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Electronic Supplementary Information

Fluorescence from an H-aggregated Naphthalenediimide based peptide: Photophysical and Computational investigation of this Rare Phenomenon

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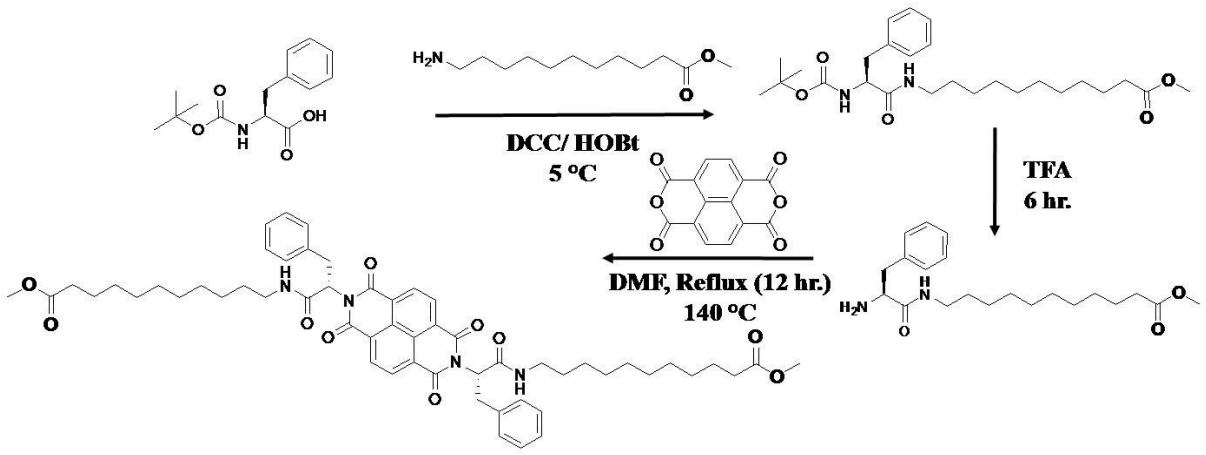
Materials:

L-Phenylalanine (Phe), 11-aminoundecanoic acid (Und) and 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NDA) were purchased from Aldrich. 1-Hydroxybenzotriazole (HOBt), *N*, *N*′-Dicyclohexylcarbodiimide (DCC) and all solvents were purchased from SRL, India.

Synthetic procedure:



Scheme S1. Chemical structure and synthesis of the peptide **1.**

Boc-Phe-OH: A solution of phenylalanine (1.65 g, 10 mmol) in a mixture of dioxane (20 ml), water (10 ml) and 1N NaOH (10 ml) was stirred and cooled in an ice-water bath. Ditertbutylpyrocarbonate (2.39 g, 11 mmol) was added and stirring was continued at room temperature for 6h. Then the solution was concentrated in vacuum to about 20 ml to 30 ml, cooled in an ice water bath, covered with a layer of ethyl acetate (about 50 ml) and acidified with a dilute solution of $KHSO_4$ to pH 2-3 (Congo red). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na_2SO_4 and evaporated in vacuum. A white material was obtained. Yield: 2.3 g, (8.6 mmol, 86 %).

Boc-Phe-Und-OMe: 2.3 g (8.6 mmol) of Boc-Phe-COOH was dissolved in 10 ml of DMF in an ice water bath. H-Und-OMe was isolated from 4.7 g (20 mmol) of the corresponding methyl ester hydrochloride by neutralization and subsequent extraction with ethyl acetate and ethyl acetate extract was concentrated to 10 ml. It was then added to the reaction mixture, followed immediately by 1.85 g (9 mmol) DCC and 1.37 g (9 mmol) of HOBt. The reaction mixture was allowed to come to room temperature and stirred for 3 days. The residue was taken up in ethyl acetate (40 ml) and dicyclohexylurea (DCU) was filtered off. The organic layer was washed with 1N HCl (3 × 30 ml),

brine (1 × 30 ml), 1M sodium carbonate (3 × 30 ml) and brine (2 × 30 ml) and dried over anhydrous Na_2SO_4 and evaporated in vacuum. A white material was obtained. Yield: 2.4 g (5.2 mmol, 60.4 %).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.30-7.19 (5H, aromatic Hs, m), 5.66 (1H, NH, br), 5.11 (1H, NH, br), 4.26-4.24 (1H, $^{\alpha}$H, m), 3.66 (3H, OCH_3, s), 3.14-2.99 (4H, $^{\beta}$Hs and $^{\alpha}CH_2$, m), 2.31-2.28 (2H, $^{\alpha}CH_2$, t, J = 7.5), 1.64-1.58 (2H, $^{\beta}CH_2$, m), 1.41(9H, Boc, s), 1.33-1.15 (14H, CH_2, m). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 174.44, 171.06, 137.05, 129.46, 128.78, 127.04, 111.67, 56.29, 51.56, 39.61, 38.95, 34.25, 33.75, 29.52, 29.47, 29.33, 29.25, 28.43, 26.88, 25.07. HRMS (m/z): 485.3493 $[M+Na]^+$, 501.3396 $[M+K]^+$.

NH_2-Phe-Und-OMe: To 2.4 g (5.2 mmol) of Boc-Phe-Und-OMe, 4 ml of trifluoroacetic acid (TFA) was added and removal of Boc group was monitored by TLC. After 8 h, TFA was removed under *vacuum*. The residue was taken in water (20 ml) and covered with ethyl acetate (about 50 ml) and basified with a solution of $NaHCO_3$. The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na_2SO_4 and evaporated in *vacuum*. A white material was obtained. Yield: 1.08 g (3.0 mmol, 57.6 %).

^{1}H NMR (500 MHz, DMSO-D_6, 25 °C): δ 7.75-7.73 (1H, NH, t, J = 5.5), 7.27-7.16 (5H, aromatic Hs, m), 3.57 (3H, OCH_3, s), 3.35-3.32 (3H, $^{\alpha}$H and NH_2, m) 3.04-2.86 (4H, $^{\beta}$Hs and $^{\alpha}CH_2$, m), 2.29-2.26 (2H, $^{\alpha}CH_2$, t, J = 7.5), 1.62 (2H, $^{\beta}CH_2$, br), 1.52-1.49 (2H, $^{\beta}CH_2$, m), 1.35-1.16 (12H, CH_2, m). ^{13}C NMR (125 MHz, DMSO-D_6, 25 °C): δ 173.96, 173.27, 138.74, 129.20, 127.94, 125.92, 56.26, 51.06, 41.29, 38.23, 33.22, 29.01, 28.83, 28.75, 28.66, 28.59, 28.39, 26.27, 25.27, 24.36. HRMS (m/z): 363.0826 $[M+H]^+$.

OMe-Und-Phe-NDI-Phe-Und-OMe (1): NH_2-Phe-Und-OMe (0.43 g, 1.20 mmol) and NDA (0.130 g, 0.5 mmol) were placed in a round-bottomed flask along with dry DMF (15 ml) and the reaction mixture was stirred for 12 h at 140 °C under N_2 atmosphere. The heating was stopped and the solution was allowed to cool to room temperature and poured over cold water. A precipitate was appeared. The precipitate was washed with 1N HCl (3 × 30 ml), cold water (3 × 30 ml) and dried in air. The product was further purified by column chromatography by using silica gel as stationary phase and $CHCl_3$ as eluent. Yield: 0.15 g (0.16 mmol, 32 %).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 (4H, NDI, s), 7.26-7.07 (10H, aromatic Hs, m), 5.99-5.95 (2H, NH, t, J = 7.8), 5.86 (2H, $^{\alpha}$H, m), 3.67-3.47 (7H, OCH_3, $^{\beta}$Hs, m), 3.27-3.23 (4H, $^{\alpha}CH_2$, m), 2.30-2.26 (4H, $^{\alpha}CH_2$, t, J = 7.6), 1.61-1.56 (4H, $^{\beta}CH_2$, m), 1.46-1.43(4H, $^{\beta}CH_2$, m), 1.33-1.24 (24H, CH_2, m). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.44, 168.31, 162.80, 136.97, 131.26, 129.04, 128.91, 127.22,

126.77, 126.50, 56.21, 51.54, 40.13, 35.07, 34.22, 32.05, 31.76, 29.81, 29.74, 29.63, 29.52, 29.48, 29.43, 29.31, 29.23, 26.91, 25.06, 22.81, 14.22. MALDITOF MS: 979.725 $[M+Na]^+$.

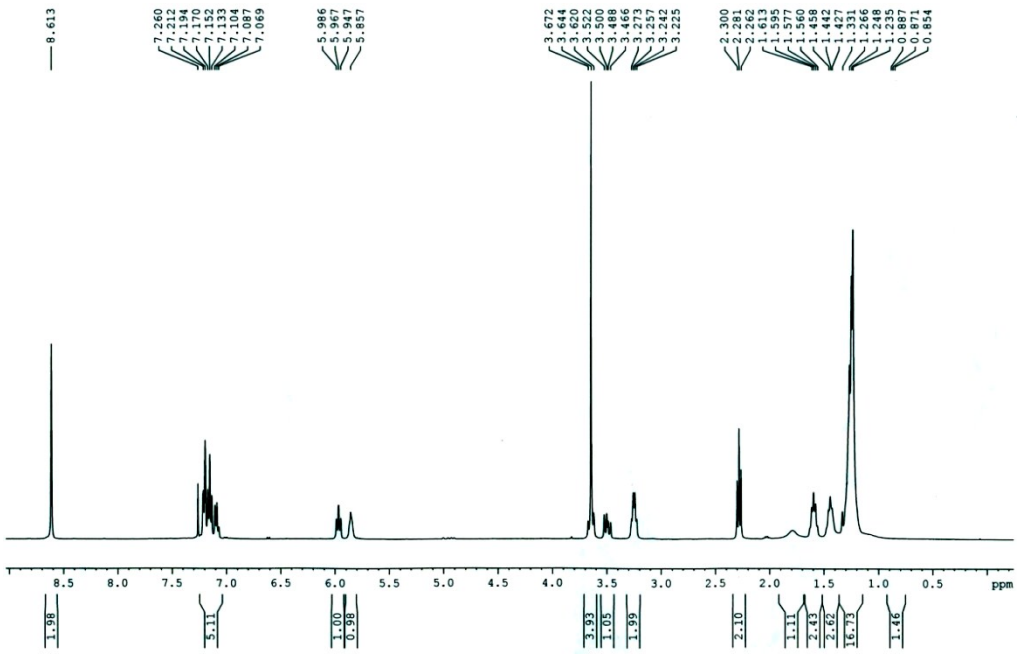


Fig. S1. ^1H NMR spectrum in $CDCl_3$ of **1** recorded in 500 MHz.

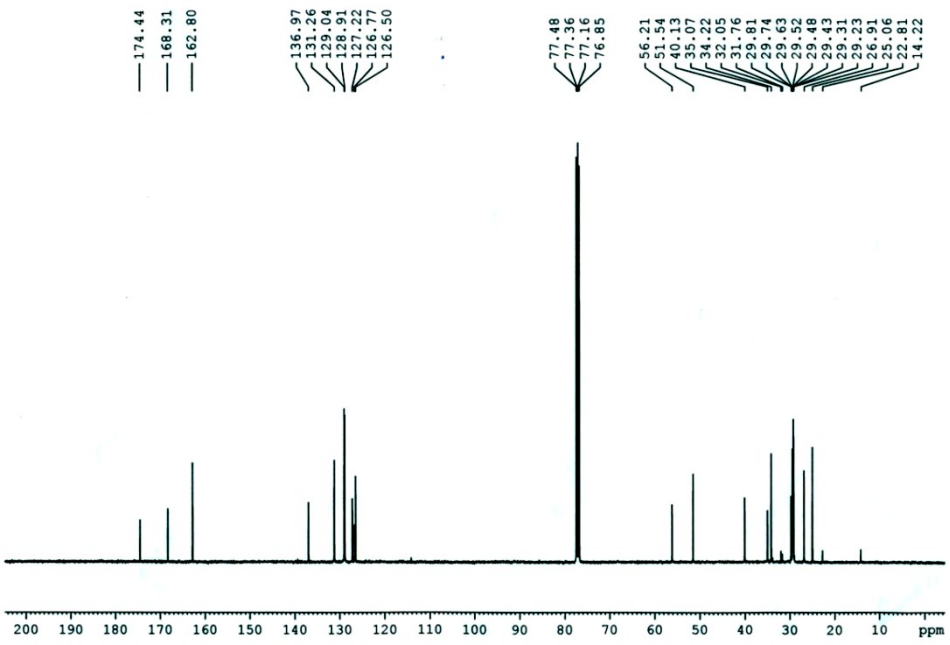


Fig. S2. ^{13}C NMR spectrum in $CDCl_3$ of **1** recorded in 125 MHz.

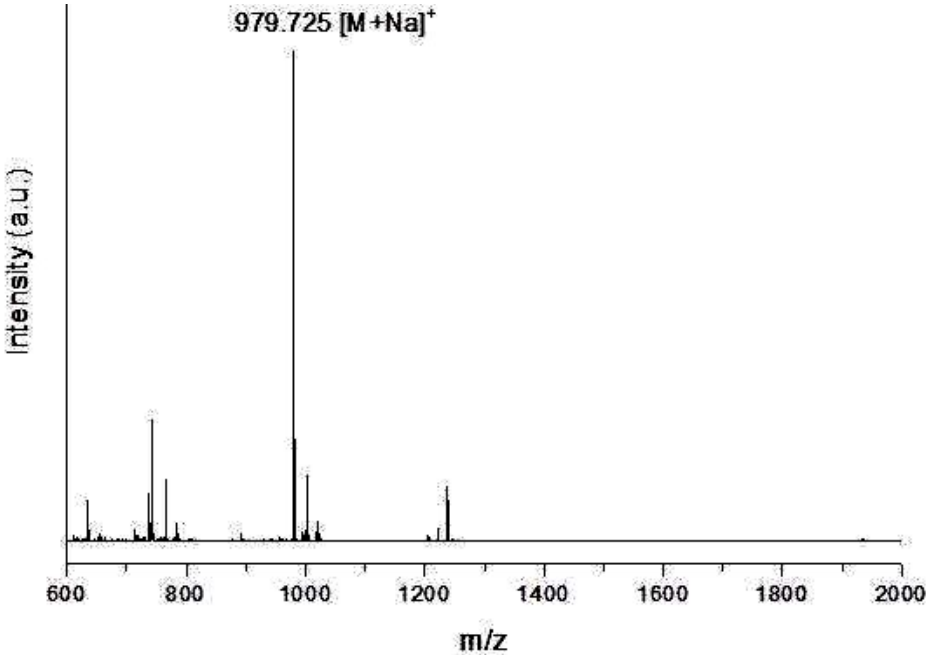


Fig. S3. MALDI-TOF MS spectra of **1**.

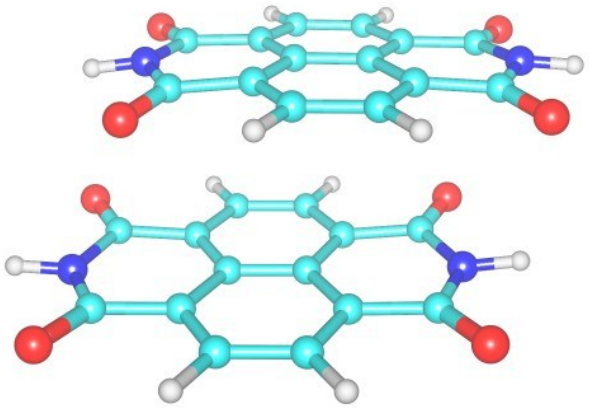


Fig. S4. Slipped parallel arrangement of NDI molecules (the alkyl groups are substituted by H).

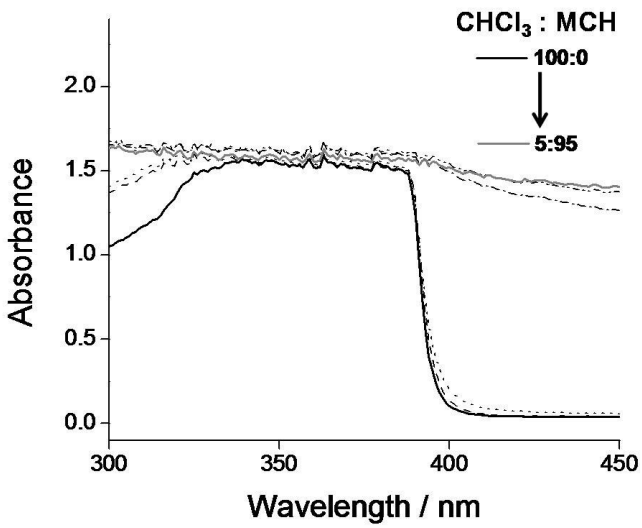


Fig. S5. The UV-vis spectra of peptide **1** in different composition of $CHCl_3$ and MCH at 0.2 mM concentration.

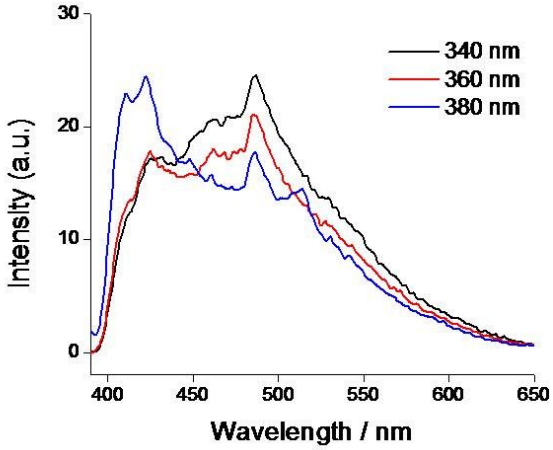


Fig. S6. The fluorescence spectra of peptide **1** solution ($CHCl_3$: MCH, 10:90) excited at 340 nm (black line), 360 nm (red line) and 380 nm (blue line).

Cartesian Coordinates for Optimized model NDI Dimer at 4.06 Å in M062X/6-31+ g(d,p) level

C	3.04009200	1.61376500	0.06185400
C	1.99748100	0.94879300	0.75575100
C	2.17241300	-0.35474600	1.28512900
C	2.84161700	2.86726900	-0.47265400
C	0.74480000	1.58845500	0.89436400
C	0.56297500	2.87870900	0.33563700
C	1.59104300	3.50607800	-0.33377100
C	-0.31447500	0.89718900	1.53546100
C	-0.11852600	-0.36330800	2.05774100
C	1.13777000	-0.99533300	1.93296100
H	1.29930300	-1.99879300	2.31893700
H	-0.95405000	-0.87238100	2.53142100
H	3.66003500	3.34718700	-1.00060300
H	5.35463700	-0.79159900	0.33065800
H	1.41789300	4.49211000	-0.75468100

H	-2.69240700	3.20676300	1.03420600
N	-1.75888200	2.80202700	1.06970500
N	4.47408700	-0.30901900	0.48970600
C	3.47012500	-1.06052600	1.07721400
O	3.65323100	-2.21912900	1.39340500
C	4.36388700	0.94809100	-0.09644500
O	5.30239400	1.45339500	-0.67098300
C	-1.67252600	1.50880300	1.55852600
O	-2.66468500	0.91831600	1.94304300
C	-0.76624100	3.54205900	0.43090500
O	-1.00167900	4.64142300	-0.01941000
C	0.31334200	-0.87719200	-1.53068400
C	-0.73781500	-1.57694900	-0.88659500
C	-0.54573400	-2.86782700	-0.33233200
C	0.10524200	0.38242800	-2.05014000
C	-2.00188400	-0.95629600	-0.75686100
C	-2.18615400	0.34944700	-1.27751500
C	-1.15578000	1.00369300	-1.91888300
C	-3.03976000	-1.63393300	-0.06888600
C	-2.82881400	-2.88576400	0.46460900
C	-1.56990700	-3.50906500	0.32996400
H	-1.38755000	-4.49502500	0.74721200
H	-3.64378000	-3.37657800	0.98781500
H	0.93461500	0.89883200	-2.52675100
H	2.70666700	-3.17642800	-1.05377200
H	-1.32543900	2.00866700	-2.29752300
H	-5.37350400	0.75355800	-0.32648000
N	-4.49020400	0.27793200	-0.49111800
N	1.77170000	-2.77435400	-1.07677500
C	0.78808800	-3.52106100	-0.43174400

O	1.03331400	-4.61911700	0.01628300
C	1.67412300	-1.48210000	-1.56666000
O	2.65922100	-0.88878900	-1.96429000
C	-4.37107000	-0.98240000	0.08586400
O	-5.30726800	-1.50070900	0.65277700
C	-3.48811500	1.04496500	-1.06171800
O	-3.67584300	2.20812200	-1.35802800

SI (***) : TD-DFT Results of model NDI Dimer at 4.06Å (Absorption)

Excited State 1: Singlet-A 3.4409 eV 360.32 nm f=0.0000

HOMO-1 ->LUMO+1 0.12166

HOMO ->LUMO 0.68131

Excited State 2: Singlet-A 3.6805 eV 336.87 nm f=0.3163

HOMO-1 ->LUMO 0.68911

Excited State 3: Singlet-A 3.8506 eV 321.98 nm f=0.0000

HOMO-3 ->LUMO+1 0.15975

HOMO-2 ->LUMO 0.59838

HOMO-1 ->LUMO+1 0.25166

Excited State 4: Singlet-A 3.9420 eV 314.52 nm f=0.0024

HOMO-9 ->LUMO+7 0.10445

HOMO-8 ->LUMO+6 -0.13278

HOMO-7 ->LUMO -0.16050

HOMO-6 ->LUMO 0.34058

HOMO-6 ->LUMO+1 -0.29167

HOMO-5 ->LUMO -0.15799

HOMO-5 ->LUMO+1 0.13280

HOMO-4 ->LUMO -0.25493

HOMO-4 ->LUMO+1 0.12795

Excited State 5: Singlet-A 3.9427 eV 314.46 nm f=0.0050

HOMO-9 ->LUMO+6 -0.13308

HOMO-8 ->LUMO+7 0.10676

HOMO-7 ->LUMO 0.31271

HOMO-7 ->LUMO+1 0.26161

HOMO-6 ->LUMO 0.23180

HOMO-5 ->LUMO -0.16149

HOMO-4 ->LUMO 0.22389

HOMO-4 ->LUMO+1 0.20035

Excited State 6: Singlet-A 4.0357 eV 307.22 nm f=0.1014

HOMO-9 ->LUMO+1 -0.18180

HOMO-8 ->LUMO 0.24856

HOMO-6 ->LUMO 0.13110

HOMO-3 ->LUMO -0.26836

HOMO-2 ->LUMO+1 -0.22718

HOMO ->LUMO+1 0.39679

Excited State 7: Singlet-A 4.0666 eV 304.88 nm f=0.0001

HOMO-9 ->LUMO 0.43926

HOMO-8 ->LUMO+1 -0.31450

HOMO-7 ->LUMO -0.10320

HOMO-7 ->LUMO+7 -0.12236

HOMO-6 ->LUMO+1 -0.11053

HOMO-6 ->LUMO+6 -0.14181

HOMO-4 ->LUMO+7 -0.11346

HOMO-1 ->LUMO+1 0.12020

Excited State 8: Singlet-A 4.0795 eV 303.92 nm f=0.0432

HOMO-9 ->LUMO+1 -0.25318

HOMO-8 ->LUMO 0.37737

HOMO-6 ->LUMO+7 0.10764

HOMO-3 ->LUMO 0.22626

HOMO-2 ->LUMO+1 0.21238

HOMO ->LUMO+1 -0.24410

Excited State 9: Singlet-A 4.2052 eV 294.84 nm f=0.0029

HOMO-9 ->LUMO -0.10966

HOMO-2 ->LUMO -0.22033

HOMO-1 ->LUMO+1 0.59869

HOMO ->LUMO -0.14314

Excited State 10: Singlet-A 4.2177 eV 293.96 nm f=0.0855

HOMO-3 ->LUMO 0.33402

HOMO-2 ->LUMO+1 0.28725

HOMO-1 ->LUMO -0.11785

HOMO ->LUMO+1 0.48272

HOMO ->LUMO+5 -0.10795

SI(*****) : TD-DFT Results of model NDI Dimer at 4.06 Å (Emission)

Excited State 1: Singlet-A 3.4387 eV 360.56 nm f=0.0000

HOMO-1 ->LUMO+1 0.12154

HOMO ->LUMO 0.68129

Excited State 2: Singlet-A 3.6776 eV 337.13 nm f=0.2655

HOMO-1 ->LUMO 0.68911

Excited State 3: Singlet-A 3.8481 eV 322.20 nm f=0.0000

HOMO-3 ->LUMO+1 0.15997

HOMO-2 ->LUMO 0.59849

HOMO-1 ->LUMO+1 0.25126

Excited State 4: Singlet-A 3.9398 eV 314.70 nm f=0.0025

HOMO-9 ->LUMO+7 0.10224

HOMO-8 ->LUMO+6 -0.13133

HOMO-9 ->LUMO -0.16480

HOMO-6 ->LUMO 0.32944

HOMO-6 ->LUMO+1 -0.28057

HOMO-5 ->LUMO -0.16876

HOMO-5 ->LUMO 0.13874

HOMO-4 ->LUMO -0.25987

HOMO-4 ->LUMO+1 0.13811

Excited State 5: Singlet-A 3.9405 eV 314.64 nm f=0.0048

HOMO-9 ->LUMO+6 -0.13183

HOMO-8 ->LUMO+7 0.10432

HOMO-7 ->LUMO 0.29598

HOMO-7 ->LUMO+1 0.24826

HOMO-6 ->LUMO 0.23735

HOMO-6 ->LUMO+1 0.11050

HOMO-5 ->LUMO -0.17019

HOMO-4 ->LUMO 0.23472

HOMO-4 ->LUMO+1 0.20352

Excited State 6: Singlet-A 4.0337 eV 307.37 nm f=0.1017

HOMO-9 ->LUMO+1 -0.18105

HOMO-8 ->LUMO 0.24708

HOMO-6 ->LUMO 0.13450

HOMO-6 ->LUMO+7 0.10009

HOMO-3 ->LUMO -0.27003

HOMO-2 ->LUMO+1 -0.22835

HOMO ->LUMO+1 0.39645

Excited State 7: Singlet-A 4.0648 eV 305.02 nm f=0.0001

HOMO-9 ->LUMO 0.43976

HOMO-8 ->LUMO+1 -0.31399

HOMO-7 ->LUMO -0.10417

HOMO-7 ->LUMO+7 -0.12072

HOMO-6 ->LUMO+1 -0.11433

HOMO-6 ->LUMO+6 -0.14269

HOMO-4 ->LUMO+7 -0.11759

HOMO-1 ->LUMO+1 0.12038

Excited State 8: Singlet-A 4.0775 eV 304.07 nm f=0.0430

HOMO-9 ->LUMO+1 -0.25405

HOMO-8 ->LUMO 0.37777

HOMO-6 ->LUMO+7 0.10749

HOMO-4 ->LUMO+6 0.10364

HOMO-3 ->LUMO 0.22607

HOMO-2 ->LUMO+1 0.21197

HOMO ->LUMO+1 -0.24164

Excited State 9: Singlet-A 4.2030 eV 294.99 nm f=0.0028

HOMO-9 ->LUMO -0.11005

HOMO-2 ->LUMO -0.21979

HOMO-1->LUMO+1 0.59864

HOMO ->LUMO -0.14301

Excited State 10: Singlet-A 4.2155 eV 294.12 nm f=0.0856

HOMO-3 ->LUMO 0.33319

HOMO-2 ->LUMO+1 0.28597

HOMO-1 ->LUMO -0.11786

HOMO ->LUMO+1 0.48407

HOMO ->LUMO+5 -0.10774