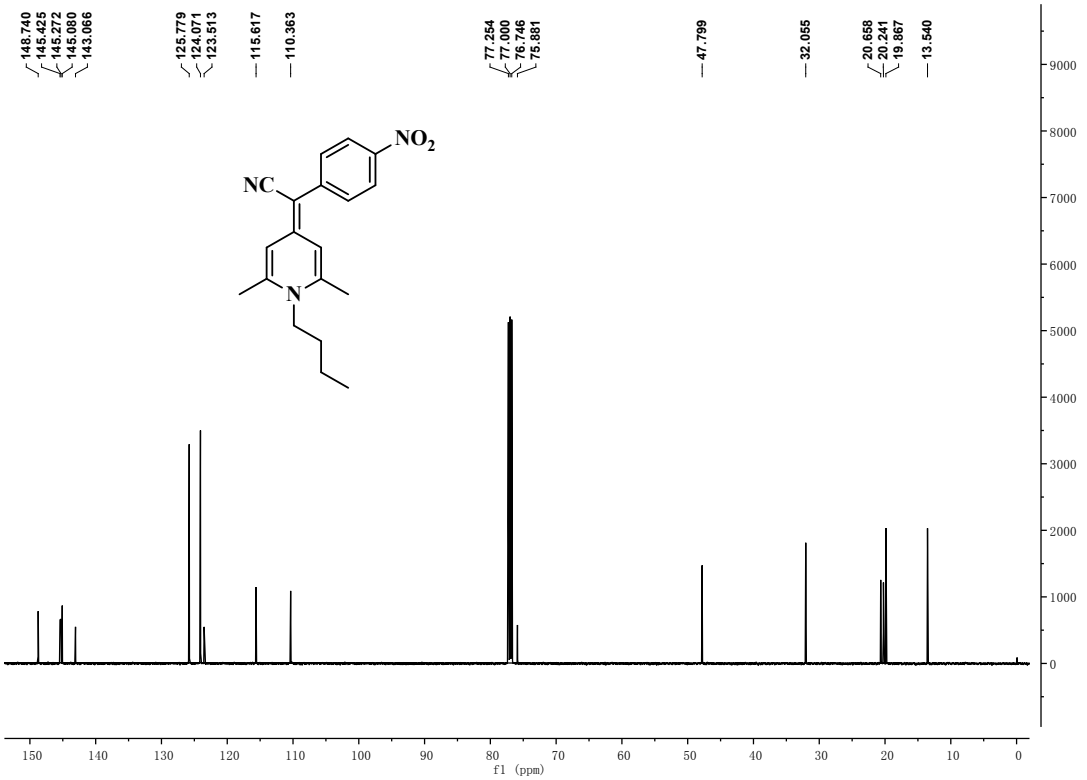


Fig. S53 ^{13}C NMR of **NDHP-C*4*** ($CDCl_3$, 125 MHz).

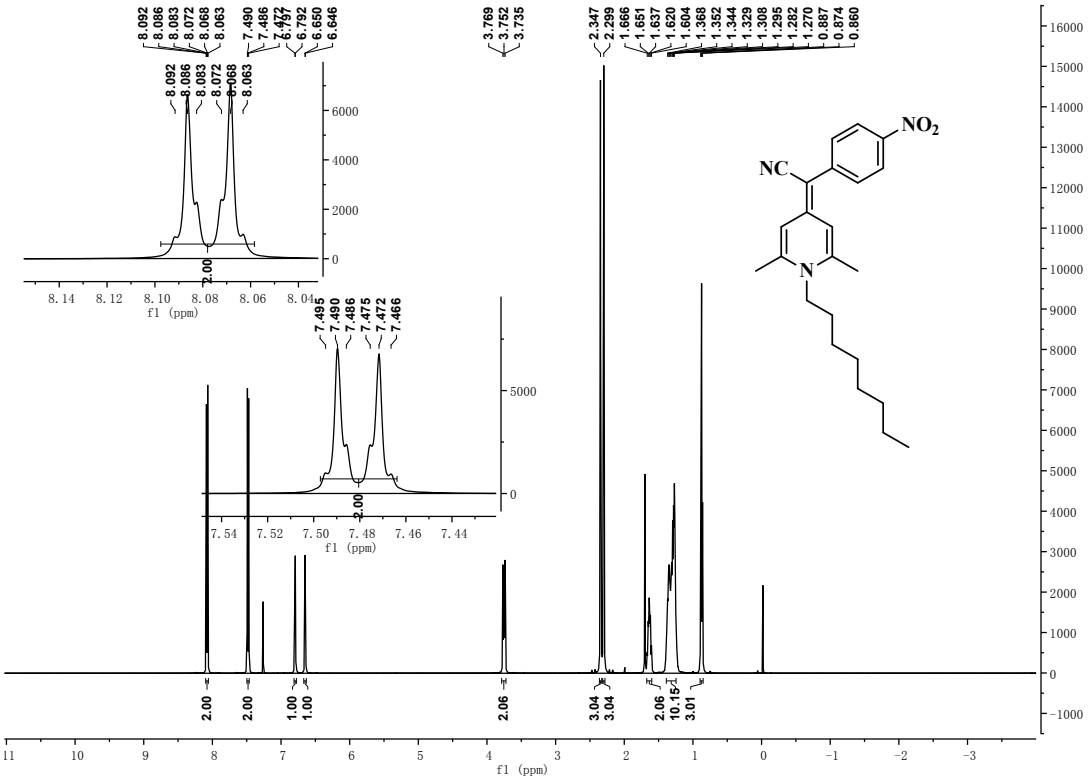


Fig. S54 ^{1}H NMR of **NDHP-C*8*** ($CDCl_3$, 500 MHz).

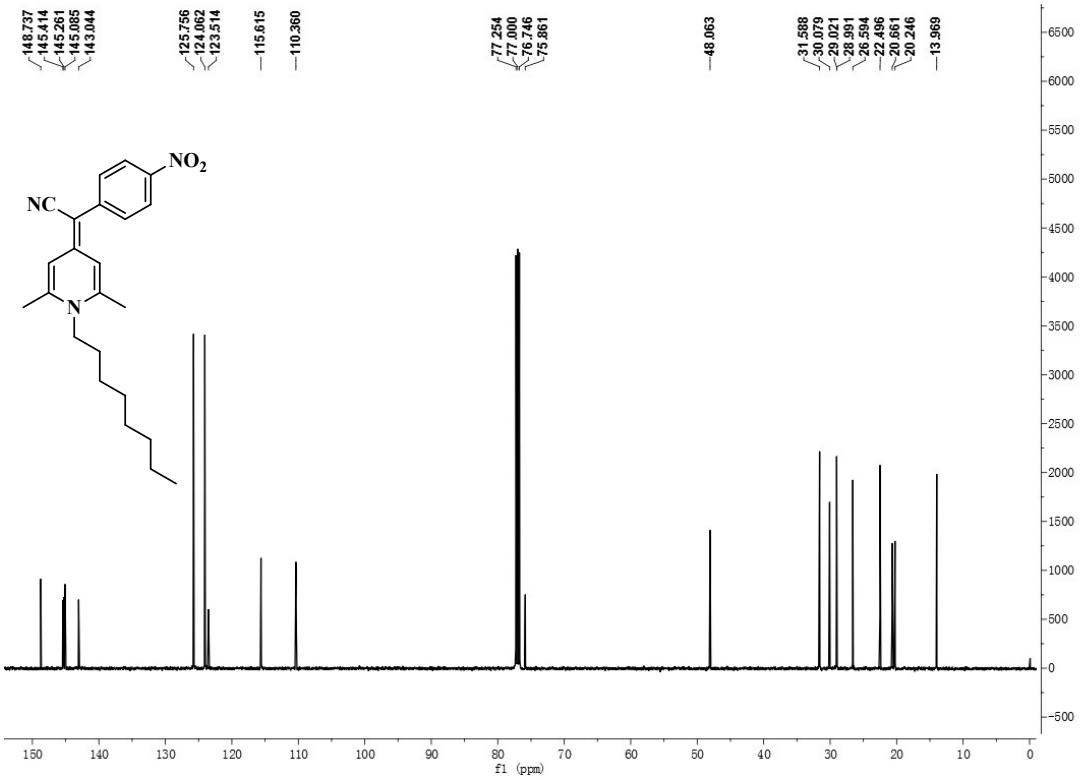


Fig. S55 ^{13}C NMR of **NDHP-C*8*** ($CDCl_3$, 125 MHz).