Supplementary Materials

Optical properties of 3-substituted indole

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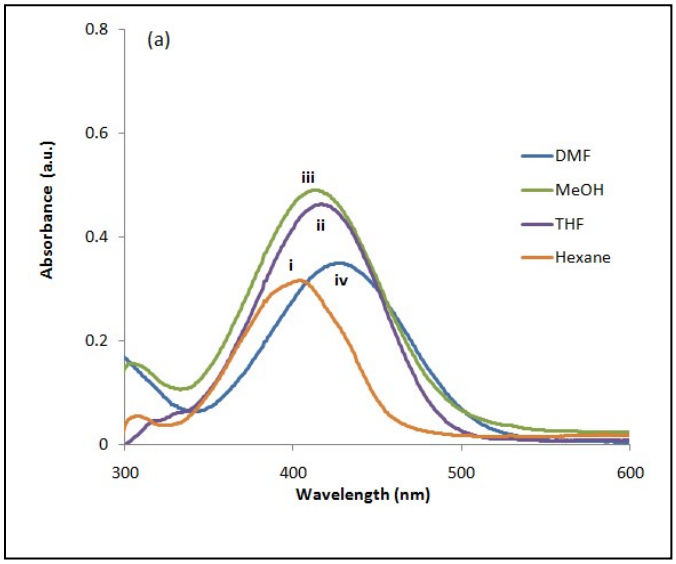
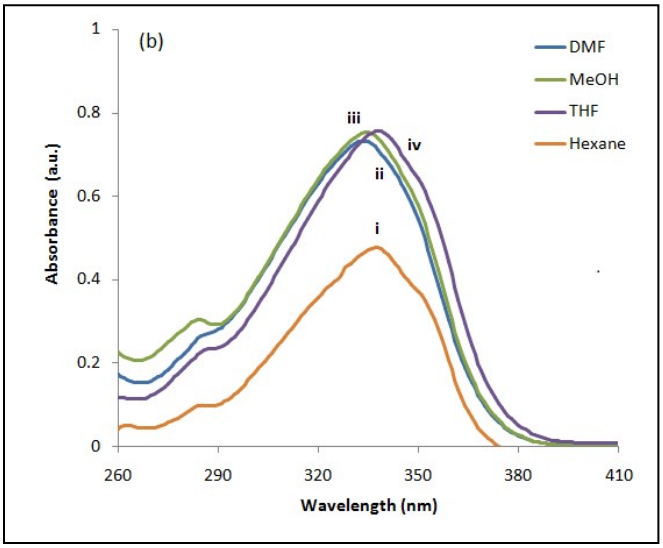
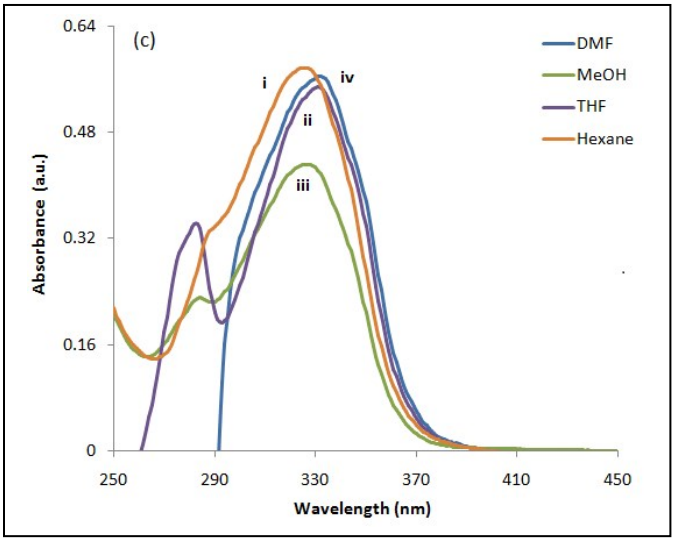
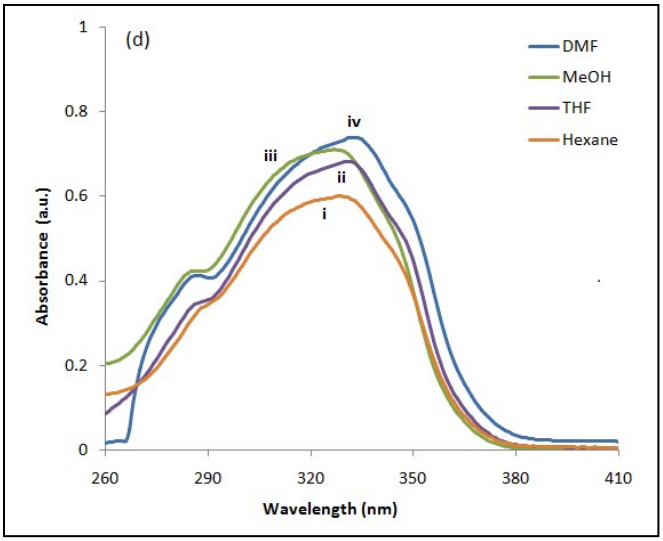
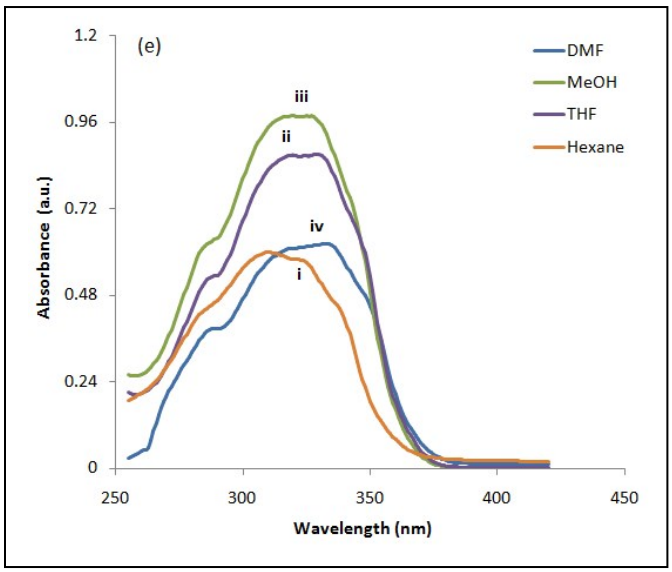
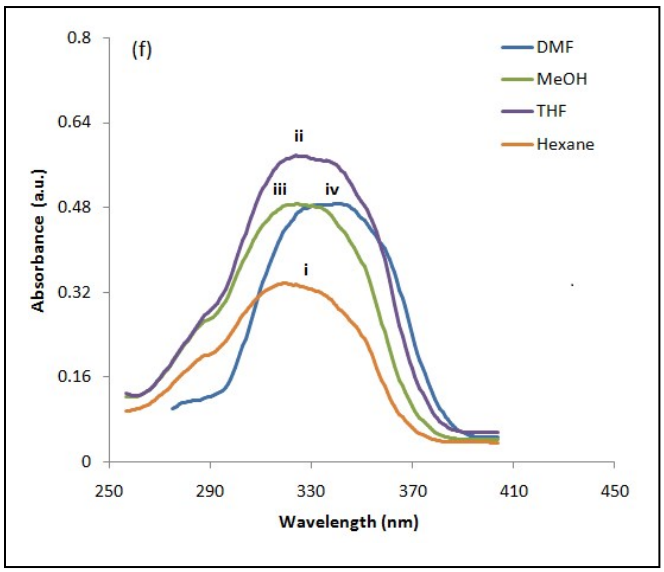












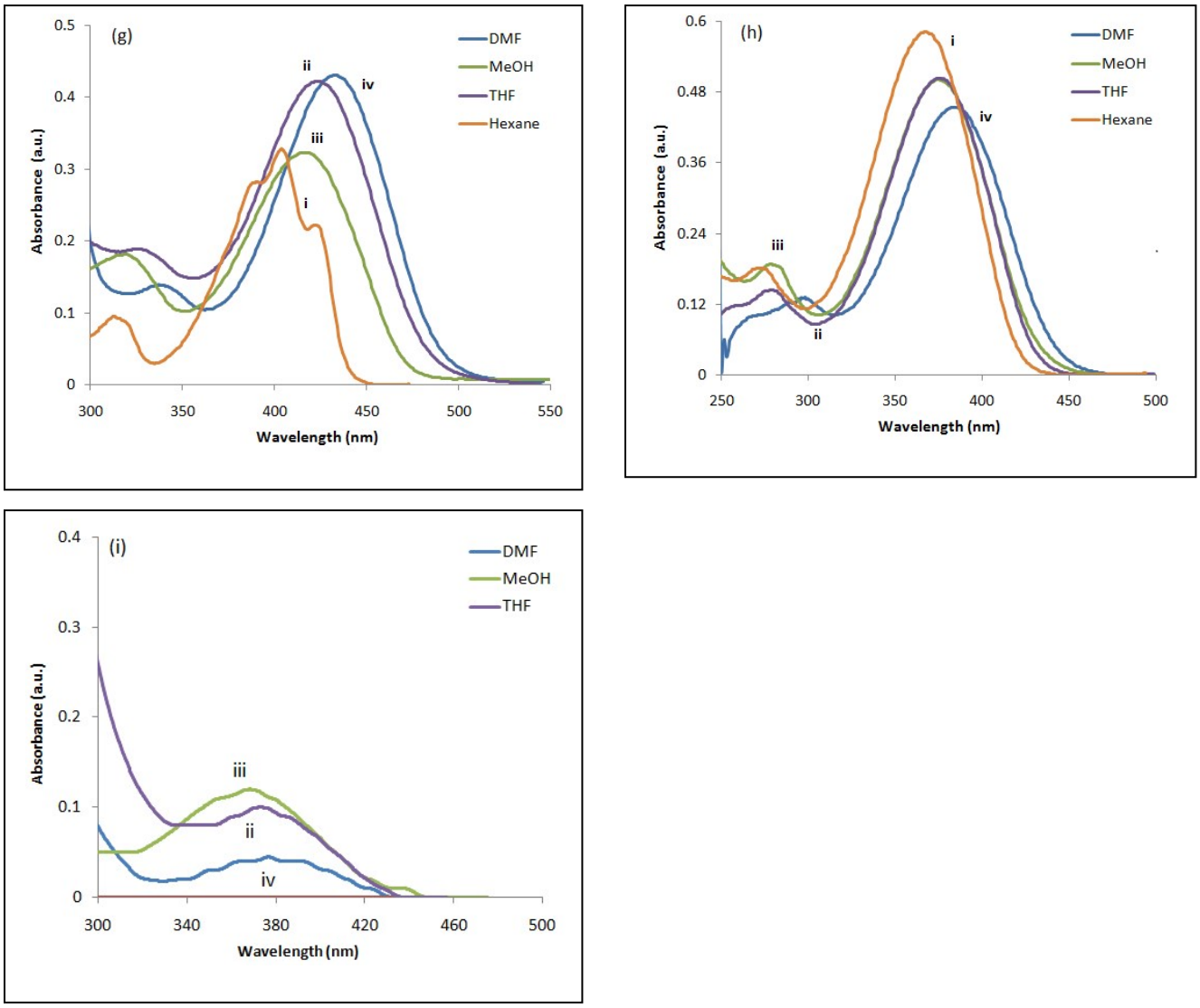
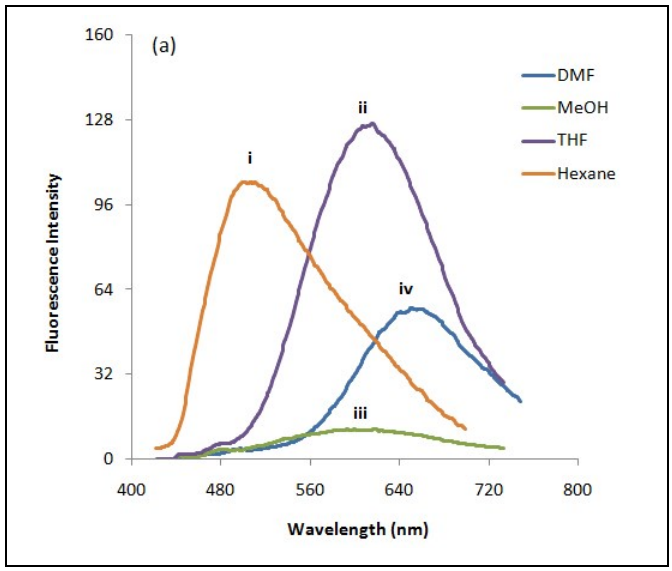
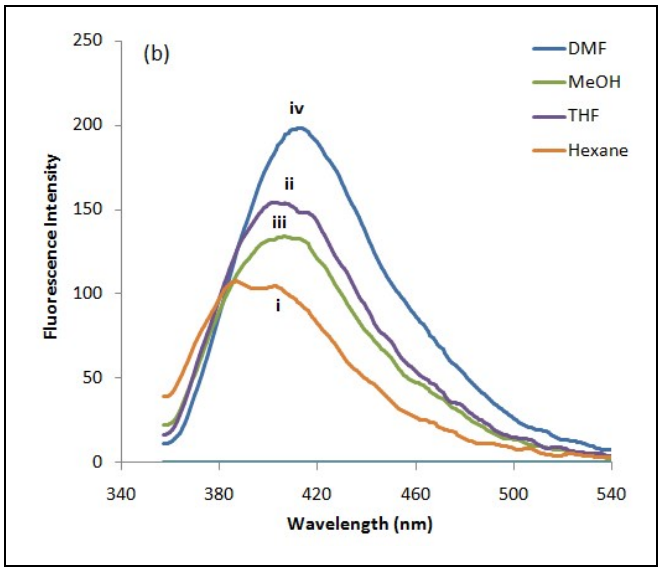
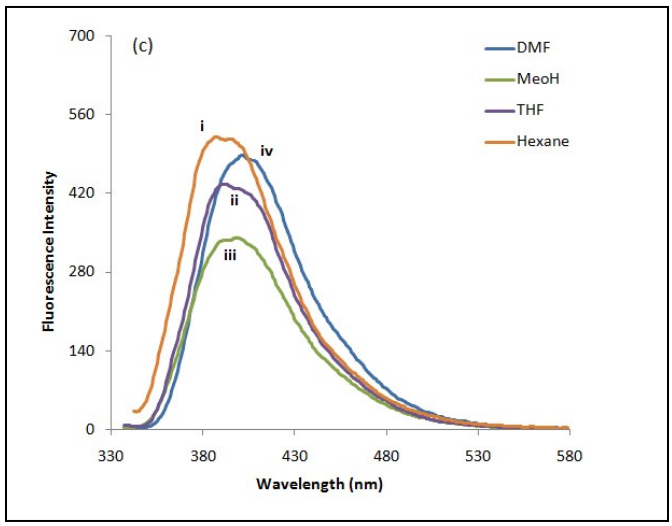
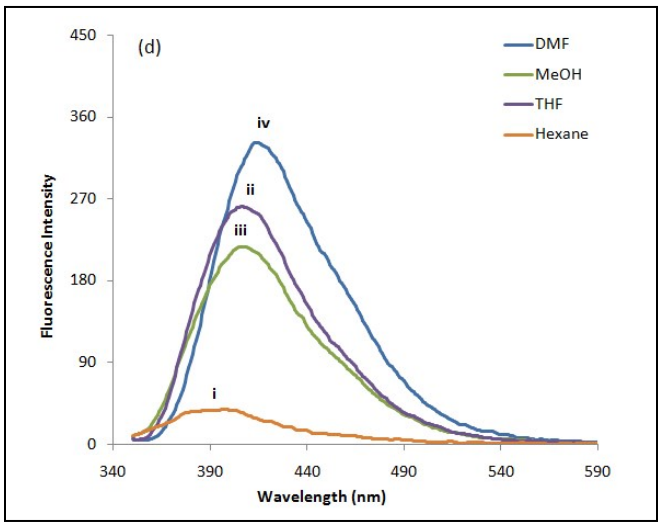


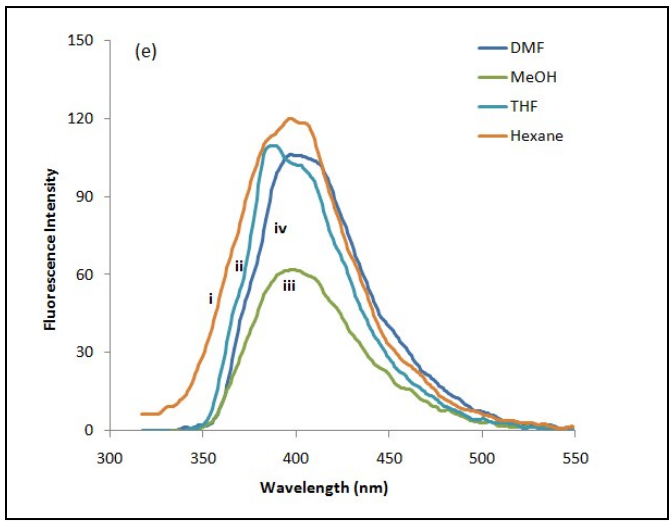
Figure S1. Absorption spectra of compounds, 2-4 (x 10^{-5}M) in (i) hexane (ii) THF (iii) MeOH and (iv) DMF; (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6**, (g) **7**, (h) **8**, (i) **9**.

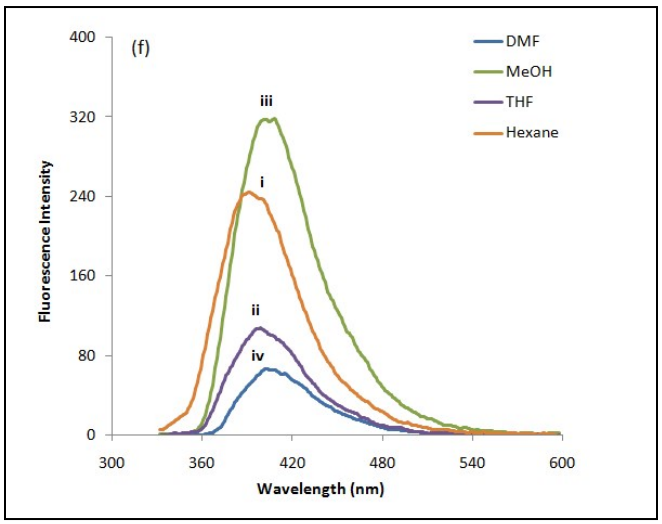

(a)
DMF
MeOH
THF
Hexane
i
ii
iii
iv
Fluorescence Intensity
Wavelength (nm)
0
32
64
96
128
160
400
480
560
640
720
800


(b)
DMF
MeOH
THF
Hexane
i
ii
iii
iv
Fluorescence Intensity
Wavelength (nm)
0
50
100
150
200
250
340
380
420
460
500
540


(c)
DMF
MeOH
THF
Hexane
i
ii
iii
iv
Fluorescence Intensity
Wavelength (nm)
0
140
280
420
560
700
330
380
430
480
530
580


(d)
DMF
MeOH
THF
Hexane
i
ii
iii
iv
Fluorescence Intensity
Wavelength (nm)
0
90
180
270
360
450
340
390
440
490
540
590


(e)
DMF
MeOH
THF
Hexane
i
ii
iii
iv
Fluorescence Intensity
Wavelength (nm)
0
30
60
90
120
150
300
350
400
450
500
550


(f)
DMF
MeOH
THF
Hexane
i
ii
iii
iv
Fluorescence Intensity
Wavelength (nm)
0
80
160
240
320
400
300
360
420
480
540
600

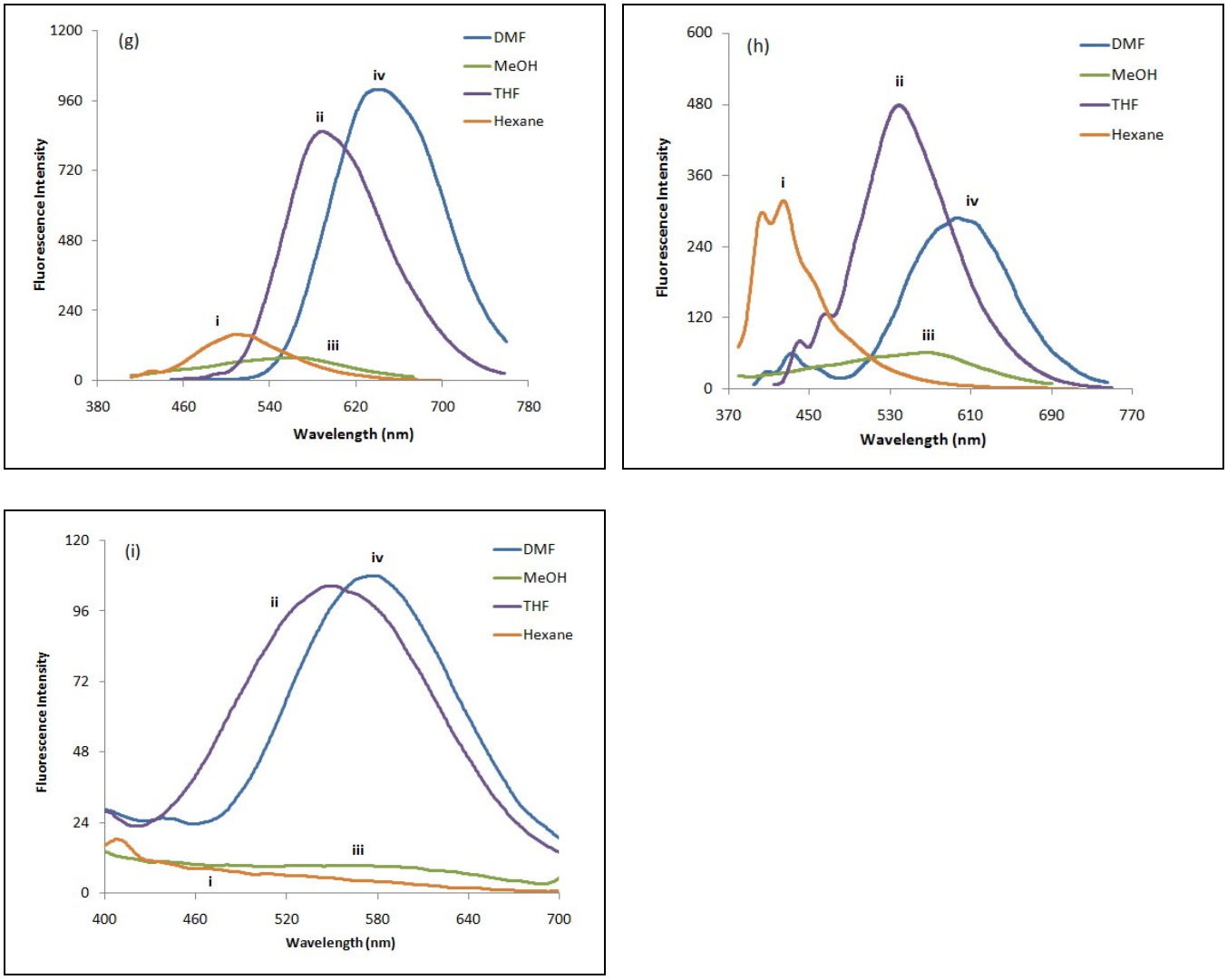


Figure S2. Fluorescence spectra of compounds (0.5 x 10^{-5}M) in (i) hexane (ii) THF (iii) MeOH and (iv) DMF; (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, (f) **6**, (g) **7**, (h) **8**, (i) **9**.

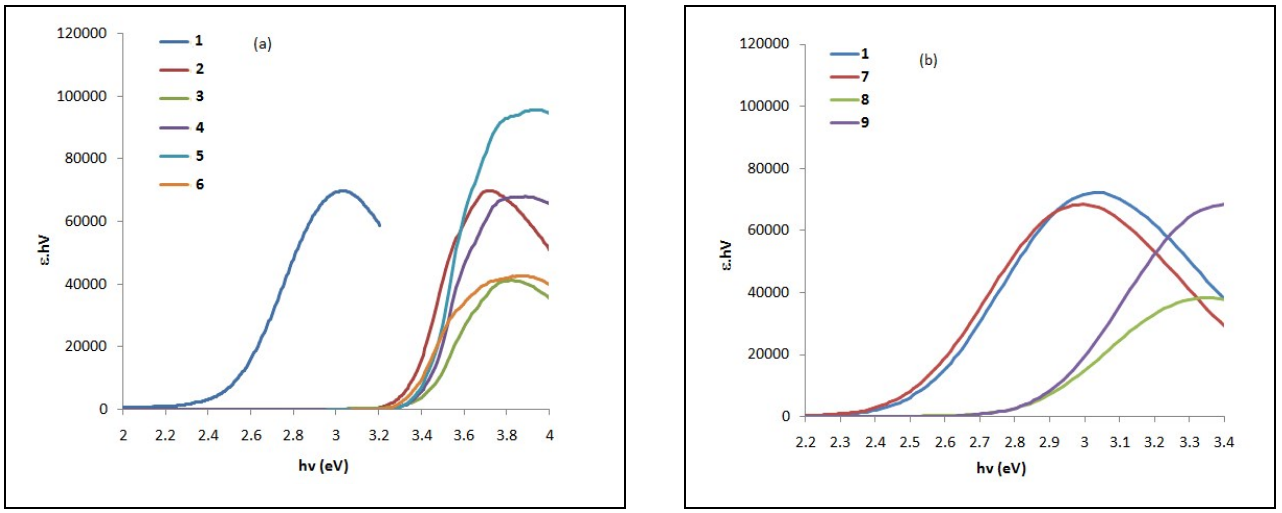


Figure S3. Tauc plot, εhv *vs*. hv (eV) of ethenyl indoles (a) **1-6** (b) **1, 7-9**.

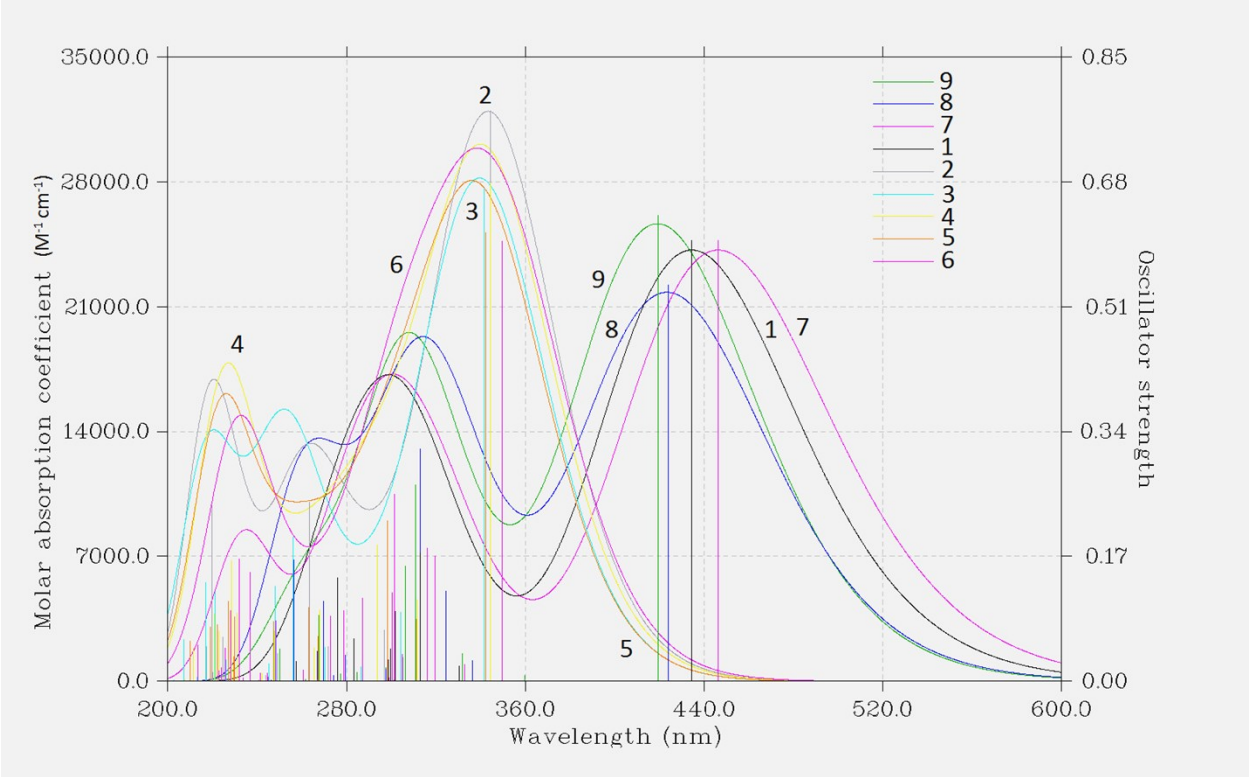


Figure S4. TDDFT computed absorption spectrum, molar absorption coefficient and oscillator strength of **1-9.**

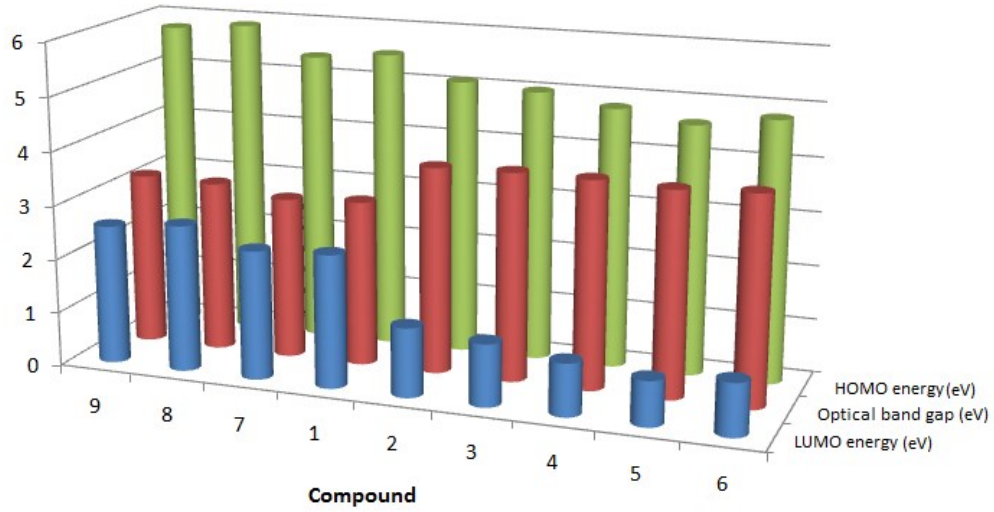


Figure S5. Comparative chart of TDDFT computed optical band gap and HOMO-LUMO energy of **1-9.**

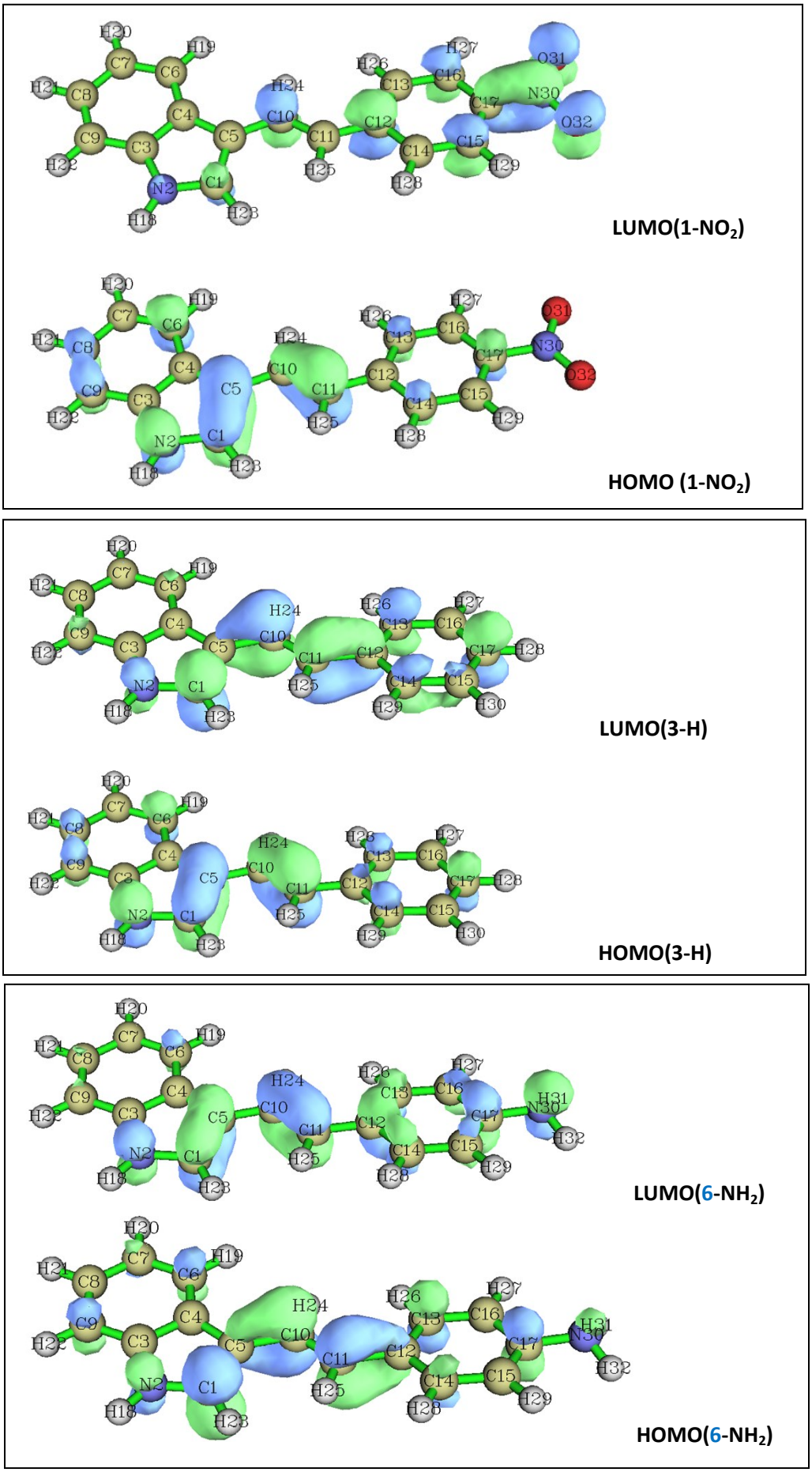
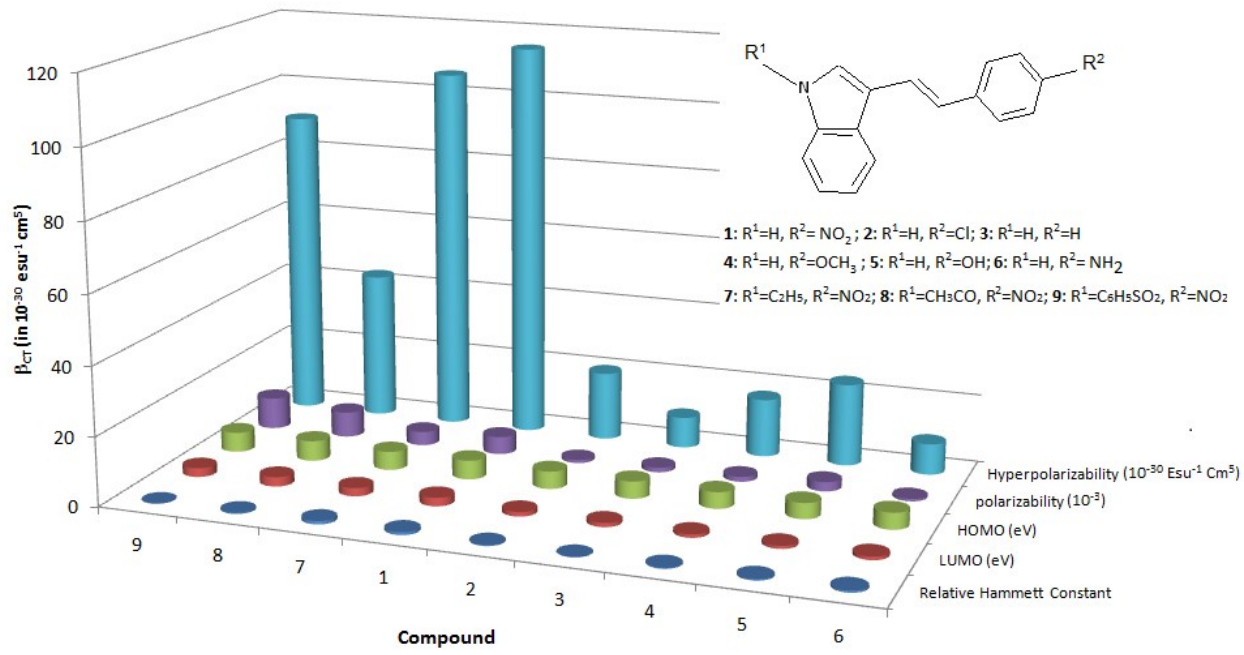


Figure S6. Molecular orbital (HOMO, LUMO) diagram of indole compounds **1** (nitro), **3** (-H) and **6** (amine).

(a)



(b)

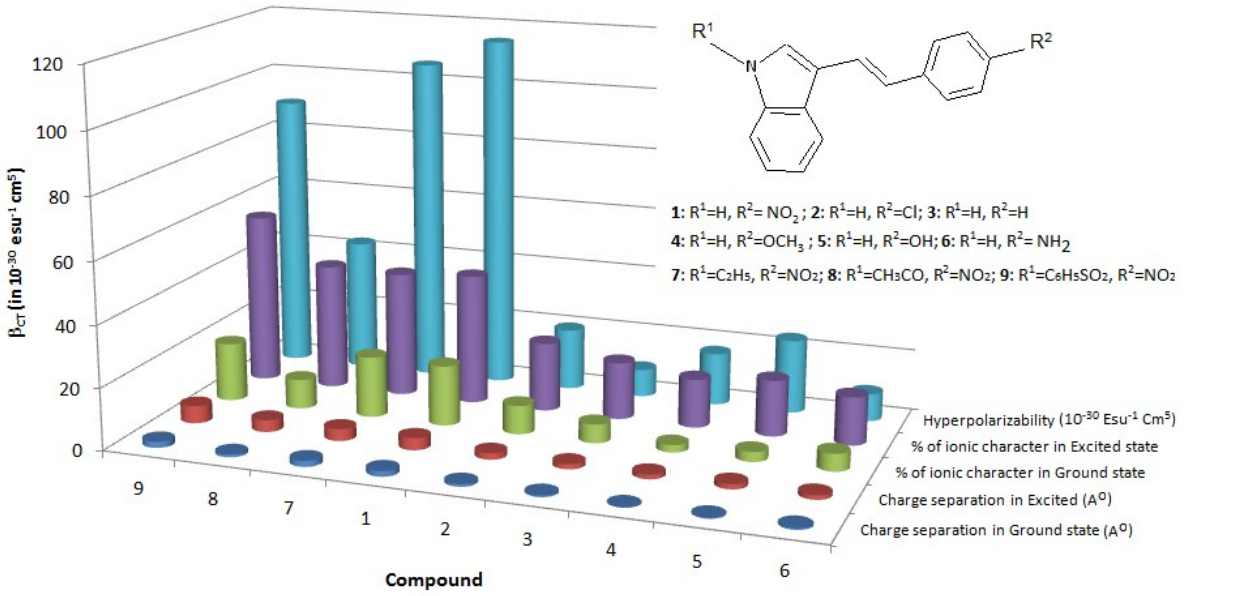


Figure S7. Comparative chart of first hyperpolarizability (β_{CT}) of **1–9** with (a) polarizability, HOMO, LUMO energy and relative Hammett substituent constant, (b) polarizability, and % of ionic character and % of charge separation in the ground and excited state of **1–9**.

Table S1. Change of dipole moment ($\Delta\mu$) obtained from the slope of the McRay plot, Stokes' shift vs. solvent polarity parameter, F(ε,n), polarizibility (π^*) and the ground state dipole moment (μ_g) obtained from TDDFT calculation of **1-9** (No. of points used, N = 4)

	Radius of molecule (A^o)	μ_g (Debye)	F(ε,n)		$\Delta\mu$ (Debye)	μ_e (Debye)	π^*	
			Slope (m_1)	R			Slope (10^{-3})	R
1	4.53	8.39	4245	0.91	9.86	18.25	-5.14	0.98
2	4.47	3.99	1384	0.99	5.52	9.51	-0.93	0.85
3	4.38	2.57	1304	0.99	5.19	7.76	-1.32	0.99
4	4.55	1.05	1434	0.99	5.77	6.82	-1.43	0.99
5	4.43	1.37	-1847	0.92	6.29	7.66	-2.69	0.91
6	4.45	2.44	805	0.85	4.18	6.62	-0.71	0.96
7	4.74	8.94	3397	0.92	9.44	18.38	-4.03	0.94
8	4.75	4.34	7645	0.97	14.21	18.55	-7.38	0.98
9	5.12	9.32	9563	0.95	17.78	27.10	-9.22	0.97

Table S2. TDDFT computed absorption wavelength maximum ($\lambda_{abs\ max}$), electronic transition energy (ΔE, eV), oscillator strength (*f*), ground state dipole moment (μ_g), highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy.

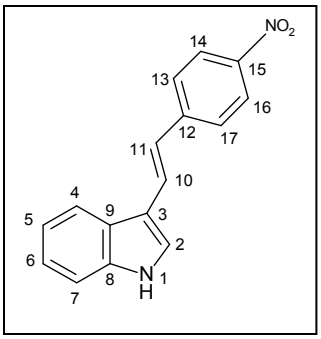
Com	$\lambda_{abs\ max}$ (nm)	*f*	Major transition (HOMO→ LUMO) (%)	HOMO (eV)	LUMO (eV)	(ΔE) (eV)	(μ_g) Debye	(β)* (in 10^{-30}) $Esu^{-1}.cm^5$
1	434.3	0.59	>99%	-5.51	-2.46	3.05	8.39	115
2	343.4	0.77	>99%	-5.10	-1.28	3.82	3.99	20
3	339.4	0.66	>99%	-5.01	-1.15	3.86	2.57	9
4	339.8	0.67	>99%	-4.81	-0.97	3.84	1.05	17
5	336.2	0.59	>99%	-4.62	-0.83	3.79	1.37	24
6	338.6	0.60	>99%	-4.82	-0.97	3.85	2.44	9
7	446.1	0.59	>99%	-5.38	-2.39	2.99	8.94	106
8	423.6	0.53	>99%	-5.89	-2.72	3.17	4.34	43
9	419.3	0.63	>99%	-5.77	-2.58	3.19	9.32	90

* first hyperpolarizability (β) obtained experimentally using solvatochromism method

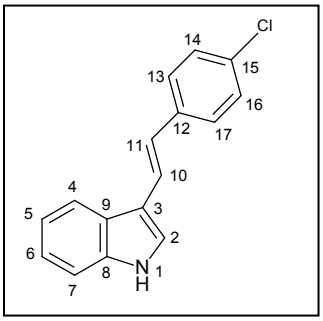
Table S3. Absorption, fluorescence wavelength, relative Hammett constant, % of charge separation (% of ionic character) of **1-9**.

Compound	Absorption nm (eV)	Emission nm (eV)	Relative Hammett constant	% of charge separation (% ionic character)		(β) (in 10^{-30}) $Esu^{-1}.cm^5$
				Ground State Aº	Excited State Aº	
1	413 (3.00)	590 (2.10)	0.81	1.76 (19.5)	3.84 (42.4)	115
2	335 (3.70)	395 (3.14)	0.24	0.84 (9.3)	2.00 (22.4)	20
3	327 (3.79)	396 (3.13)	0	0.54 (6.1)	1.63 (18.6)	9
4	327 (3.79)	404 (3.07)	-0.28	0.22 (2.4)	1.43 (15.8)	17
5	322 (3.85)	390 (3.18)	-0.38	0.29 (3.2)	1.61 (18.2)	24
6	324 (3.82)	405 (3.06)	-0.57	0.51 (5.7)	1.39 (15.6)	9
7	418 (2.96)	558 (2.22)	0.95	1.88 (19.8)	3.87 (40.8)	106
8	374 (3.31)	563 (2.20)	0.34	0.91 (9.6)	3.90 (41.1)	43
9	370 (3.35)	588 (2.11)	0.08	1.96 (19.1)	5.70 (55.7)	90

Characterization data of synthesized ethenyl indoles (1-9)[1,2]



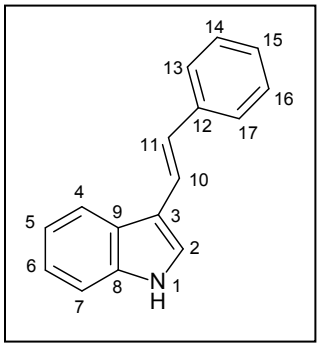
3-(4-Nitrophenylethenyl-*E*)-N-H-indole (1)[1,2]: Yield 31%; M.p. 195-196 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 413 (27,900); IR (KBr): ν_{max} (cm^{-1}) 3370 (NHst), 3048 (C-Hst), 1626 (vinyl C=Cst), 1585, 1490, 1425 (Ar C=Cst), 1520 (Ar-NO_2, N=O Asym-st), 1330 (Ar-NO_2, N=O Sym-st); ^{1}H NMR ($CDCl_3$, 500 Hz): □δ 7.17 (1H, d, J = 15.8 Hz, -C=CH-Ar), 7.27-7.31 (2H, m, -C_5-H, and -C_6-H), 7.44 (1H, d, J= 7.5 Hz, -C_4-H), 7.47 (1H, d, J = 2.7 Hz, -C_2-H), 7.50 (1H, d, J = 15.8 Hz, -CH=C-Ar), 7.61 (2H, d, J = 8.9 Hz, -Ar), 8.01 (1H, d, J= 6.9 Hz, -C_7-H), 8.21 (2H, d, J = 8.9 Hz, -ArNO_2), 8.35 (1H, s, br, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 145.8 (-C_{15}), 145.3 (-C_{12}), 136.9 (-C_8), 126.7 (-C_{11}), 125.8 (-C_{13}, -$C_{17,}$ -C_2), 125.7 (-C_9), 125.2 (-C_{10}), 123.1 (-C_{14}, -C_{16}), 122.8 (-C_6), 121.0 (-C_5), 120.2 (-C_4), 115.0 (-C_7), 111.7 (-C_3); MS (EI^{+}): m/z 264 (M^{+}); Analytical CHNS calculated for **1**: $C_{16}H_{12}N_2O_2$ (264.24) (%) C 72.71, H 4.57, N 10.59, Found C 72.65, H 4.55, N 10.58.



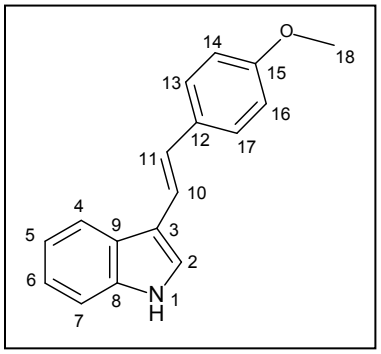
3-(4-Chlorophenylethenyl-*E*)-N-H-indole (2)[2]: Yield 56%; M.p. 191-192 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 335 (18,800); IR (KBr): ν_{max} (cm^{-1}) 3381 (NHst), 3048 (C-Hst), 1632 (vinyl C=Cst), 1524, 1488, 1455, 1403 (Ar, C=Cst); ^{1}H NMR ($CDCl_3$, 500 Hz): □δ 7.08 (1H, d, J = 16.5 Hz, -C=CH-Ar), 7.22-7.26 (2H, m, -C_5-H, -C_6-H), 7.29 (1H, d, J = 16.5 Hz, -CH=C-Ar), 7.31 (2H, d, J = 8.2 Hz, -Ar), 7.38 (1H, d, J = 2.0 Hz, -C_2-H), 7.41 (1H, d, J= 7.6 Hz, -C_4-H), 7.44 (2H, d, J = 8.2 Hz, -Ar-Cl), 7.98 (1H, d, J= 8.2 Hz, -C_7-H), 8.21 (1H, s, br, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 137.0 (-C_8), 136.8 (-C_{12}), 131.9 (-C_{15}), 131.2, 128.7 (-C_{13} , C_{17}), 126.8, 125.3 (-C_{14} , C_{16}), 124.2 (-C_{11}), 124.0 (-C_9), 122.8 (-C_{10}), 122.3 (-C_6), 120.5 (-C_5), 120.1 (-C_4), 115.3 (-C_7), 111.4 (-C_3); MS (EI^{+}): m/z 253 (M^{+});

Analytical CHNS calculated for **2**: $C_{16}H_{12}NCl$ (253.69) (%) C 75.73, H 4.76, N 5.52, Found C 75.70, H 4.74, N 5.51.

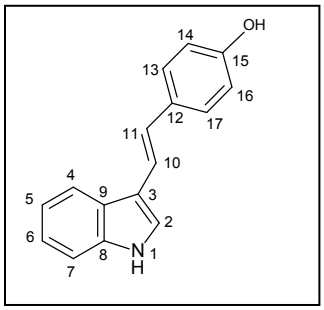
3-(phenylethenyl-*E*)-N-H-indole (3)[2]: Yield 45%; M.p. 209-210 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 327 (10,800); IR (KBr): ν_{max} (cm^{-1}) 3381 (NHst), 3036 (C-Hst), 1630 (vinyl C=Cst), 1594, 1524, 1455, 1418 (Ar, C=Cst); ^{1}H NMR ($CDCl_3$, 500 Hz): δ 7.08 (1H, d, J = 15.8 Hz, -C=CH-Ar), 7.15-7.22 (3H, m, -C_5-H, -C_6-H and -Ar-H), 7.29 (1H, d, J = 2.7 Hz, -C_2-H), 7.31 (2H, d, J = 7.5 Hz, -Ar), 7.33 (1H, d, J = 15.8 Hz, -CH=C-Ar), 7.34 (1H, d, J= 9.0 Hz, -C_4-H), 7.47 (2H, d, J = 7.5 Hz, -Ar), 7.95 (1H, d, J= 7.6 Hz, -C_7-H), 8.11 (1H, s, br, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 138.5 (-C_{12}), 136.8 (-C_8), 128.6 (-C_{11}), 126.6 (-C_{14} , C_{16} , C_2), 125.7 (-C_{13} , C_{17}), 125.5 (-C_{15}), 123.7 (-C_9), 122.7 (-C_{10}), 121.6 (-C_6), 120.4 (-C_5), 120.2 (-C_4), 115.6 (-C_7), 111.4 (-C_3); MS (EI^{+}): m/z 219 (M^{+}); Analytical CHNS calculated for **3**: $C_{16}H_{13}N$ (219.25) (%) C 87.63, H 5.97, N 6.38, Found C 87.53, H 5.96, N 6.37.



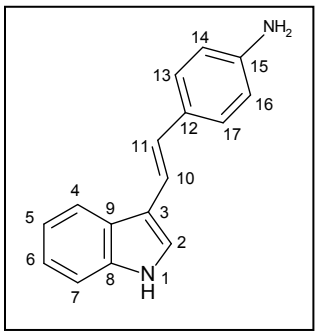
3-(4-Methoxyphenylethenyl-*E*)-N-H-indole (4)[2]: Yield 34%; M.p. 232-233 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 327 (17,800); IR (KBr): ν_{max} (cm^{-1}) 3377 (NHst), 3034 (C-Hst), 1634 (vinyl C=Cst), 1604,1574, 1505, 1456, 1428 (Ar, C=Cst), 1244 (Ar-O-Cst); ^{1}H-NMR ($CDCl_3$, 500 Hz): δ 3.83 (3H, s, -OCH_3), 6.90 (2H, d, J = 8.9 Hz, -Ar-OCH_3), 7.09 (1H, d, J = 16.4 Hz, -CH=C-Ar), 7.19 (1H, d, J = 16.4 Hz, -C=CH-Ar), 7.21-7.25 (2H, m, -C_5-H, -C_6-H), 7.35 (1H, d, J=2.7 Hz, -C_2-H), 7.39 (1H, d, J = 7.6 Hz, -C_7-H), 7.46 (2H, d, J = 8.9 Hz, -Ar), 7.99 (1H, d, J = 7.6 Hz, -C_4-H), 8.16 (1H, br, s, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 158.5 (-C_{15}), 136.8 (-C_8), 131.3 (-C_{11}), 130.4 (-C_{13} , C_{17}), 126.8 (-C_{12}), 125.6 (-C_2), 125.2 (-C_9), 123.1 (-C_{10}), 122.6 (-C_6), 120.3 (-C_5), 120.1 (-C_4), 119.6,



115.8 (-$C_{14,}$ C_{16}), 114.0 (-C_7), 111.3 (-C_3), 55.3 (-C_{18}); MS (EI^+): m/z 249 (M^+); Analytical CHNS calculated for **4**: $C_{17}H_{15}NO$ (249.27) (%) C 81.89, H 6.06, N 5.61, Found C 81.81, H 6.04, N 5.60.



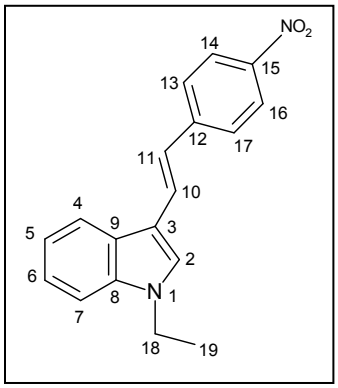
3-(4-Hydroxyphenylethenyl-*E*)-N-H-indole (5)[2]: Yield 33%; M.p. 225-226 ^oC; UV-vis (MeOH): λ_{max} nm (ε, l $mol^{-1}cm^{-1}$) 322 (24,400); IR (KBr): □ν_{max} (cm^{-1}) 3379 (NHst), 3126 (OHst), 3030 (C-Hst), 1636 (vinyl C=Cst), 1587, 1540, 1505, 1456, 1420, 1358 (Ar, C=Cst); ^{1}H-NMR ($CDCl_3$, 500 Hz): □δ 4.74 (3H, s, -OH), 6.83 (2H, d, J = 8.2 Hz, -Ar-OH), 7.08 (1H, d, J = 16.5 Hz, -CH=C-Ar), 7.18 (1H, d, J = 16.5 Hz, -C=CH-Ar), 7.21-7.23 (2H, m, -C_5-H, -C_6-H), 7.35 (1H, d, J=2.7 Hz, -C_2-H), 7.39 (1H, d, J = 6.2 Hz, -C_7-H), 7.41 (2H, d, J = 8.2 Hz, -Ar), 7.98 (1H, d, J = 8.2 Hz, -C_4-H), 8.16 (1H, br, s, -NH); MS (EI^+): m/z 235 (M^+); Analytical CHNS calculated for **5**: $C_{16}H_{13}NO$ (235.25) (%) C 81.67, H 5.57, N 5.95, Found C 81.61, H 5.55, N 5.93.



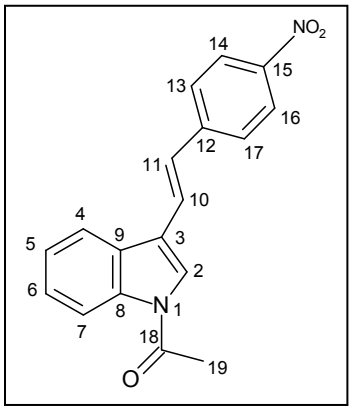
3-[4-Aminophenylethenyl-*E*]-N-H-indole (6)[1,2]: Yield 47%; M.p. 263-264 ^oC; UV-vis (MeOH): λ_{max} nm (ε, l $mol^{-1}cm^{-1}$) 324 (12,200); IR (KBr): □ν_{max} (cm^{-1}) 3394, 3341 (H-N-Hst), 3026 (C-Hst), 1610 (vinyl C=Cst), 1507, 1456, 1420, 1337 (Ar, C=Cst); ^{1}H-NMR ($CDCl_3$, 500 Hz): □δ 3.70 (2H, br, s, -NH_2), 6.69 (2H, d, J = 8.2 Hz, -Ar-NH_2), 7.05 (1H, d, J = 15.8 Hz, -CH=C-Ar), 7.14 (1H, d, J = 15.8 Hz, -C=CH-Ar), 7.18-7.25 (2H, m, -C_5-H, -C_6-H), 7.33 (1H, d, J=2.7 Hz, -C_2-H), 7.34 (2H, d, J = 8.9 Hz, -Ar), 7.38 (1H, d, J = 7.5 Hz, -C_7-H), 7.97 (1H, d, J = 7.5 Hz, -C_4-H), 8.13 (1H, br, s, -NH); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 145.2 (-C_{15}), 136.7 (-C_8), 129.3 (-C_{11}), 126.9 (-C_{13}, C_{17}), 125.8 (-C_2), 125.6 (-C_9), 122.7 (-C_{10}), 122.5 (-C_{12}), 120.2 (-C_6), 120.1 (-C_5), 118.1 (-C_4), 115.9 (-$C_{14,}$ C_{16}), 115.3 (-

C_7), 111.3 (-C_3); MS (EI^+): m/z 234 (M^+); Analytical CHNS calculated for **6**: $C_{16}H_{14}N_2$ (234.26) (%) C 82.01, H 6.02, N 11.95, Found C 81.95, H 6.01, N 11.93.

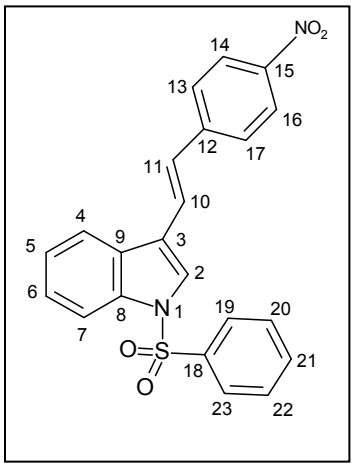
3-[4-Nitrophenylethenyl-*E*]-N-ethyl indole (7)[1] : Yield 80%; M.p. 135-136 ^oC; UV-vis (MeOH) λ_{max}/nm (ε, l $mol^{-1}cm^{-1}$): 418 (18,823); IR (KBr) ν_{max}, (cm^{-1}): 1596,1331 (NO_2), 1627 (C=C); ^1H NMR ($CDCl_3$, 300 Hz): δ 1.51 (t, J = 7.32 Hz, 3H, -CH_3), 4.21 (q, J = 7.32 Hz, 2H, -CH_2), 7.12 (d, J = 16.1 Hz, 1H, -CH=C-ArNO_2), 7.23-7.34 (m, 2H, -C_5C_6), 7.38 (s, 1H, -C_7), 7.40 (s, 1H, -C_2), 7.49 (d, J = 16.4 Hz, 1H, -C=CH-ArNO_2), 7.59 (d, J = 8.7 Hz, 2H, -Ar), 7.98-8.00 (m, 1H, -C_4), 8.20 (d, J = 8.7 Hz, 2H, -ArNO_2); Analytical CHNS calculated for **7**: $C_{18}H_{16}N_2O_2$ (292.3)(%): C 73.99, H 5.51, N 9.58; found C 73.99, H 5.09, N 9.51.



3-[4-Nitrophenylethenyl-*E*]-N-acetyl indole (8): Yield 83%; M.p.: 216-218 ^oC; UV-vis (MeOH) λ_{max}/nm (ε, l $mol^{-1}cm^{-1}$): 373 (9464); IR (KBr) ν_{max}, (cm^{-1}): 1584, 1334 (NO_2) 1643 (C=C), 1703 (C=O); ^1H-NMR ($CDCl_3$, 300 MHz): δ 2.69 (3H, s, -$COCH_3$), 7.27 (1H, d, J = 16.48 Hz, -CH=C-ArNO_2), 7.39 (1H, d, J = 16.48, -C=CH-ArNO_2), 7.40-7.47 (2 H, m, H at -C_5 and -C_6), 7.64 (2H, d, J = 8.79 Hz, -Ar), 7.66 (1H, s, H-C_2), 7.90-7.93 (1H, m, H-C_7), 8.24 (2H, d, J = 8.79 Hz, -ArNO_2), 8.50 (1H, m, H-C_4); Analytical CHN calculated for **8**: $C_{18}H_{14}N_2O_3$ (306.3)(%) C, 70.58; H, 4.61; N, 9.15. Found C, 70.55; H, 4.60; N, 9.11.



3-[4-Nitrophenylethenyl-*E*]-N-benzene sulphonyl-indole (9)[1]: Yield 80%; M.p. 263-264 ^{o}C; UV-vis (MeOH): λ_{max} nm (ε, l mol^{-1}cm^{-1}) 370 (21,500); IR (KBr): ν $_{max}$ (cm^{-1}) 3100 (C-Hst), 1620 (vinyl C=Cst), 1588, 1421 (Ar C=Cst), 1505 (Ar-NO_2, N=O Asym-st), 1340 (Ar-NO_2, N=O Sym-st), 1180 (S=Ost); ^{1}H NMR ($CDCl_3$, 500 Hz): δ 7.22 (1H, d, J = 15.8 Hz, -C=CH-Ar), 7.34 (1H, d, J = 15.8 Hz, -CH=C-Ar), 7.34-7.40 (2H, m, -C_5-H, and -C_6-H), 7.40 (1H, t, J= 7.5 Hz, -$ArSO_2$), 7.47 (1H, t, J= 7.5 Hz, -$ArSO_2$), 7.57 (1H, t, J= 7.5 Hz, -$ArSO_2$), 7.63 (2H, d, J= 7.5 Hz, -$ArSO_2$), 7.93 (2H, d, J = 8.9 Hz, -Ar), 8.23 (2H, d, J = 8.9 Hz, -$ArNO_2$), 7.82 (1H, s, -C_2-H), 7.86 (1H, d, J= 6.9 Hz, -C_7-H), 8.04 (1H, d, J= 7.5 Hz, -C_4-H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 146.7 (-C_{15}), 143.8 (-C_{12}), 137.8 (-C_{18}), 135.5 (-C_8), 134.1 (-C_{21}), 129.4 (-C_{11}), 128.5 (-$C_{20,}$ C_{22}), 127.1 (-$C_{13,}$ C_{17}, C_2), 126.8 (-C_9), 126.5 (-$C_{19,}$ C_{23}), 125.5 (-C_{10}), 125.4 (-C_4), 124.2 (-C_6), 123.9 (-C_{14} ,C_{16}), 120.4 (-C_5), 119.9 (-C_7), 113.8 (-C_3); Analytical CHNS calculated for **9**: $C_{22}H_{16}N_2O_4S$ (404.39) (%) C 65.33, H 3.98, N 6.92, S 7.92 Found C 65.31, H 3.96, N 6.92, S 7.90.



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1. (a) A. K. Singh, P.K. Hota, Photoreactivity of donor-acceptor ethenes. Indian J. Chem. B. 42 (2003) 2048-2053, (b) A. K. Singh, P.K. Hota, Fluorescence and photoisomerization studies of *p*-nitrophenyl substituted indolic ethenes, J. Phys. Org. Chem. 19 (2006) 43-52.
2. J. Kumar, N. Kumar, N. Sati, P. K. Hota, Antioxidant Properties of ethenyl indole: DPPH assay and TDDFT studies, New J. Chem. 44 (2020) 8960-8970.