Phenazines and Thiazine: Green Synthesis, Photophysical Properties and Dichroic Behavior in Nematic Host

Amol S. Choudhary[1], Manoj K. Malik[2], Sharad R. Patil[1], K. H. Prabhu[3], Rajendra R. Deshmukh[2], and Nagaiyan Sekar*[1]

[1]Tinctorial Chemistry Group, Department of Dyestuff and Intermediate Technology, Institute of Chemical Technology, Matunga, Mumbai – 400 019, India.

[2] Department of Physics, Institute of Chemical Technology, Matunga, Mumbai-400 019, India.

[3] Department of Textile Design & Color, Wool Research Association, Kolshet Road, Thane-400 607, India.

*n.sekar@ictmumbai.edu.in

This file includes:

1. Experimental Details:

2-Hydroxy 1, 4-napthaquinone (Lawsone) was procured from Sigma Aldrich. The nematic liquid crystal (LC) E7 used for dichroism measurement was procured form E. Merck, Japan.

Ultrasound set-up.

The ultrasound for sonochemical synthesis is generated with the help of ultrasonic instrument set-up (horn type). The schematic representation of the set-up is shown in Figure 2. The specification and details of the set-up, processing parameters used during the experiments are as follows:

Ultrasonic bath: *Make.*

Sonic and Materials, USA. Frequency: 20 kHz. Dimensions of bath: 0.15 m, 0.15 m and 0.14 m. Surface area of ultrasound irradiating face: 2.25×10^{-2} $m^{2.}$

Ultrasonic horn: Make. Ace. Frequency: 20 kHz, Rated output power: 750 W.

Sonicator Probe. 13 mm tip diameter, 136 mm length and 340 g weight made of Titanium alloy Ti-6Al-4V.

Dichroic measurement.

The **e**xactly 0.5 wt% dye was dissolved in the host LCE7 by stirring above the clearing temperature (T_c) for about an hour. Dye-LCE7 mixture was then filled by capillary action above the T_c of the LCE7 in glass cells (with 6 µm gap and spin-coated with polyimide orienting layer rubbed unidirectional), followed by slow cooling to induce a planar orientation. The absorption of the polarized light was measured parallel and perpendicular to the direction of rubbing. A cell containing only the LC was used as a reference. The dichroic ratio $R = (A_{II} / A_{\perp})$ was calculated from the absorption of light polarized parallel (A_{II}) and perpendicular ($A_{\perp}$) to the orientation of dye. The order parameter (S) of the dye with respect to liquid crystal director was determined form the equation $S = (R\text{-}1) / (R\text{+}2)$.

Computational methods.

All computations were performed using the Gaussian 09 package. The ground state (S_0) geometry of the synthesized dyes in their C1 symmetry was optimized in the gas phase using density functional theory (DFT). The functional used was B3LYP. The B3LYP method combines Becke's three parameter exchange functional (B3), the nonlocal correlation functional by Lee, Yang and Parr (LYP). The basis set used for all the atoms was 6-31G(d). The vibrational analysis was performed at the same level of theory to verify that the optimized structures correspond to local minima on the energy surface. The vertical excitation energies and oscillator strengths were obtained for the lowest 20 singlet-singlet transitions at the optimized ground state equilibrium geometries by using time dependent density functional theory (TDDFT) using the same hybrid functional and basis set. The low-lying first singlet excited states (S_1) of the dye TMS1 was relaxed using TDDFT to obtain its minimum energy geometry. The difference between the energies of the optimized geometries at first singlet excited state and the ground state was used to calculate the emission. The frequency computations were also carried out on Franck-Condon

excited state of the dyes. All the computations in solvents of different polarities were carried out using the Self Consistent Reaction Field (SCRF) under the Polarizable Continuum Model (PCM). The vertical electronic excitation spectra, including wavelengths, oscillators strengths, and main configuration assignments were systematically investigated using TDDFT with PCM model on the basis of the optimized ground state geometries.

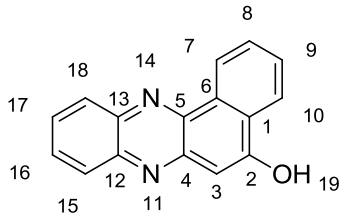
2. Typical synthetic procedure

2.1 General Procedure for the Synthesis of phenazines (4a-h, 5a-h).

The 2-hydroxy 1, 4-naphthoquinone (Lawsone) **1** (1 mmol) or 3-Nonyl-2, 5-dihydroxy 1, 4-qinone (Embellin) **2** (1 mmol) was added slowly to the substituted 1, 2-diaminobenzene derivatives **3a-h** (1 mmol) in water (10 mL) under sonication using an ultrasonic horn (ACE horn, 20 kHz frequency) at 40 % amplitude for 2 min with a 5 sec ON and 5 sec OFF cycle from time t = 0 h. After complete addition (addition time 2 min), the reaction mixture was again exposed to acoustic cavitations (by using ACE ultrasonic horn) for further 4 min, by keeping sonication parameter constant which was second-hand during mixing. After completion of the reaction (TLC), a separated solid was filtered on Buchner funnel, washed well with water, and dried to obtain pure product **(4a-h, 5a-h)**. The temperature of the process was maintained at 30 ± 2^0C by means of supplying water to the jacketed reactor used for the synthesis. Reaction was completed within 20-40 min. Reaction time was estimated by repeating the same reaction condition for three times. The isolated products were subjected to recrystallization (aqueous EtOH) to afford analytically pure products. The structures of the prepared products were assigned on the basis of their spectral data by FTIR, ^{1}HNMR, ^{13}CNMR, Mass spectral and elemental analysis.

2.2 Analytical data of synthesized compounds 4a-4h and 5a-5h

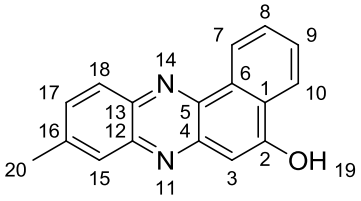
benzo[a]phenazin-5-ol (4a)[1, 2]



Molecular formula: - $C_{16}H_{10}N_2O$; Color: - orange crystals; m.p.: 251-253 ^{0}C; FTIR (KBr, ν_{max} in

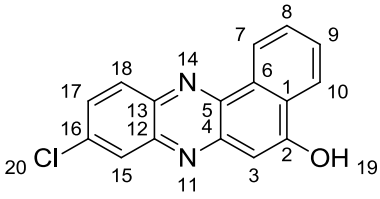
cm^{-1}):- 3347.00 (Ar, -OH str.), 1609.00 (-C=N), 1557.10, 1508.20 (-C=C-);
1HNMR (500 MHz, DMSO, δ, ppm) δ 9.215 (br, s, 1H, -OH), δ 7.213 (s, 1H, H^3), δ 8.837 (m, 2H, J = 8 Hz, $H^{8, 9}$), δ 8.163 (dd, 1H, J = 8 Hz, H^{10}) δ 9.265 (dd, 1H,H^7) δ 7.925 – 7.902 (m, 4H, J = 8.13Hz, $H^{15, 16, 17, 18}$); ESIMS: Calculated for $C_{16}H_{10}N_2O$ + 246.0855, Found 246.0937;

9-methylbenzo[a]phenazin-5-ol (4b) [1, 2]



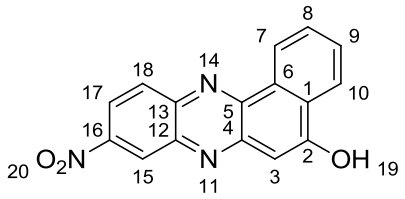
Molecular formula:- $C_{17}H_{12}N_2O$; Color:- orange crystals; m.p.: 255-257 ^{0}C; FTIR (KBr, νmax in cm^{-1}):– 3052.00 (Ar, -CH str.), 2963.60-2923.70 (-CH str., -CH3), 1602.00 (-C=N), 1557.10, 1508.20 (-C=C-); 1HNMR (500 MHz, DMSO, δ, ppm) δ 9.217 (br, s, 1H, -OH), δ 7.14 (s, 1H, H^3), δ 8.113 (m, 2H, J = 8 Hz, $H^{8, 9}$), δ 8.027 (dd, 1H, J = 8 Hz, H^{10}) δ 8.137 (dd, 1H,H^7) δ 7.252 – 7.223 (m, 4H, J = 8.13Hz, $H^{15, 16, 17, 18}$), δ 2.644 (s, 3H, H^{20});
+ESIMS:- Calculated for $C_{17}H_{12}N_2O$ 260.09, Found 260.13;

9-chlorobenzo[a]phenazin-5-ol (4c) [1, 2]



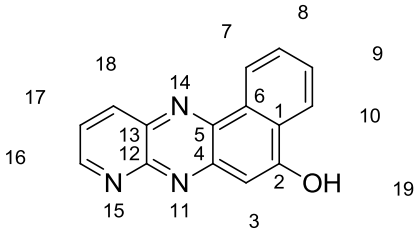
Molecular formula: - $C_{16}H_9ClN_2O$; Color: - yellowish-orange crystals; m.p.: 259-261 ^{0}C; FTIR (KBr, ν_{max} in cm^{-1}):- 3347.00 (Ar, -OH str.), 1621.00 (-C=N), 1559.10, 1507.20 (-C=C-),
1HNMR (500 MHz, DMSO-d6) :- 9.21 (br s,1H,-OH),8.161 (m, 2H, $H^{17,18}$),8.314 (m,1H,H^7),7.90 (m, 4H, $H^{7,8,9,10}$), 7.15 (s,1H, H^3); ESIMS: Calculated for $C_{16}H_{10}N_2O$ + 280.04, Found 280.056;

9-nitrobenzo[a]phenazin-5-ol (4d) [1, 2]



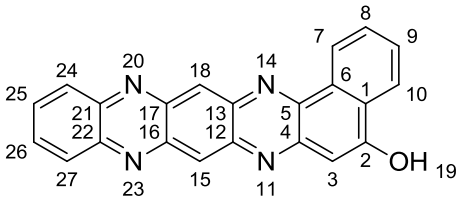
Molecular formula: - $C_{16}H_9N_3O_3$; Color: - yellowish-orange crystals; m.p.: 243-246 ^{0}C; FTIR (KBr, ν_{max} in cm^{-1}):- 3347.00 (Ar, -OH str.), 1621.00 (-C=N), 1559.10, 1507.20 (-C=C-),
1HNMR (DMSO) :- 9.583) (br,d,1H,-OH^{19}) d 8.921 (s,1H, H^{15}), 8.407 (m,1H, H^{17}), 7.963 (m,1H,H^{18}), 7.613 (m,4H,$H^{7,8,9,10}$), 7.117 (s,1H,),
ESIMS: Calculated for $C_{16}H_{10}N_2O$ + 291.06, Found 291.056;

Benzo[f]pyrido[2,3-b]quinoxalin-5-ol (4e)



Molecular formula: - $C_{15}H_9N_3O$; Color: - dark red crystals; m.p.: 221-223 ^{0}C;
Elemental Analysis: - Calculated: C (72.87 %), H (3.67 %), N (16.99 %), and O (6.47 %); Found: C (72.52%), H (3.71%), N (17.13%), O (6.22%);
FTIR (KBr, ν_{max} in cm^{-1}):- 3038.80 (Ar, -CH str.); 2969.40-2924.50 (-CH str., -CH3); 1671.40 (-C=O), 1610 and 1602.00 (-C=N), 1561.20, 1528.60 (-C=C-),
1HNMR (DMSO) :- δ 9.641 (br,s,1H,-OH^{19}), δ 7.582 (s,1H, H^3), δ 7.936 (m,2H,$H^{8,9}$), δ 8.307 (m,1H, H^7) δ 8.135 (m,1H,H^{10}) , δ 8.572 (t,1H,H^{18}), δ 8.315 (m,1H,H^{17}), δ 8.527 (d,1H,H^{18}) ; +ESIMS:Calculated for $C_{15}H_9N_3O$ + 247.07, Found 247.12;

Benzo[a]quinoxalino[2,3-i]phenazin-5-ol (4f)

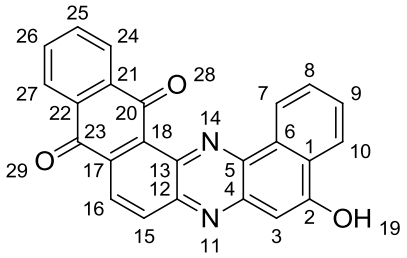


Molecular formula: - $C_{22}H_{12}N_4O$; Color: - dark green crystals; m.p.: 281-283 ^{0}C;

1HNMR (DMSO-d6):- δ 9.421(br, s, 1H, -OH^{19}), δ 8.325 (m, 1H, H^7), δ 8.172 (m, 1H, H^{10}), 7.843-7.81 (m, 2H, H^{8,9}), δ 7.234 (s,1H, H^3), δ 8.864 (s,1H, H^{18}), δ 8.861 (s,1H, H^{15}), δ 8.183-8.103 (m, 4H, H^{24,25,26,27}) ;

Elemental Analysis: - Calculated: C (72.87 %), H (3.67 %), N (16.99 %), and O (6.47 %); Found: C (72.52%), H (3.71%), N (17.13%), O (6.22%);

5-Hydroxybenzo[a]naphtho[2,3-j]phenazine-10,15-dione (4g)

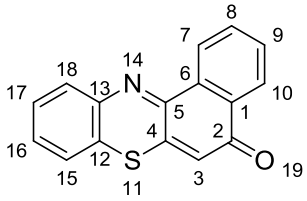


Molecular formula: - $C_{22}H_{12}N_4O$; Color: - dark blue crystals; m.p.: 301-305 ^{0}C;

1HNMR (DMSO-d6):- 1HNMR (500 MHz, DMSO, δ, ppm) δ 10.105 (br, s, 1H, -OH), δ 7.531 (s, 1H, H^3), δ 8.849 (m, 2H, J = 8 Hz, H^{8,9}), δ 8.602 (dd, 1H, J = 8 Hz, H^{10}) δ 8.965 (dd, 1H,H^7) δ 8.735 – 8.702 (dd, 2H, J = 8.13Hz, H^{15,16}); δ 7.794-7.763 (m,4H,H^{24,25,26,27})

Elemental Analysis: - Calculated: C (72.87 %), H (3.67 %), N (16.99 %), and O (6.47 %); Found: C (72.52%), H (3.71%), N (17.13%), O (6.22%);

5H-Benzo[a]phenothiazin-5-one (4H)



Molecular formula: - $C_{22}H_{12}N_4O$; Color: - dark blue crystals; m.p.: 301-305 ^{0}C;

1HNMR (DMSO-d6):- δ 7.351-7.318 (m, 4H, H^{15,16,17,18}), δ 7.981 (s,1H,H^3), 7.526-7.493

(m,4H,$H^{7,8,9,10}$)

Elemental Analysis: - Calculated: C (72.87 %), H (3.67 %), N (16.99 %), and O (6.47 %); Found: C (72.52%), H (3.71%), N (17.13%), O (6.22%);

3. Computational data of the synthesized compounds (Figures S1-S24)

Figure S1: Calculated energy of HOMO (H), LUMO (L) and band gap (H-L) the dye 4e in different polarity of the solvents

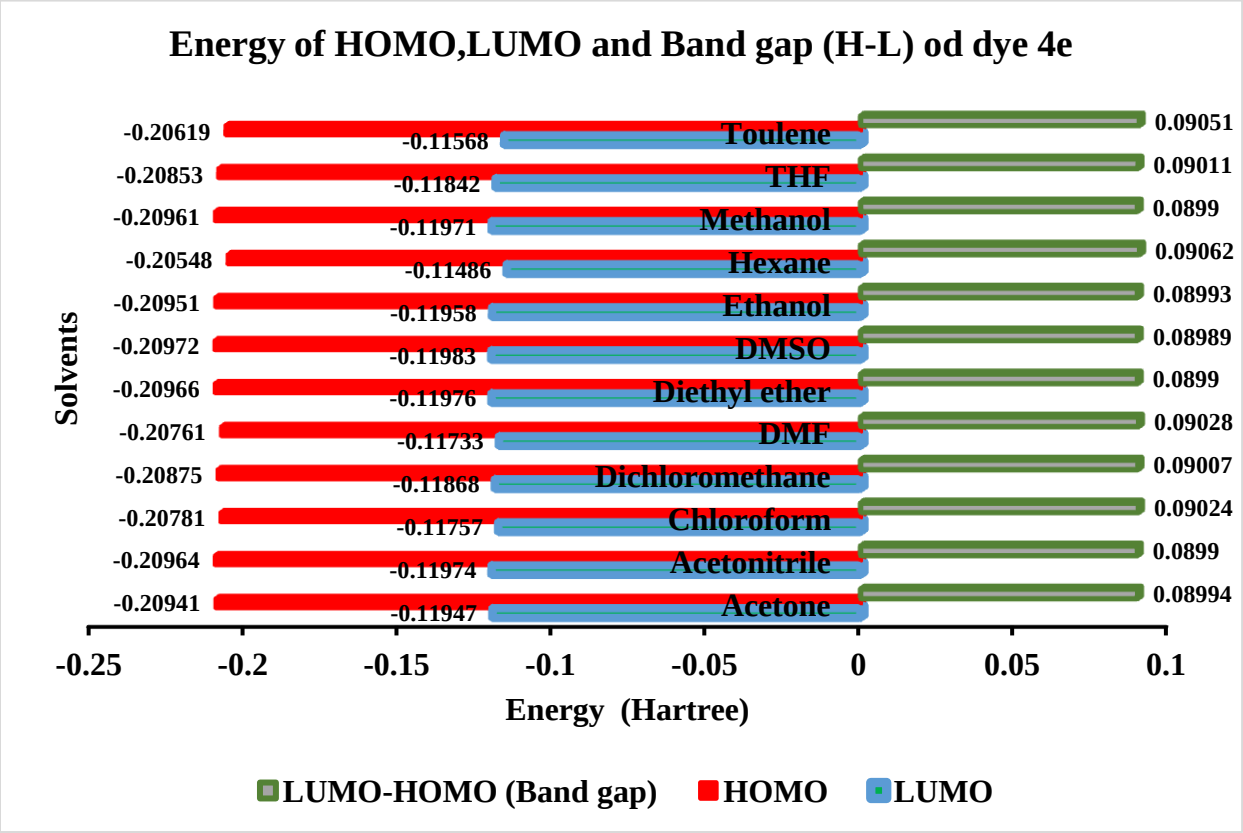


Figure S2: Calculated energy of HOMO (H), LUMO (L) and band gap (H-L) the dye 4f in

different polarity of the solvents

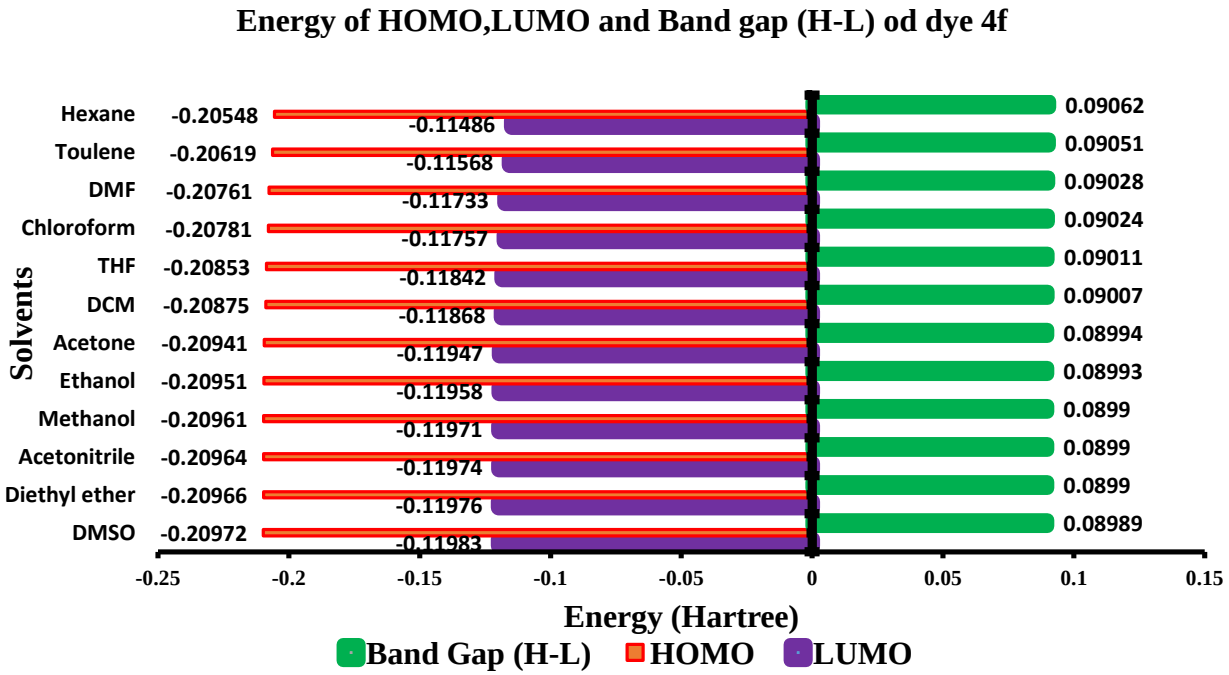


Figure S3: Calculated energy of HOMO (H), LUMO (L) and band gap (H-L) the dye 4g in different polarity of the solvents

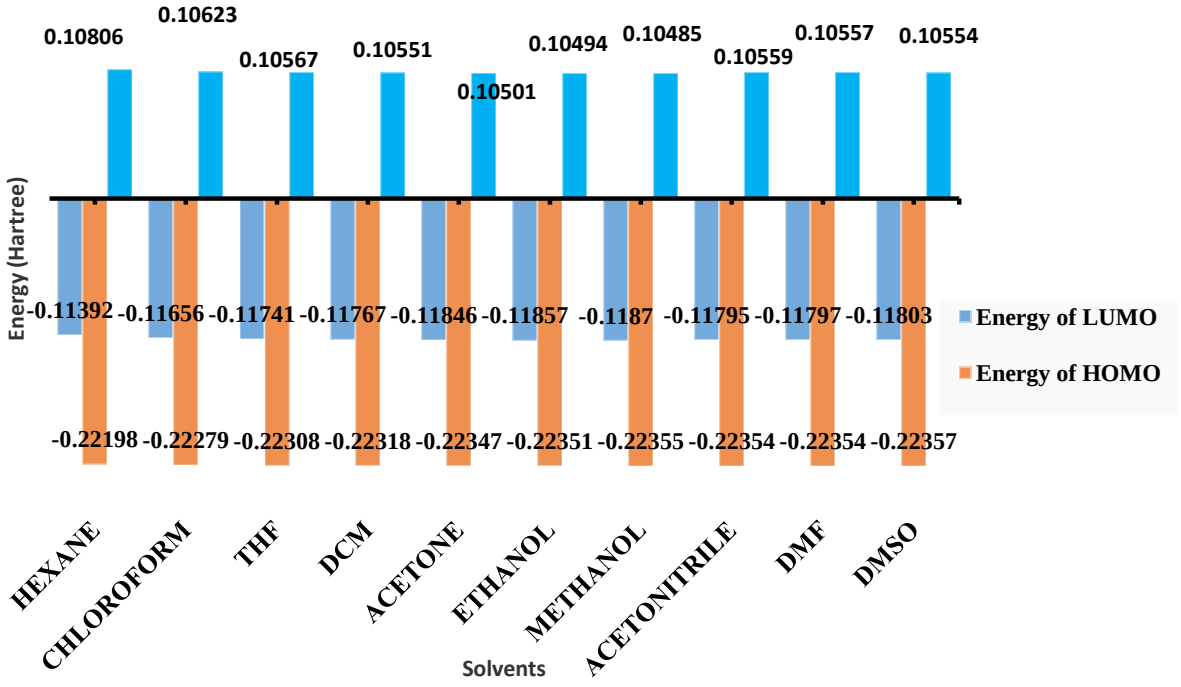


Figure S4: Calculated energy of HOMO (H), LUMO (L) and band gap (H-L) the dye 4h in different polarity of the solvents

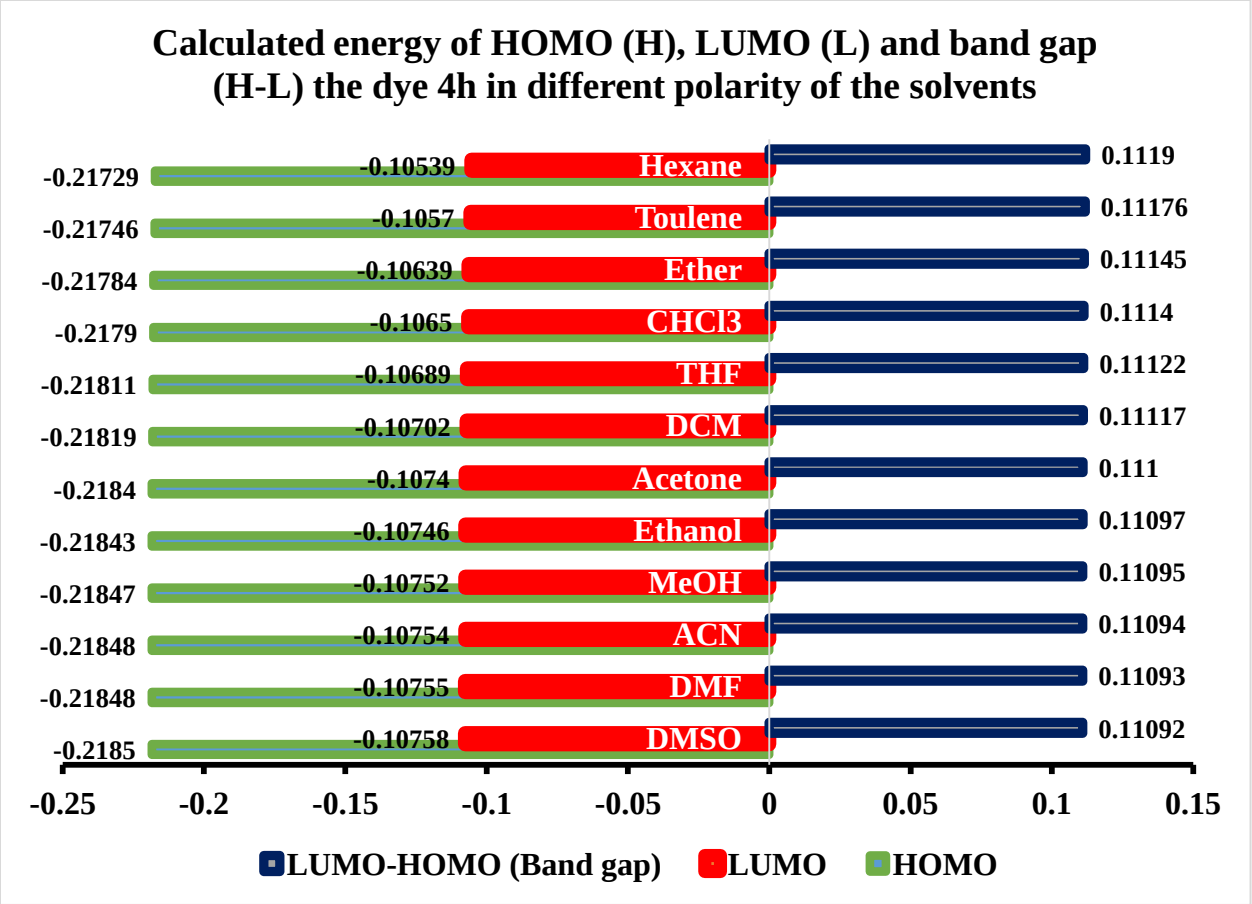

Calculated energy of HOMO (H), LUMO (L) and band gap (H-L) the dye 4h in different polarity of the solvents
-0.21729
-0.10539
Hexane
0.1119
-0.21746
-0.1057
Toulene
0.11176
-0.21784
-0.10639
Ether
0.11145
-0.2179
-0.1065
CHCl3
0.1114
-0.21811
-0.10689
THF
0.11122
-0.21819
-0.10702
DCM
0.11117
-0.2184
-0.1074
Acetone
0.111
-0.21843
-0.10746
Ethanol
0.11097
-0.21847
-0.10752
MeOH
0.11095
-0.21848
-0.10754
ACN
0.11094
-0.21848
-0.10755
DMF
0.11093
-0.2185
-0.10758
DMSO
0.11092
-0.25
-0.2
-0.15
-0.1
-0.05
0
0.05
0.1
0.15
LUMO-HOMO (Band gap)
LUMO
HOMO

Figure S5: Calculated dipole moment of the dye 4e in different polarity of the solvents

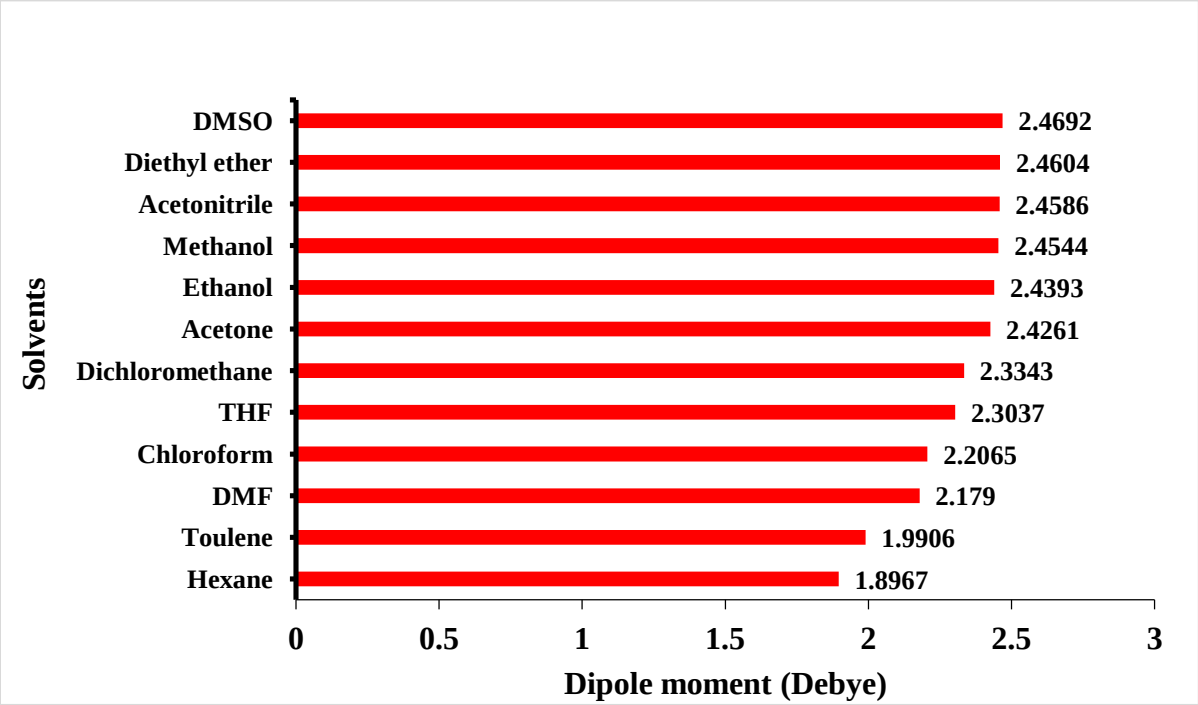


Figure S6: Calculated dipole moment of the dye 4f in the different polarity of the solvents

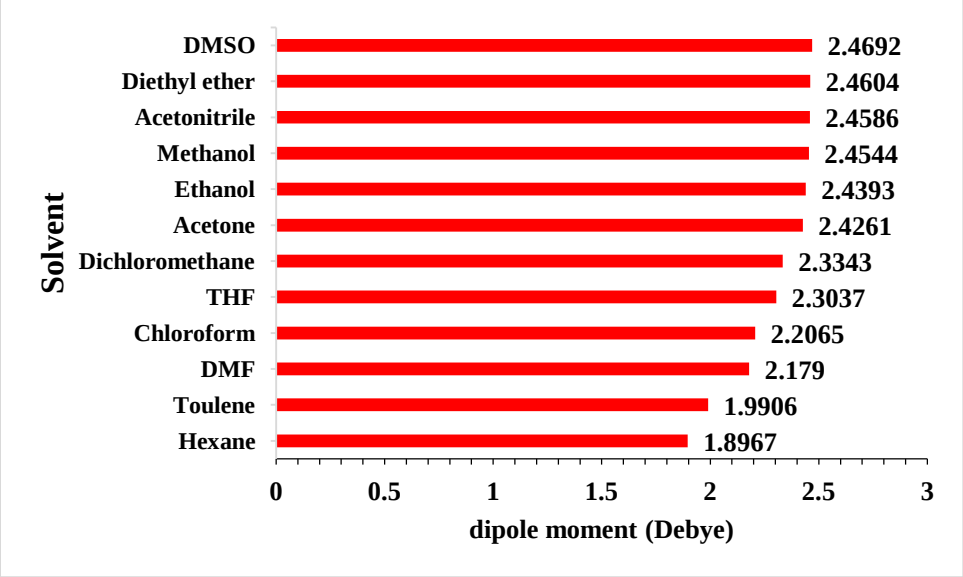


Figure S7: Calculated dipole moment of the dye 4g in the different polarity of the solvents

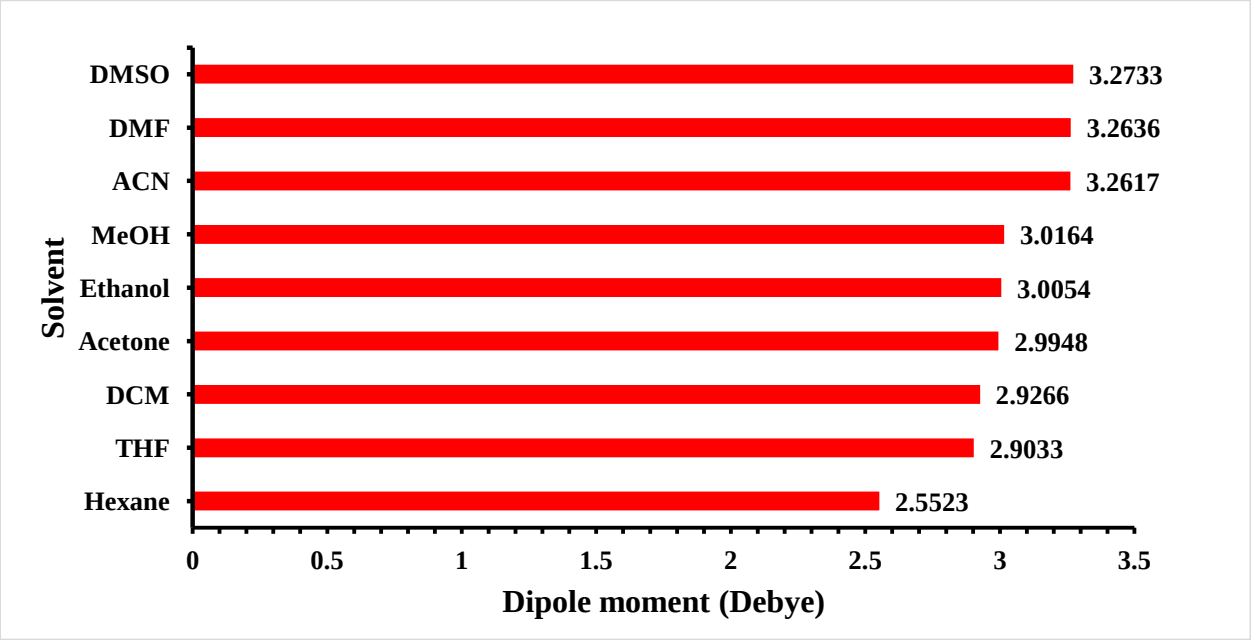


Figure S8: Calculated dipole moment of the dye 4h in the different polarity of the solvents

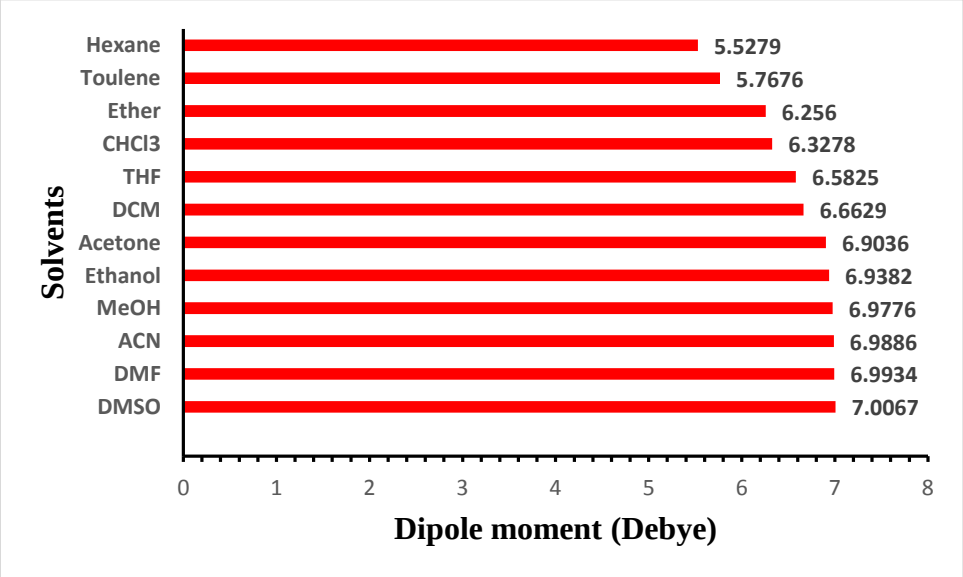


Figure S9: Calculated ground state energy of the dye 4e in the different polarity of the solvents

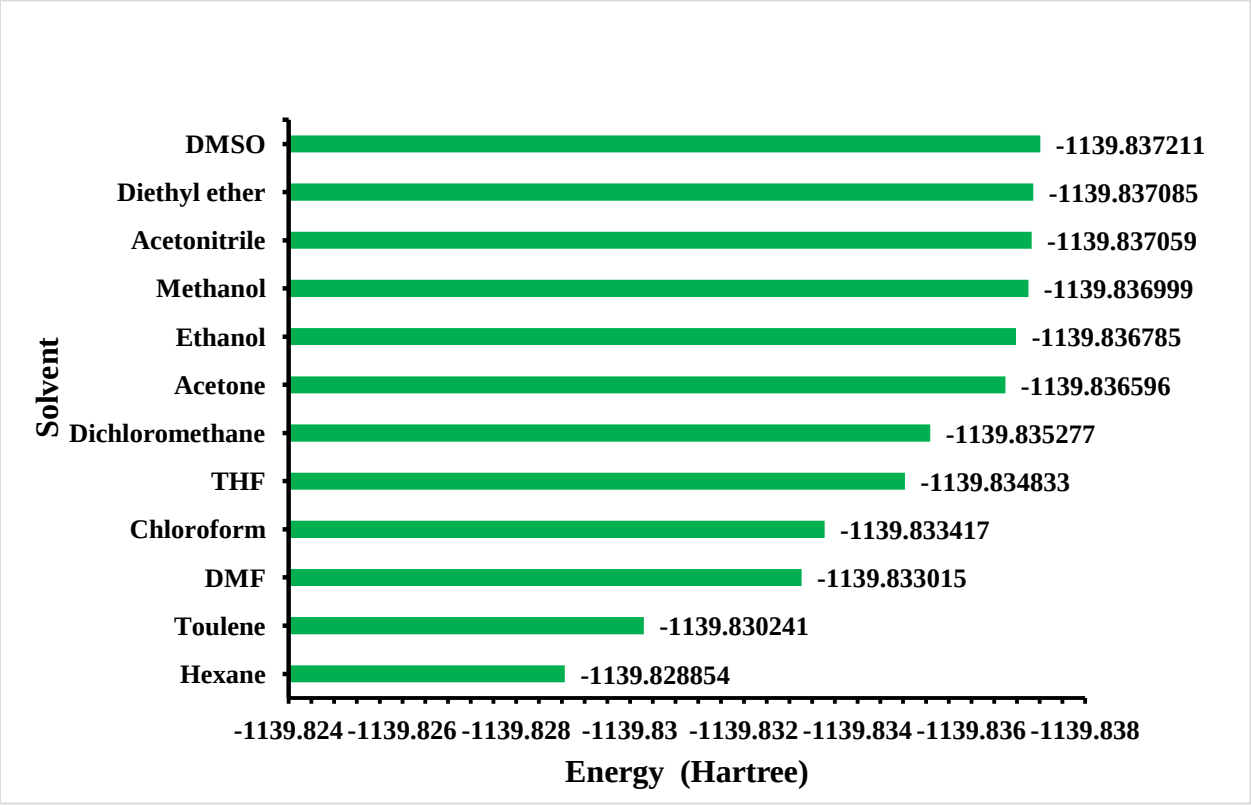


Figure S10: Calculated ground state energy of the dye 4f in the different polarity of the solvents

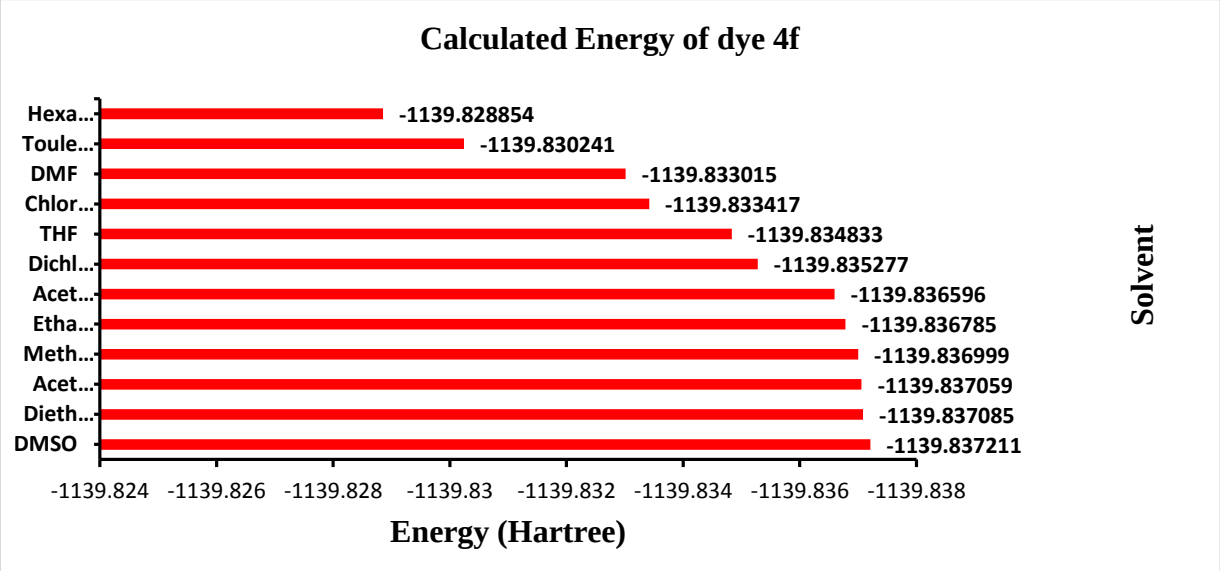


Figure S11: Calculated ground state energy of the dye 4g in the different polarity of the solvents

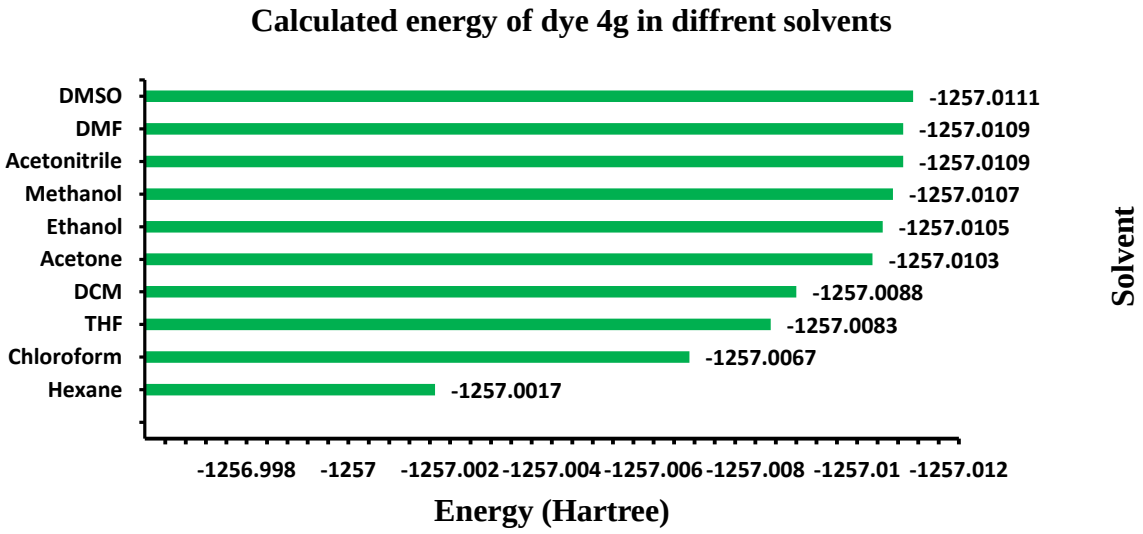


Figure S12: Calculated ground state energy of the dye 4h in the different polarity of the solvents

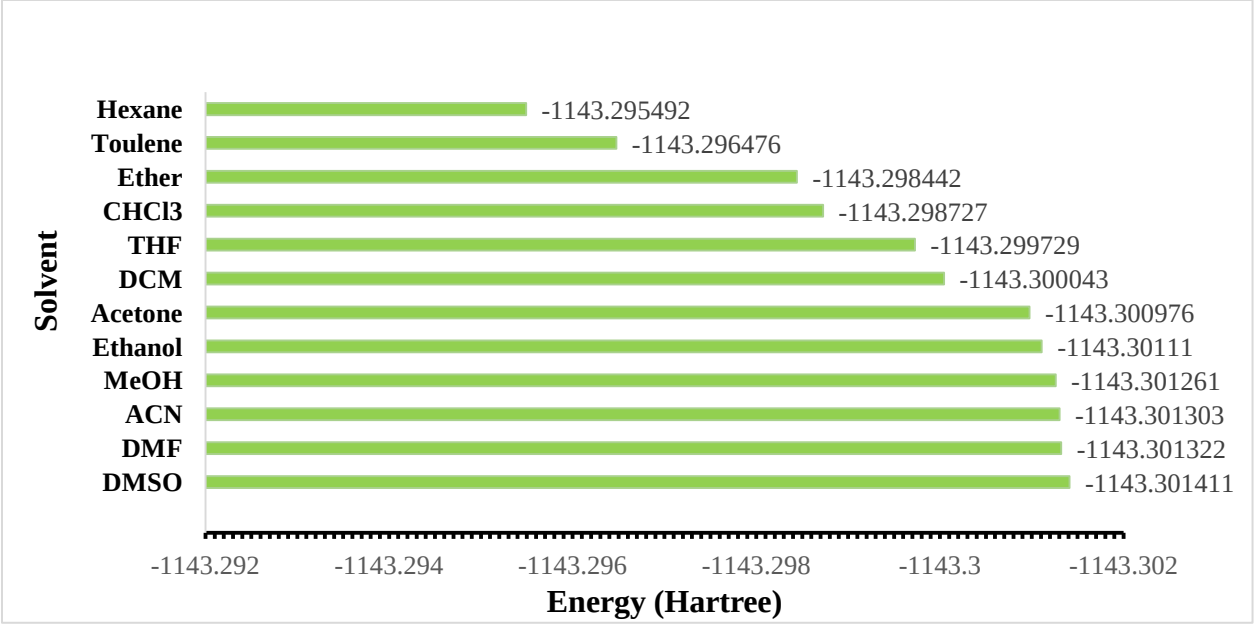


Figure S13: calculated ground state dipole moment of the dye 4f in different solvents

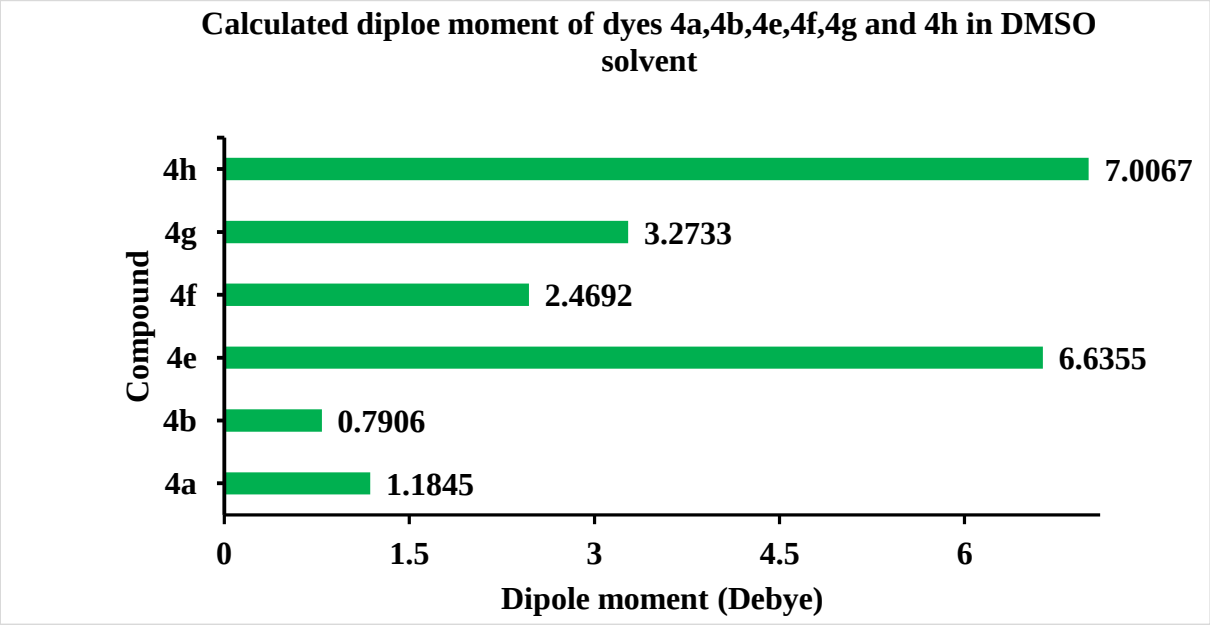


Figure S14: calculated ground state energy of the dye 4a,4b,4e,4f4g and 4h in different solvents

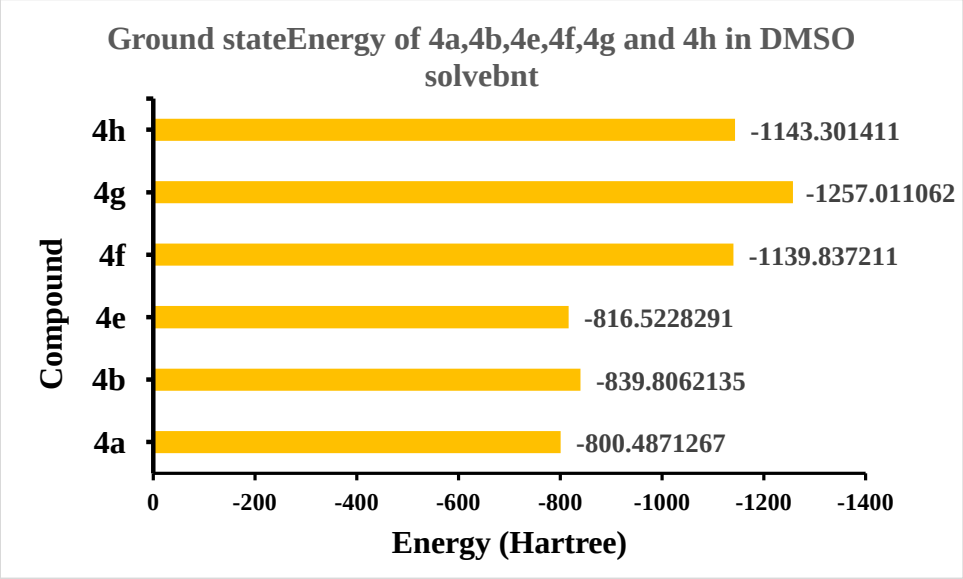


Figure S15: optimized geometry of the dye 4g and 4h in DMSO solvent

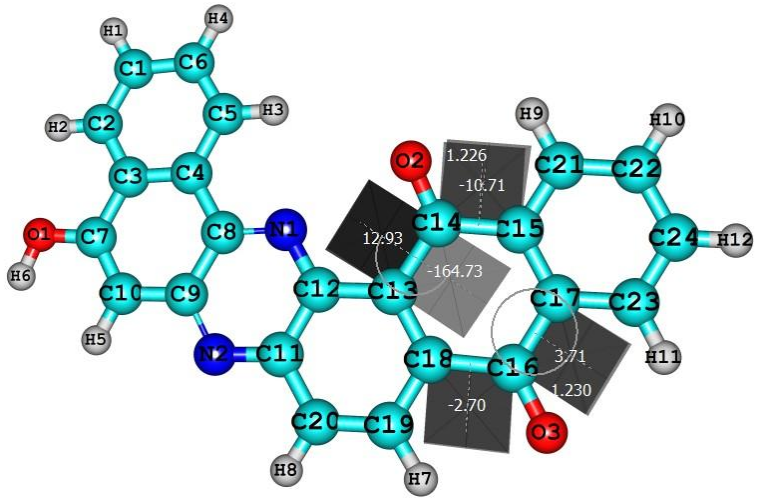


Figure S16: Photophysical properties of dye 4e: Experimental and theoretical

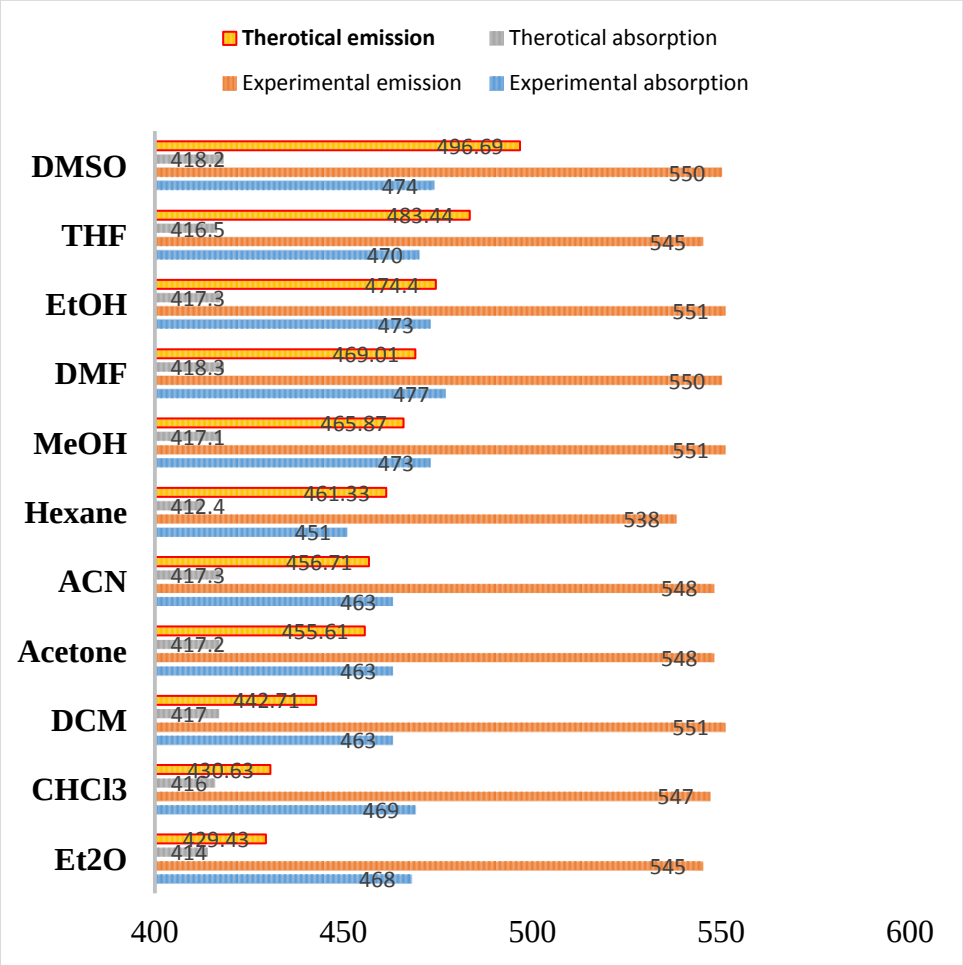


Table S1: optimized geometry bond angle, bond length, dihedral angle of the dye 4g in different polarity of solvents

Solvents	Inter atomic distance		Bond angle		Dihedral angle	
	Atoms	Å	Atoms	^{o}		
DMSO	14C-2O	1.22619	13C-14C-2O	123.084	12C-13C-14C-2O	12.930
	14C-3O	1.22988	9C-2N-11C	117.579	18C-13C-14C-2O	164.73
DMF	14C-2O	1.22617	13C-14C-2O	123.090	12C-13C-14C-2O	12.859
	14C-3O	1.22986	9C-2N-11C	117.579	18C-13C-14C-2O	164.820
ACN	14C-2O	1.22617	13C-14C-2O	123.090	12C-13C-14C-2O	12.843
	14C-3O	1.22986	9C-2N-11C	117.578	18C-13C-14C-2O	164.837
MeOH	14C-2O	1.22618	13C-14C-2O	123.320	12C-13C-14C-2O	4.832
	14C-3O	1.23002	9C-2N-11C	117.617	18C-13C-14C-2O	174.371
Ethanol	14C-2O	1.22612	13C-14C-2O	123.324	12C-13C-14C-2O	4.815
	14C-3O	1.22998	9C-2N-11C	117.613	18C-13C-14C-2O	174.390
Acetone	14C-2O	1.22606	13C-14C-2O	123.327	12C-13C-14C-2O	4.751
	14C-3O	1.22995	9C-2N-11C	117.609	18C-13C-14C-2O	174.462
DCM	14C-2O	1.22570	13C-14C-2O	123.352	12C-13C-14C-2O	4.722
	14C-3O	1.22970	9C-2N-11C	117.583	18C-13C-14C-2O	174.484
THF	14C-2O	1.22558	13C-14C-2O	123.359	12C-13C-14C-2O	4.742
	14C-3O	1.22962	9C-2N-11C	117.575	18C-13C-14C-2O	174.459
$CHCl_3$	14C-2O	1.22522	13C-14C-2O	123.382	12C-13C-14C-2O	4.794
	14C-3O	1.22933	9C-2N-11C	117.548	18C-13C-14C-2O	174.385
Hexane	14C-2O	1.22410	13C-14C-2O	123.454	12C-13C-14C-2O	4.768
	14C-3O	1.22836	9C-2N-11C	117.464	18C-13C-14C-2O	174.402

Table S2. Calculated ground state energy of dyes **4e** in different polarity of solvent

Solvents	Energy	Dipole moment	Energy of HOMO		Energy of LUMO		Band Gap	
	Hartree	Debye	Hartree	eV	Hartree	eV	Hartree	eV
DMSO	-816.5228	6.6355	-0.2213	-6.0229	-0.09527	-2.5924	-0.1261	3.4305
DMF	-816.5227	6.6147	-0.2213	-6.0216	-0.0952	-2.5905	-0.1261	3.4311
Acetonitrile	-816.5226	6.6104	-0.2213	-6.02133	-0.09518	-2.5899	-0.1261	3.4313
Methanol	-816.5226	6.6004	-0.2213	-6.0207	-0.09515	-2.5891	-0.1261	3.4318
Ethanol	-816.5223	6.5651	-0.2212	-6.0186	-0.09503	-2.5889	-0.1262	3.4296
Acetone	-816.5221	6.5339	-0.2211	-6.0169	-0.09493	-2.58318	-0.1262	3.4338
DCM	-816.5206	6.3188	-0.2206	-6.0042	-0.09421	-2.5636	-0.1264	3.4406
THF	-816.5201	6.2473	-0.2205	-6.0001	-0.09397	-2.5571	-0.1265	3.4431
CHCl3	-816.5184	6.0226	-0.22	-5.9871	-0.09322	-2.5366	-0.1268	3.4504
Et_2O	-816.518	5.9598	-0.2199	-5.9837	-0.09302	-2.5312	-0.1268	3.4525
Toluene	-816.5149	5.5373	-0.2191	-5.9612	-0.09167	-2.4944	-0.1274	3.4667
Hexane	-816.5134	5.3336	-0.2187	-5.9514	-0.09105	-2.4776	-0.1276	3.4738

Table S3. Calculated ground state energy of dyes **4f** in different polarity of solvent

Solvents	Energy	Dipole moment	Energy of LUMO		Energy of HOMO		Band Gap	
	Hartree	Debye	Hartree	eV	Hartree	eV	Hartree	eV
DMSO	-1139.8372	2.4692	-0.1198	-3.2607	-0.2097	-5.7068	0.0899	2.4460
Et_2O	-1139.8371	2.4604	-0.1198	-3.2588	-0.2097	-5.7051	0.0899	2.4463
Acetonitrile	-1139.8371	2.4586	-0.1197	-3.2583	-0.2096	-5.7046	0.0899	2.4463
Methanol	-1139.837	2.4544	-0.1197	-3.2575	-0.2096	-5.7038	0.0899	2.4463
Ethanol	-1139.8368	2.4393	-0.1196	-3.2539	-0.2095	-5.7011	0.0899	2.4471
Acetone	-1139.8366	2.4261	-0.1195	-3.2509	-0.2094	-5.6983	0.0899	2.4474
DCM	-1139.8353	2.3343	-0.1187	-3.2294	-0.2088	-5.6804	0.0901	2.4509
THF	-1139.8348	2.3037	-0.1184	-3.2224	-0.2085	-5.6744	0.0901	2.4520
CHCL3	-1139.8334	2.2065	-0.1176	-3.1992	-0.2078	-5.6548	0.0902	2.4556
DMF	-1139.833	2.179	-0.1173	-3.1927	-0.2076	-5.6494	0.0903	2.4566
Toluene	-1139.8302	1.9906	-0.1157	-3.1478	-0.2062	-5.6107	0.0905	2.4629
Hexane	-1139.8289	1.8967	-0.1149	-3.1255	-0.2055	-5.5914	0.0906	2.4659

Table S4. Calculated ground state energy of dyes **4g** in different polarity of solvent

Solvent	Energy	Dipole Moment	Energy of HOMO		Energy of LUMO		Band gap	
	Hartree	Debye	Hartree	eV	Hartree	eV	Hartree	eV
DMSO	-1257.0111	3.2733	-0.2236	-6.0836	-0.1180	-3.2118	0.1055	2.8719
DMF	-1257.0109	3.2636	-0.2235	-6.0828	-0.1180	-3.2101	0.1056	2.8727
ACN	-1257.0109	3.2617	-0.2235	-6.0828	-0.1180	-3.2096	0.1056	2.8732
MeOH	-1257.0107	3.0164	-0.2236	-6.0831	-0.1187	-3.2300	0.1049	2.8531
Ethanol	-1257.0105	3.0054	-0.2235	-6.0820	-0.1186	-3.2265	0.1049	2.8556
Acetone	-1257.0103	2.9948	-0.2235	-6.0809	-0.1185	-3.2235	0.1050	2.8575
DCM	-1257.0088	2.9266	-0.2232	-6.0730	-0.1177	-3.2020	0.1055	2.8711
THF	-1257.0083	2.9033	-0.2231	-6.0703	-0.1174	-3.1949	0.1057	2.8754
Hexane	-1257.0017	2.5523	-0.2220	-6.0404	-0.1139	-3.0999	0.1081	2.9405

Table S5. Calculated ground state energy of dyes **4h** in different polarity of solvent

Solvent	Energy	Dipole Moment	HOMO		LUMO		HOMO-LUMO	
	Hartree	Debye	Hartree	eV	Hartree	eV	Hartree	eV
DMSO	-1143.3014	7.0067	-0.2185	-5.9457	-0.1076	-2.9274	0.1109	3.0183
DMF	-1143.3013	6.9934	-0.2185	-5.9451	-0.1076	-2.9266	0.1109	3.0186
ACN	-1143.3013	6.9886	-0.2185	-5.9451	-0.1075	-2.9263	0.1109	3.0188
MeOH	-1143.3013	6.9776	-0.2185	-5.9449	-0.1075	-2.9258	0.1110	3.0191
Ethanol	-1143.3011	6.9382	-0.2184	-5.9438	-0.1075	-2.9241	0.1110	3.0196
Acetone	-1143.3010	6.9036	-0.2184	-5.9430	-0.1074	-2.9225	0.1110	3.0205
DCM	-1143.3000	6.6629	-0.2182	-5.9373	-0.1070	-2.9122	0.1112	3.0251
THF	-1143.2997	6.5825	-0.2181	-5.9351	-0.1069	-2.9086	0.1112	3.0265
$CHCl_3$	-1143.2987	6.3278	-0.2179	-5.9294	-0.1065	-2.8980	0.1114	3.0313
Ether	-1143.2984	6.2560	-0.2178	-5.9277	-0.1064	-2.8950	0.1115	3.0327
Toluene	-1143.2965	5.7676	-0.2175	-5.9174	-0.1057	-2.8762	0.1118	3.0411
Hexane	-1143.2955	5.5279	-0.2173	-5.9128	-0.1054	-2.8678	0.1119	3.0450

Table S6. Computed vertical excitation, oscillator strength, % orbital contribution of the dye **4e** in different solvents.

Solvent	Orbital	Orbital Coefficient	Vertical Excitation (nm)	eV	% Orbital contribution	Oscillator strength
DMF	H-> L	0.6917	418.26	2.9643	95.70	0.2393
DMSO	H-> L	0.6916	418.20	2.9647	95.65	0.2374
Ethanol	H-> L	0.6909	417.31	2.9710	95.47	0.2276
ACN	H-> L	0.6907	417.30	2.9711	95.40	0.2252
Acetone	H-> L	0.6909	417.17	2.9721	95.46	0.2270
Methanol	H-> L	0.6905	417.08	2.9727	95.35	0.2225
DCM	H-> L	0.6917	417.02	2.9731	95.70	0.2356
THF	H-> L	0.6915	416.53	2.9766	95.64	0.2320
Chloroform	H-> L	0.6920	416.03	2.9802	95.77	0.2363
Et_2O	H-> L	0.6909	414.80	2.9890	95.47	0.2209
Toluene	H-> L	0.6925	414.46	2.9914	95.90	0.2392
Hexane	H-> L	0.6911	412.41	3.0063	95.52	0.2188

Table S7. Computed vertical excitation, oscillator strength, % orbital contribution of the dye **4g** in different solvents.

Solvent	Orbital	Orbital Coefficient	Vertical Excitation (nm)	eV	% Orbital contribution	Oscillator strength
MeOH	H -> L	0.6949	508.44	2.4385	96.58	0.1691
EtOH	H -> L	0.6952	508.36	2.4389	96.66	0.1733
Acetone	H -> L	0.6952	507.96	2.4408	96.67	0.1732
DCM	H -> L	0.6958	505.92	2.4507	96.82	0.1822
DMSO	H -> L	0.6765	504.44	2.4578	91.54	0.1774
DMF	H -> L	0.6771	504.40	2.4581	91.70	0.1792
ACN	H -> L	0.6775	503.47	2.4626	91.81	0.1694
CHCl3	H -> L	0.6958	502.24	2.4686	96.84	0.1864
Hexane	H -> L	0.6951	491.94	2.5203	96.62	0.1811

Table S8. Computed vertical excitation, oscillator strength, % orbital contribution of the dye **4h** in different solvents.

Solvent	Orbital	Orbital Coefficient	Vertical Excitation (nm)	eV	% Orbital contribution	Oscillator strength
DMF	H -> L	0.6811	466.09	2.6601	92.77	0.2817
DMSO	H -> L	0.6808	465.86	2.6614	92.71	0.2791
DCM	H -> L	0.6810	464.64	2.6684	92.76	0.2805
Ethanol	H -> L	0.6795	464.45	2.6695	92.33	0.2683
ACN	H -> L	0.6790	464.29	2.6704	92.21	0.2649
Acetone	H -> L	0.6794	464.26	2.6706	92.32	0.2678
THF	H -> L	0.6806	463.94	2.6724	92.65	0.2769
Methanol	H -> L	0.6786	463.91	2.6726	92.10	0.2618
Chloroform	H -> L	0.6816	463.77	2.6734	92.91	0.2842
Toluene	H -> L	0.6828	462.68	2.6797	93.23	0.2920
Et2O	H -> L	0.6795	461.65	2.6857	92.34	0.2664
Hexane	H -> L	0.6804	459.60	2.6976	92.58	0.2695

References:

1. Ahmad S., Gadari R., Masoud A., Helvicta Chimica Acta, **2014**, *97*, 228-236.
2. Kaupp G., Naimi-Jamal, Reza M., Eur. J. Org. Chem., **2002,** *8*, 1368-1373.