Supplementary Information for New Journal of Chemistry

Meso-Carbazole decorated BODIPYs - an Electron Donor-Acceptor System with Excellent FluoroSolvato/Vapochromic Behavior, Aggregation-Induced Emission and Antileishmanial Activity

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Characterization Data

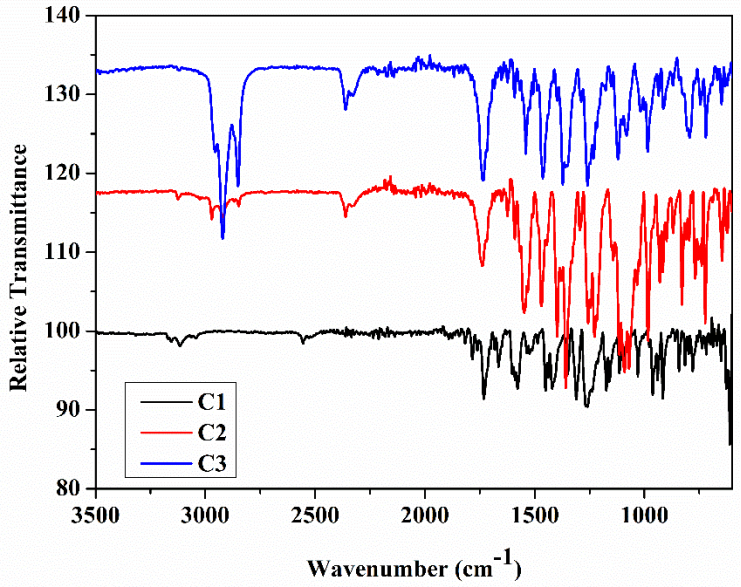


Figure S1. FTIR spectra of *meso*-carbazole substituted BODIPY (**C1**) and the corresponding brominated derivatives (**C2** and **C3**) at room temperature.

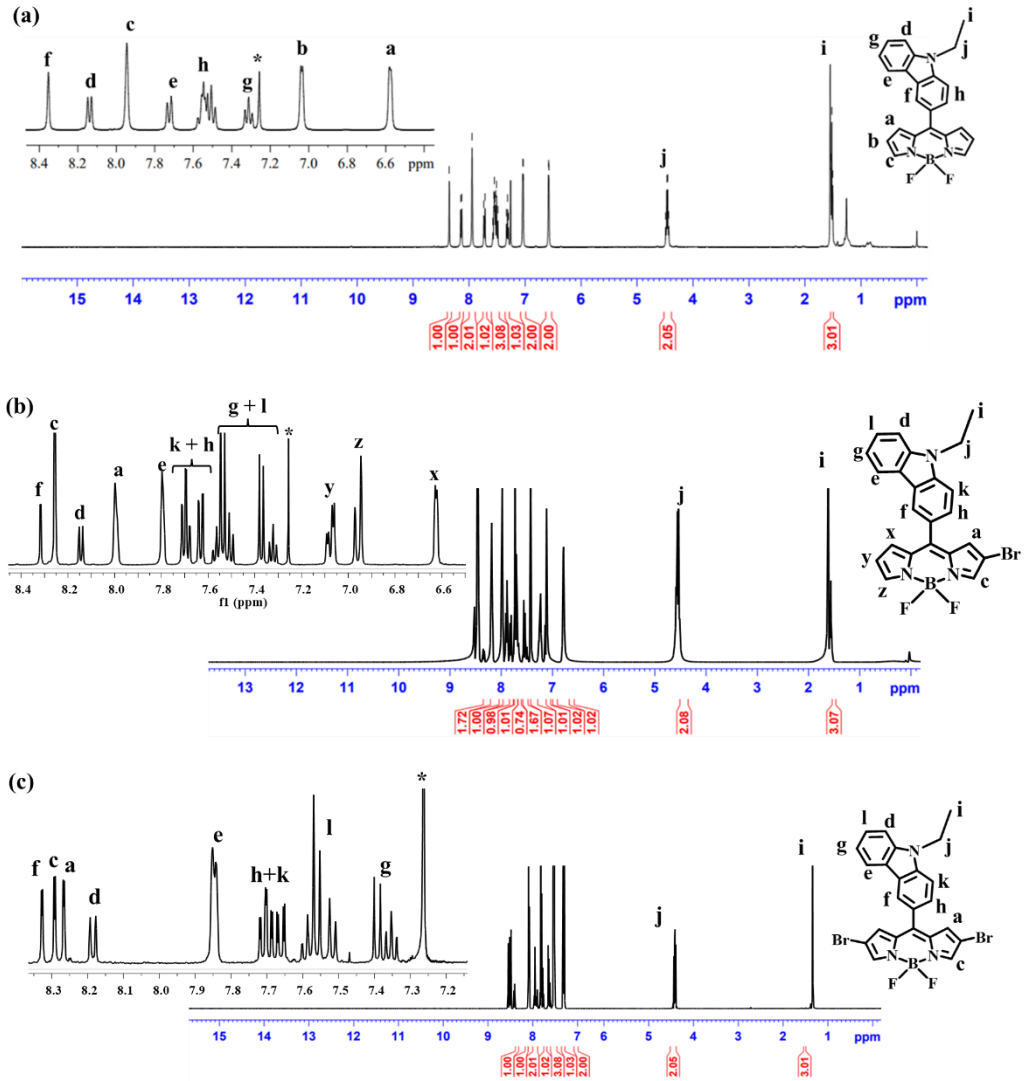


Figure S2. ^{1}H NMR spectra (500 MHz, $CDCl_3$) of (a) **C1**, (b) **C2** and (c) **C3** recorded at room temperature. Peaks marked with an asterisk (*) at 7.26 ppm indicate the residual $CDCl_3$.

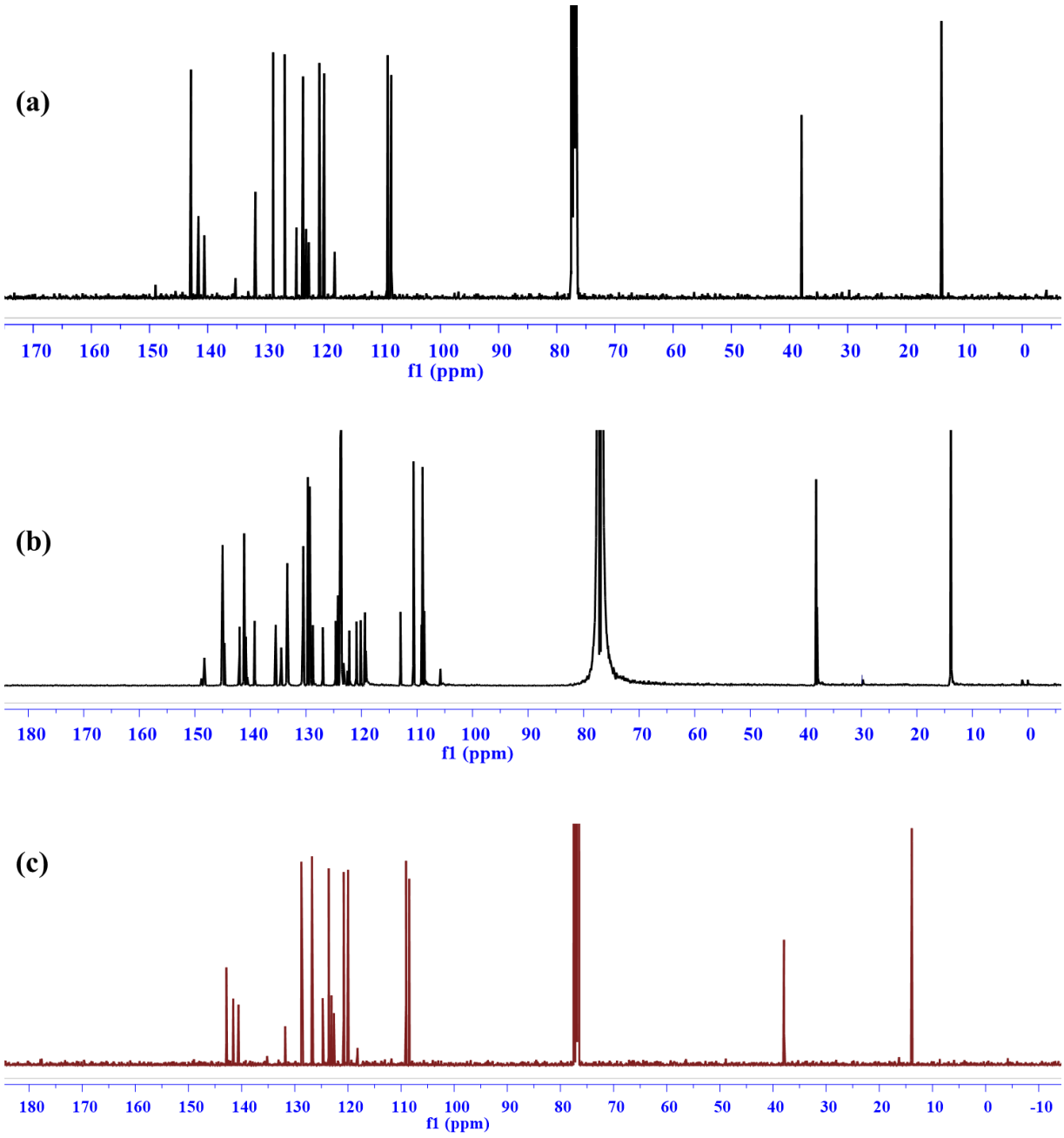
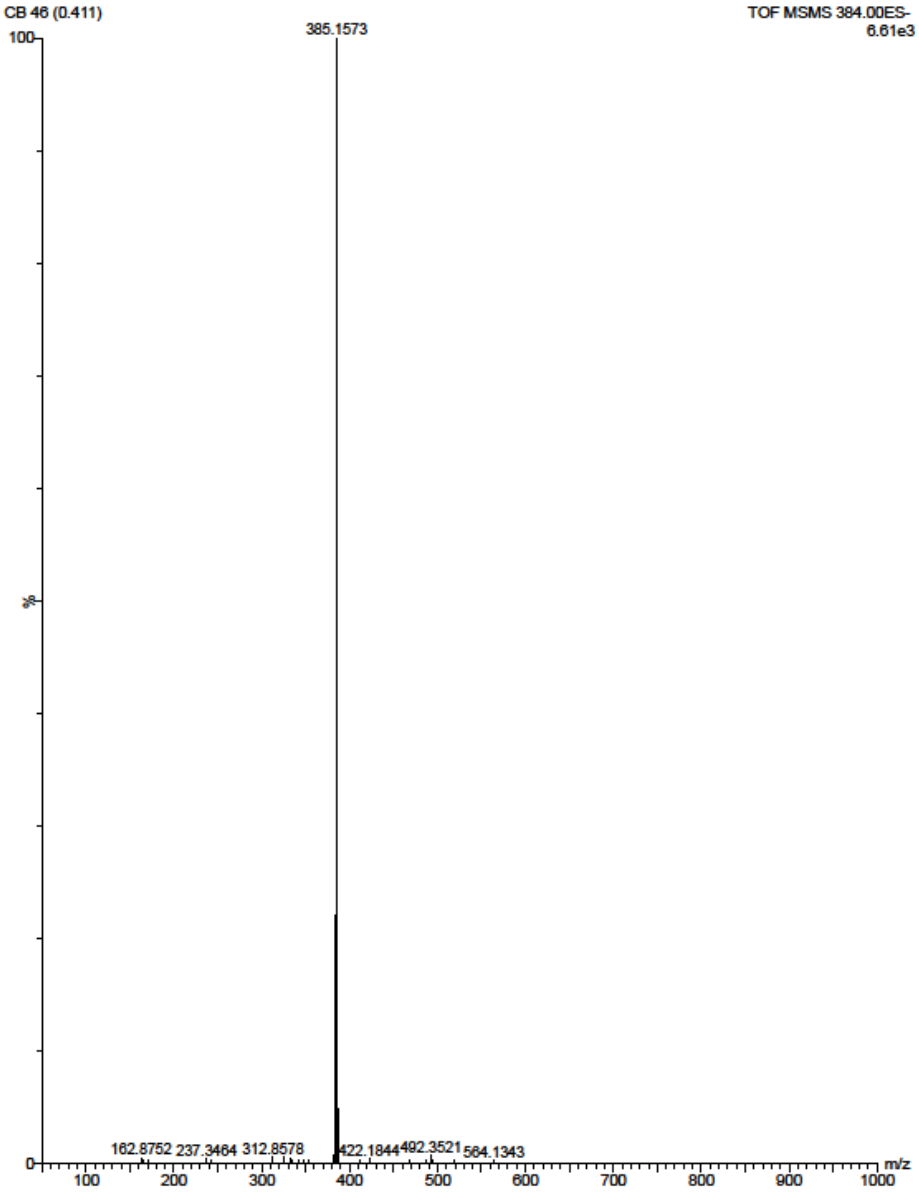


Figure S3. ^{13}C NMR spectra (500 MHz, $CDCl_3$) of (a) **C1** (b) **C2** and (c) **C3** recorded at room temperature.

(a)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100
%
0
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237.3464
312.8578
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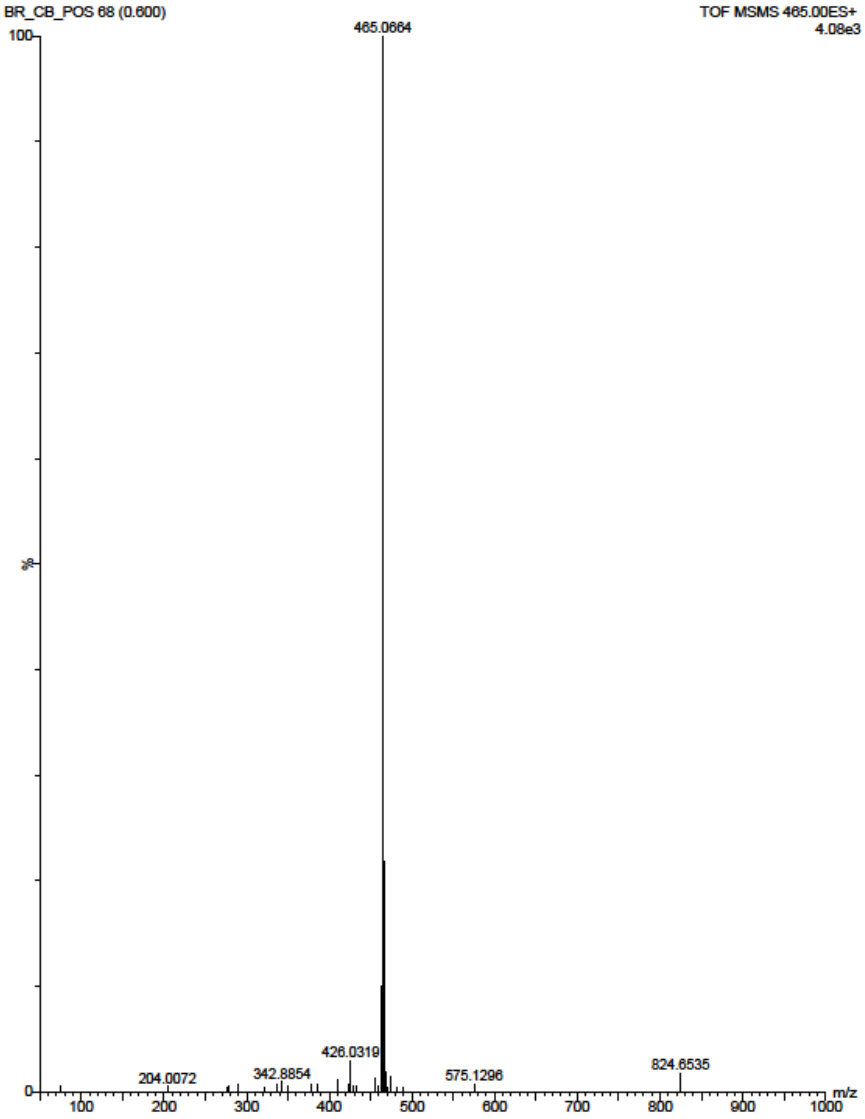
492.3521
564.1343
100
200
300
400
500
600
700
800
900
1000
m/z

(b)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200
300
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500
600
700
800
900
1000
m/z

(c)

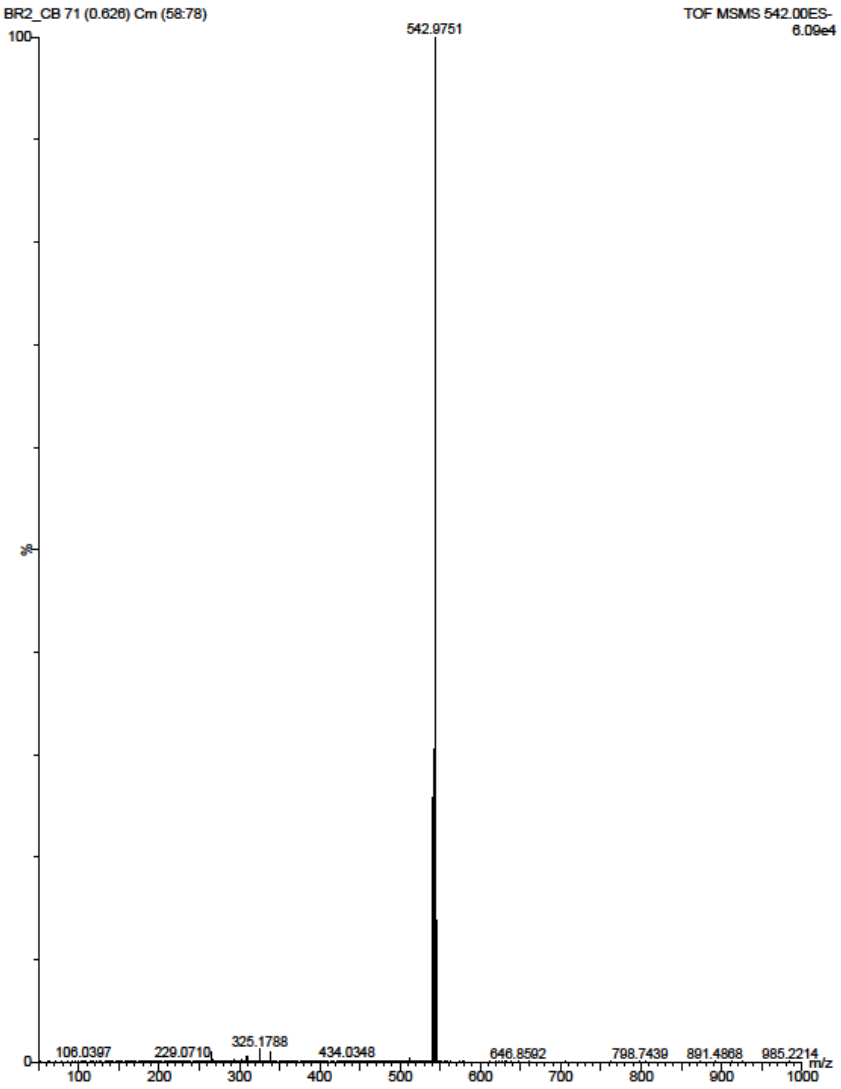


Figure S4. HRMS mass spectra of *meso*-carbazole substituted BODIPYs (a) **C1**, (b) **C2**, and (c) **C3** recorded in methanol.

Table S1. The crystallographic data of BODIPY **C1**

Parameters	**C1**
Molecular Formula	C_{23} H_{18} B F_2 N_3
Formula Number	385.21
CCDC number	2235136
Temperature/K	296 K
Crystal system	Monoclinic
Space group	P 21/c
Λ	0.1073
a (Å)	13.8926(4)
b (Å)	18.2905(10)
c (Å)	7.7364(7)
α (degree)	90
β(degree)	99.426(2)
γ(degree)	90
Volume/ ($Å^3$)	1939.3(2)

Z	4
μ / mm^{-1}	0.092
$Density_{calcd}$ / mg m^{-3}	1.319
F (000)	800.0
θ range (°)	2.227 to 24.994°.
R_{int}	0.0487
Data / restraints /parameters	3424 / 0 / 264
GOF on F2	1.004
R_1[a], wR_2[b] [I >2σ(I)]	R_1 = 0.0487, wR_2 = 0.1089
R_1, wR_2 (all data)	R_1 = 0.1193, wR_2 = 0.1479

Table S2. Selected bond lengths (Å) and bond angles (degree) of BODIPY **C1**

Parameters	C1
C_{Bod}–C_{Aryl}	1.472(3)
B–N1	1.521(4)
N1–B–N2	106.0(2)
F1–B–F2	108.5(2)
Φ_{Aryl}	46.0(3)
$\Phi_{pyrrole}$	178.5(2)

Photophysical Data

Table S3. Photophysical properties of carbazole.

Compound	Dielectric Constant	Solvent	λ_{max} (nm)	log ε	λ_{em} (nm)	Φ_f [a]	Δυ (nm) [b]
Carbazole	1.9	Hexane	293	3.13	360	0.20	18
	2.38	Toluene	292	3.10	358	0.21	16
	4.81	Chloroform	292	3.12	368	0.24	26
	6.02	Ethyl Acetate	290	3.14	366	0.26	27
	7.58	THF	289	3.15	365	0.25	22
	17.9	Isopropyl alcohol	290	3.16	360	0.24	20
	20.7	Acetone	289	3.14	359	0.27	18
	24.5	Ethanol	293	3.13	358	0.28	16
	32.7	Methanol	290	3.12	360	0.30	19
	37.5	Acetonitrile	293	3.11	362	0.25	21
	46.7	DMSO	290	3.13	361	0.27	19

[a]Fluorescence quantum yield (Φ_f) was calculated using the standard fluorescein in aqueous NaOH (0.1 N) (Φ_f = 0.90); [b]Stokes shift.

Table S4. Photophysical properties of *meso*-carbazole substituted BODIPY **C1** and its brominated derivatives **C2** and **C3**.

BODIPY	Dielectric Constant	Solvent	λ_{max} (nm)	log ε	λ_{em} (nm)	Φ_f [a]	Q[b] (%)	Δυ (nm) [c]	Δf [d]	k_r[e] (10^9 s^{-1})	k_{nr}[f] (10^9 s^{-1})	τ[g] (ns)
C1	1.9	Hexane	499	4.49	507	0.51	-	8	0.0012	2.55	2.45	0.2
	2.38	Toluene	498	4.53	520	0.53	-	22	0.014	-	-	-
	4.81	$CHCl_3$	498	4.42	578	0.62	-	80	0.1447	-	-	-

	6.02	Ethyl Acetate	497	4.15	610	0.32	-	113	0.2005	-	-	-
	7.58	THF	496	4.38	607	0.21	16	111	0.2107	0.31	1.21	0.659
	17.9	Isopropyl alcohol	495	4.12	623	0.05	79	128	-	-	-	-
	20.7	Acetone	496	4.23	634	0.05	81.4	138	0.2846	0.049	0.93	1.02
	24.5	Ethanol	494	4.22	510, 641	0.04	85.7	147	0.2884	-	-	-
	32.7	Methanol	493	4.51	507, 652	0.02	93.3	159	0.3086	-	-	-
	37.5	Acetonitrile	494	4.65	506, 659	0.03	88	165	0.3055	-	-	-
	46.7	DMSO	493	4.43	507, 675	0.02	92.5	182	0.26	0.006	0.31	3.14
C2	1.9	Hexane	516	4.12	527	0.40	-	11	0.0012	2.7	4.09	0.147
	2.38	Toluene	516	4.35	548	0.42	-	32	0.0126	-	-	-
	4.81	Chloroform	515	4.24	587	0.51	-	72	0.1447	-	-	-
	6.02	Ethyl Acetate	514	4.44	619	0.36	-	105	0.2005	-	-	-
	7.58	THF	513	4.18	618	0.46	-	105	0.2107	1.6	1.9	0.275
	17.9	Isopropyl alcohol	511	4.11	631	0.05	79.1	120	-	-	-	-
	20.7	Acetone	512	4.21	646	0.05	81.4	134	0.2846	0.037	0.71	1.33
	24.5	Ethanol	510	4.30	520, 658	0.05	82.1	148	0.2884	-	-	-
	32.7	Methanol	510	4.23	525, 667	0.02	93.3	157	0.3086	-	-	-
	37.5	Acetonitrile	507	3.99	523, 670	0.02	92	163	0.3055	-	-	-
	46.7	DMSO	508	4.28	527, 676	0.01	96.2	168	0.26	0.005	0.49	2.0
C3	1.9	Hexane	533	3.98	549	0.11	45	16	0.0012	0.017	1.76	0.659
	2.38	Toluene	532	4.19	550	0.08	61.9	18	0.0126	-	-	-
	4.81	Chloroform	534	4.32	551	0.06	75	19	0.1447	-	-	-
	6.02	Ethyl Acetate	529	4.46	559	0.05	80.7	30	0.2005	-	-	-
	7.58	THF	528	3.97	556	0.03	88	28	0.2107	0.042	1.38	0.698
	17.9	Isopropyl alcohol	527	4.10	557	0.002	99.1	30	-	-	-	-
	20.7	Acetone	526	4.11	553	0.01	96.4	27	0.2846	0.017	1.76	0.562
	24.5	Ethanol	525	4.26	554	0.02	93.3	29	0.2884	-	-	-
	32.7	Methanol	527	4.50	548	0.002	99.2	21	0.3086	-	-	-
	46.7	DMSO	526	4.36	557	0.001	99.6	31	0.3055	0.0016	1.63	0.612

[a]Fluorescence quantum yield (Φ_f) was calculated using the standard fluorescein in aqueous NaOH (0.1 N) (Φ_f = 0.90); [b]Quenching Efficiency (Q): (*Phys.Chem.Chem.Phys*., 2018, **20**, 27418); $Q = \frac{\Phi_{(Ref)} - \Phi_{(BODIPY)}}{\Phi_{(Ref)}}$

[c]Stokes shift; [d]Orientational polarizability: (*J. Mater. Chem. C*, 2017, **5**, 6136-6143; *J. Chem. Phys*., 2006, **125**, 054513). [e]Radiative ($k_r = \Phi_f / \tau$) and [f]non-radiative ($k_{nr} = (1- \Phi_f) / \tau$) decay rates; [g]fluorescence lifetime.

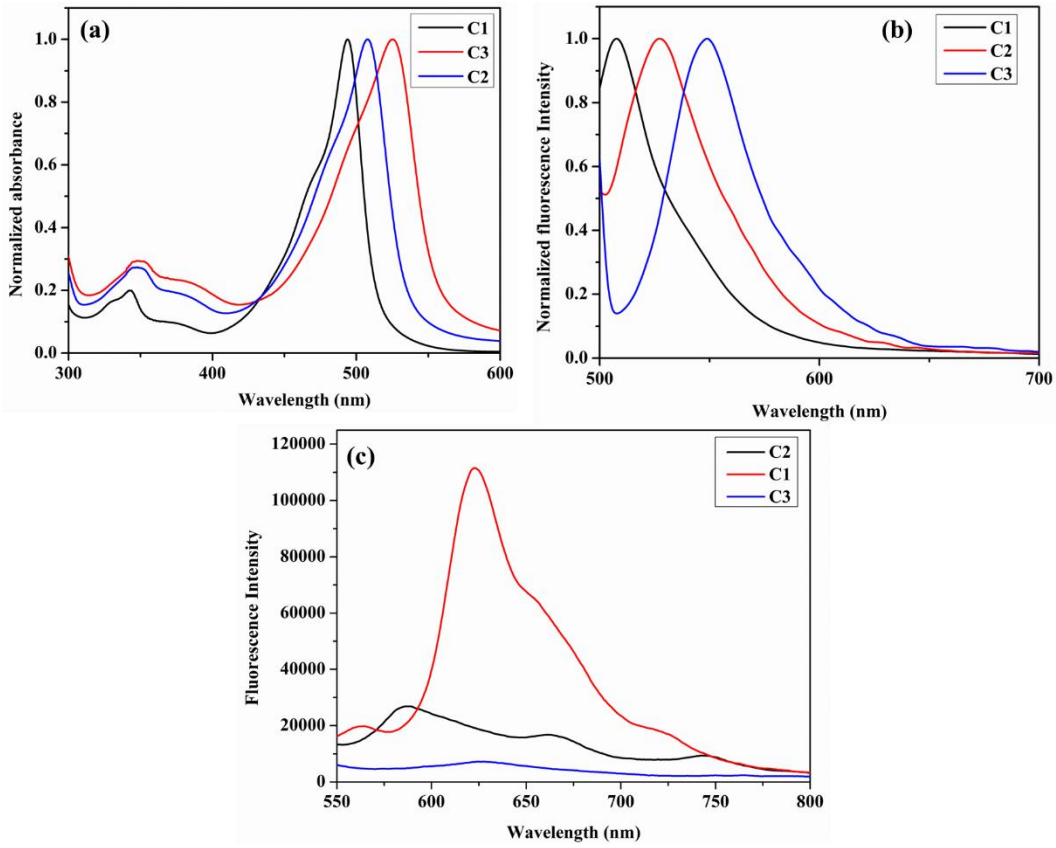


Figure S5. (a) Normalized absorption (10^{-5} M) and (b) emission spectra (10^{-7} M, λ_{ex} = 480 nm) of *meso*-carbazole appended BODIPYs **C1**, **C2**, and **C3** in hexane at room temperature; (c) Solid-state fluorescence spectra of **C1**, **C2**, and **C3** (λ_{ex} = 500 nm).

Theoretical Calculations

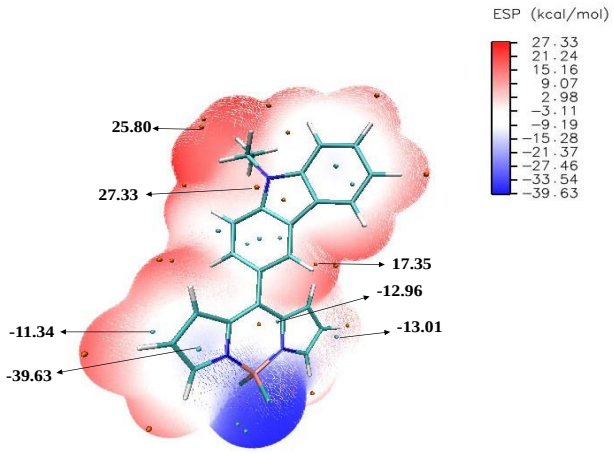


Figure S6. MESP of *meso*-carbazole substituted BODIPY **C1** calculated at M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Table S5. ESP values (M06/def2-TZVPP//BP86/def2-TZVPP) in kcal/mol at the Van der Waals surface of selected atoms in *meso*-carbazole substituted BODIPY **C1**.

Atoms	ESP (kcal/mol)
Carbazole Carbon atoms	
C2	-4.50
C4	-7.14
C6	-8.38
C8	-7.08
C13	-0.89
C15	-3.40
C18	-3.66
Pyrrole Carbon atoms	
C22 (β-pyrrole)	-8.15
C24 (β-pyrrole)	-10.04
C26 (α-pyrrole)	-10.32

Table S6. Computed absorption properties of *meso*-carbazole BODIPY in the ground state in DMSO using PCM solvent model at M06/def2TZVPP//BP86/def2-TZVPP.

BODIPY	Excited state	Oscillator strength (f)	Excitation energy (eV)	λ (nm)	Transition	Coefficient of transition	Percentage contribution
C1 λ_{exp} = 493 nm	1	0.2563	2.52	490.47	HOMO→LUMO	0.6990	97.72
	2	0.1309	2.82	439.08	HOMO-2→LUMO	0.4960	49.20
					HOMO-1→LUMO	0.4944	48.88
	3	0.3788	2.90	426.91	HOMO-2→LUMO	0.4940	48.80
					HOMO-1→ LUMO	-0.4944	48.88
	4	0.0658	3.63	341.02	HOMO-4→LUMO	0.6577	86.51
					HOMO-5→ LUMO	-0.2264	10.25
	5	0.0993	3.81	325.18	HOMO-5→LUMO	0.1480	4.38
					HOMO-4→LUMO	0.2047	8.38
					HOMO-3→LUMO	0.5334	56.90
					HOMO→LUMO+1	-0.3551	25.21
C2 λ_{exp} = 508 nm	1	0.2626	2.44	508.05	HOMO→LUMO	0.6990	97.72
	2	0.1473	2.72	458.44	HOMO-2→LUMO	0.4840	46.85
					HOMO-1 →LUMO	0.5057	51.14
	3	0.3722	2.79	443.32	HOMO-1 →LUMO	0.5062	51.24
					HOMO-2→LUMO	-0.4788	45.84
	4	0.1415	3.50	353.71	HOMO-4→LUMO	-0.1023	2.09
					HOMO-3→LUMO	0.2212	9.78
					HOMO-2→LUMO	0.6487	84.16
					HOMO→LUMO	-0.1029	2.11
	5	0.0448	3.70	334.51	HOMO-4→LUMO	0.6923	95.85
C3 λ_{exp} = 526 nm	1	0.2732	2.35	526.87	HOMO→LUMO	0.7007	98.19
	2	0.1337	2.63	470.15	HOMO-2→LUMO	0.4966	49.32
					HOMO-1→LUMO	0.4953	49.06
	3	0.4120	2.68	461.49	HOMO-4→LUMO	-0.1042	2.17
					HOMO-1→LUMO	0.4945	48.90
					HOMO-2→LUMO	-0.4919	48.39
	4	0.0786	3.42	361.64	HOMO-5→LUMO	0.2361	11.14
					HOMO-3→LUMO	0.6546	85.70
	5	0.1795	3.47	356.28	HOMO-4→LUMO	0.6890	94.94
					HOMO-1→ LUMO	-0.1039	2.15

Table S7. Computed absorption properties of *meso*-carbazole BODIPY (dihedral angle = 90°) in DMSO using PCM solvent model at M06/def2TZVPP//BP86/def2-TZVPP.

BODIPY	Excited state	Oscillator strength (f)	Excitation energy (eV)	λ (nm)	Transition	Coefficient of transition	Percentage contribution
C1	1	0.0008	2.33	530.37	HOMO-3 →LUMO	-0.1076	2.31
					HOMO→LUMO	0.6870	94.3
	2	0.0757	2.7	457.79	HOMO-2→LUMO	0.3064	18.7
					HOMO-1→LUMO	0.6227	77.5
					HOMO→LUMO	-0.1155	2.6
	3	0.4326	2.92	424.33	HOMO-4→LUMO	-0.1189	2.8
					HOMO-2→LUMO	0.6235	77.7
					HOMO-1→LUMO	-0.309	19.09
C2	1	0.0006	2.22	557.56	HOMO→LUMO	0.6878	94.6
	2	0.0654	2.59	476.99	HOMO-2→LUMO	0.2640	13.9
					HOMO-1 →LUMO	0.6423	82.5
					HOMO→LUMO	-0.1109	2.4
	3	0.4432	2.79	443.57	HOMO-3→LUMO	-0.1139	2.5
					HOMO-2 →LUMO	0.6409	82.1
					HOMO-1 →LUMO	-0.2643	13.9
C3	1	0.0006	2.11	587.5	HOMO→LUMO	0.6884	94.7
	2	0.0555	2.48	497.99	HOMO-2→LUMO	-0.2213	9.7
					HOMO-1→LUMO	0.6588	86.8
					HOMO→LUMO	0.1074	2.3
	3	0.4723	2.67	463.56	HOMO-5→LUMO	0.1058	2.2
					HOMO-2→LUMO	0.6574	86.4
					HOMO-1→LUMO	0.2220	9.8

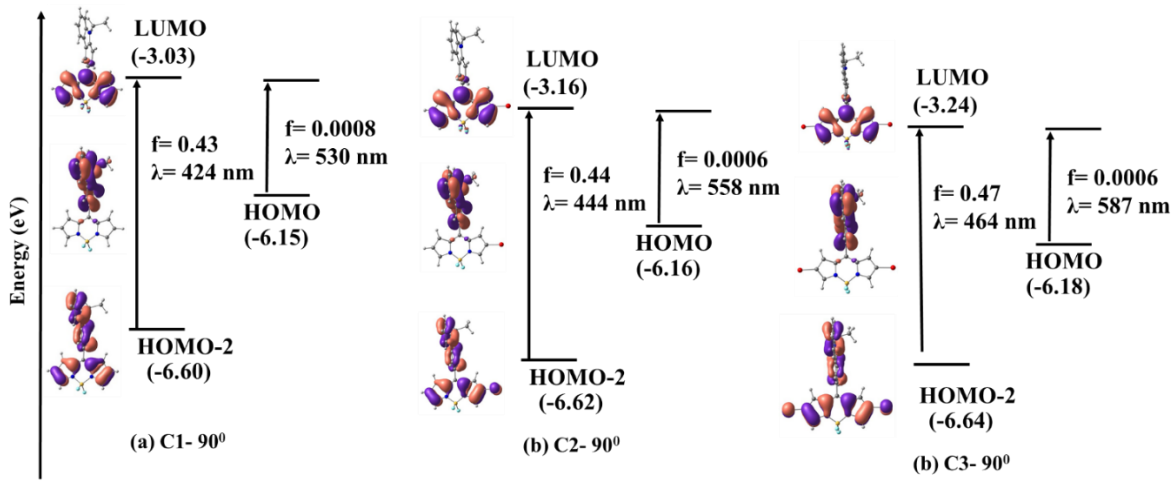


Figure S7. Important electronic transitions computed for *meso*-carbazole BODIPY derivatives (dihedral angle between BODIPY and carbazole planes fixed to 90°) using TDDFT at M06/def2TZVPP level of theory in DMSO using PCM solvent model. Eigenvalues are given in eV. The surfaces are plotted at the iso-surface value of 0.03. The corresponding wavelength (λ) in nm and oscillator strength (f) is given.

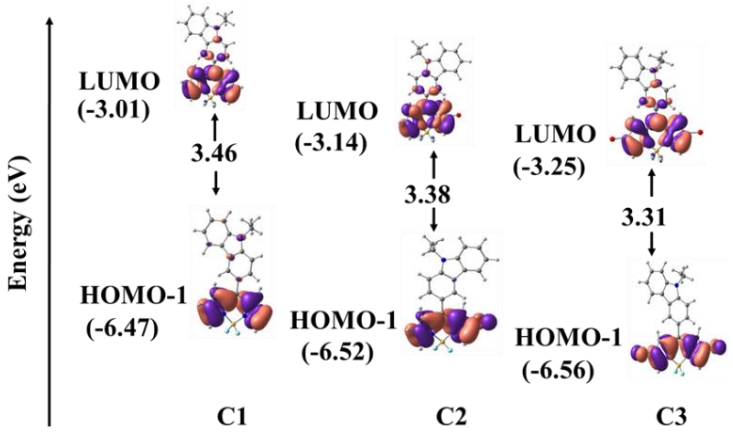


Figure S8. Selected molecular orbitals and energy gap of **C1**, **C2**, and **C3** in DMSO. Eigenvalues are given in eV.

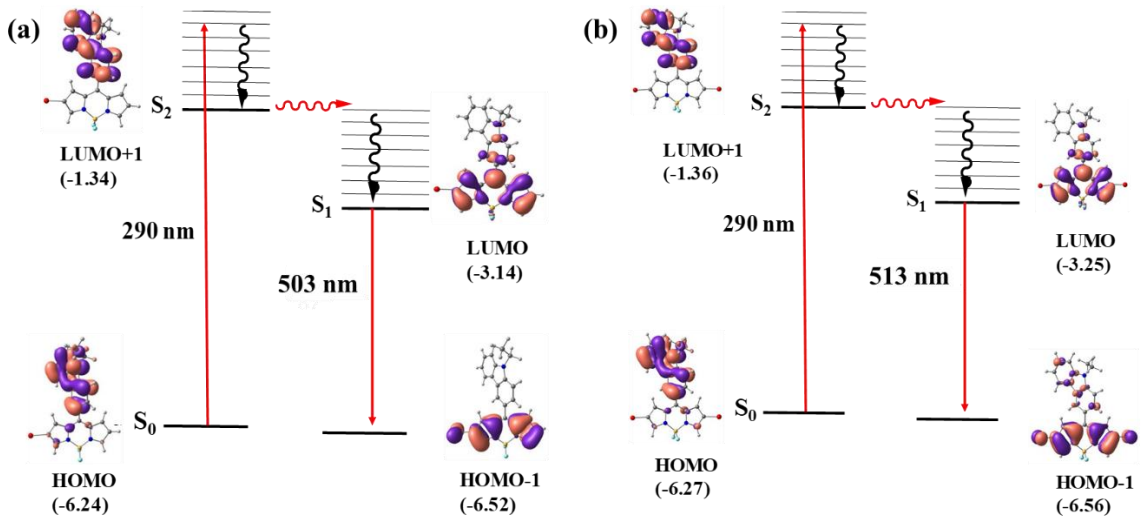


Figure S9. The electronic transitions in (a) **C2**, and (b) **C3**, calculated using TDDFT at the M06/def2TZVPP//BP86/def2-TZVPP level of theory, indicating intramolecular excitation energy transfer in **C2** and **C3**. Eigenvalues values are given in eV.

Solvatochromism

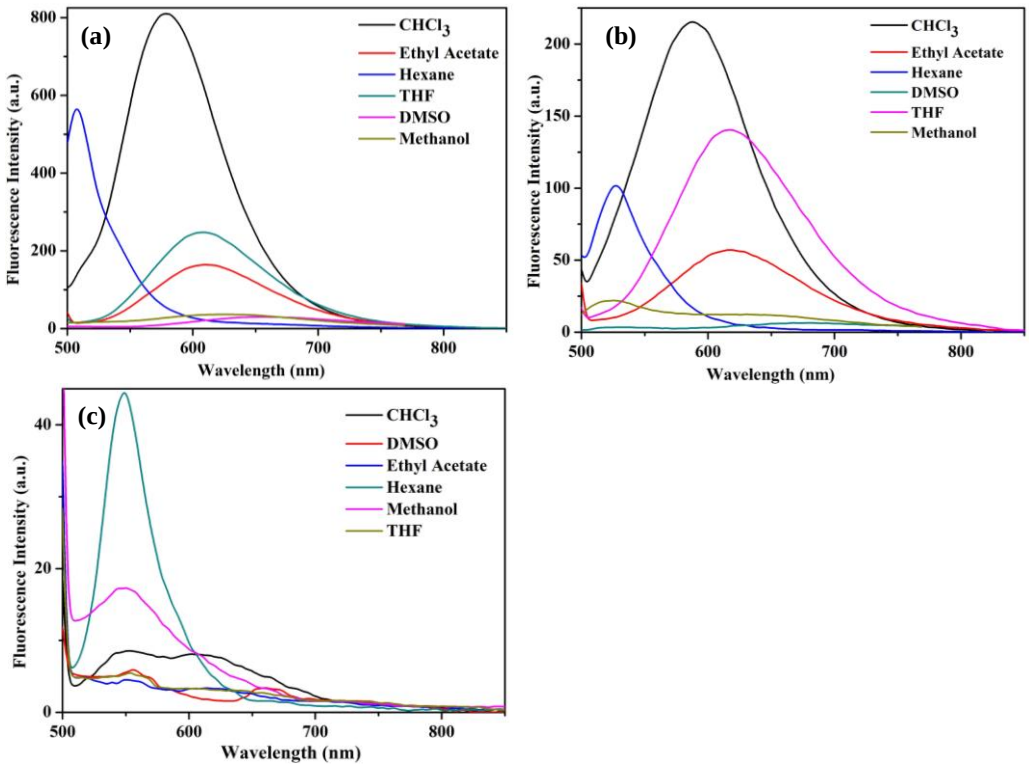


Figure S10. Fluorescence spectrum of (a) **C1** (b) **C2** (c) **C3** (10^{-7} M, λ_{ex} = 480 nm) in solvents of different polarity at room temperature.

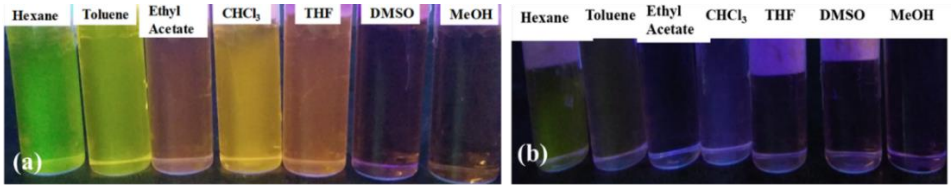


Figure S11. Photograph of (a) **C2** and (b) **C3** in various solvents under UV irradiation.

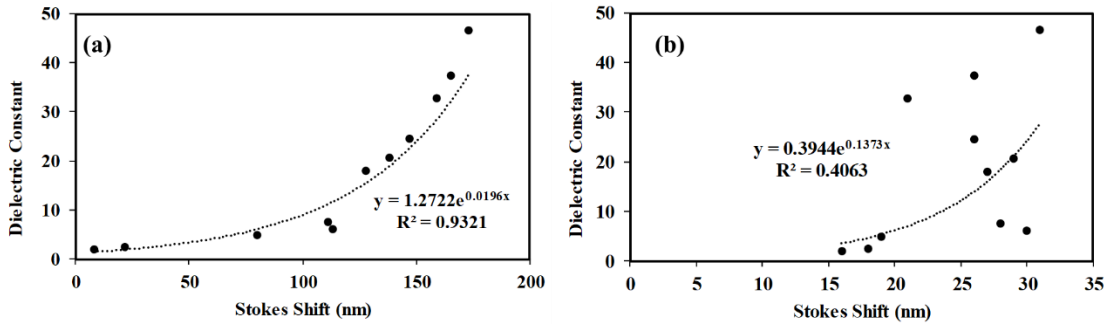


Figure S12. The plot of dielectric constant vs Stokes shift (nm) for (a) **C2** and (b) **C3**.

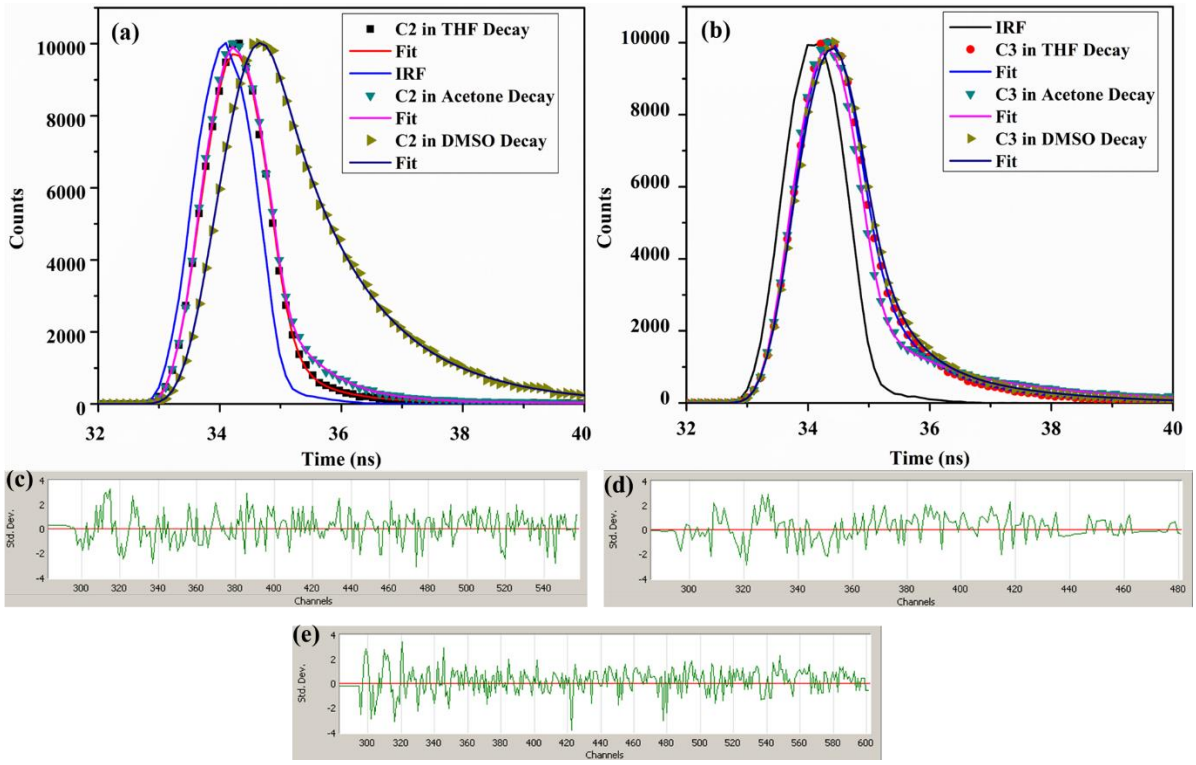


Figure S13. The fluorescence decay profiles of (a) **C2** and (b) **C3** (λ_{ex} = 460 nm) in different solvents. The instrument response function, (IRF) is shown in the blue line in **C2** and a black line in **C3**. Residuals obtained from the fit of (c) **C1**, (d) **C2** and (e) **C3** in THF are given at the bottom.

Table S8. Fitted decay time (τ_i), pre-exponential coefficients (α_i), and chi-squared (χ^2) values were obtained by fitting the emission decays (λ_{ex} = 460 nm).

Solvent	α_1	α_2	α_3	τ_1	τ_2	τ_3	χ^2	τ (ns)
C1								
THF	0.14947	0.178944	-	2.08E-10	7.62E-10		1.35	0.65
Hexane	6.43E-03	2.852009	6.04E-04	1.04E-09	8.09E-11	6.11E-09	1.10	0.2
Acetone	0.190875	-	-	1.02E-09			1.30	1.02
DMSO	0.118504	-	-	3.14E-09			1.10	3.14
C2								
THF	0.7845303	5.85E-03		1.94E-10	1.60E-09		1.22	0.27
Hexane	8.32E+00	5.61E-02	1.34E-03	4.57E-11	7.23E-10	3.42E-09	1.32	0.14
Acetone	0.006429235	2.852009	0.000603659	1.04E-09	8.0922E-11	6.10806E-09	1.22	1.33
DMSO	6.52E-02	0.111928		8.07E-10	1.49E-09		1.15	2.0
C3								
Acetone	0.4492571	3.90E-02	-	2.65E-10	1.27E-09	-	1.43	0.56
DMSO	1.08E+00	2.20E-02	-	1.39E-10	2.13E-09	-	1.03	0.61
Hexane	0.14947	0.178944	-	2.08E-10	7.62E-10	-	1.25	0.65
THF	3.40E-01	2.99E-02	-	3.55E-10	1.58E-09	-	1.05	0.69

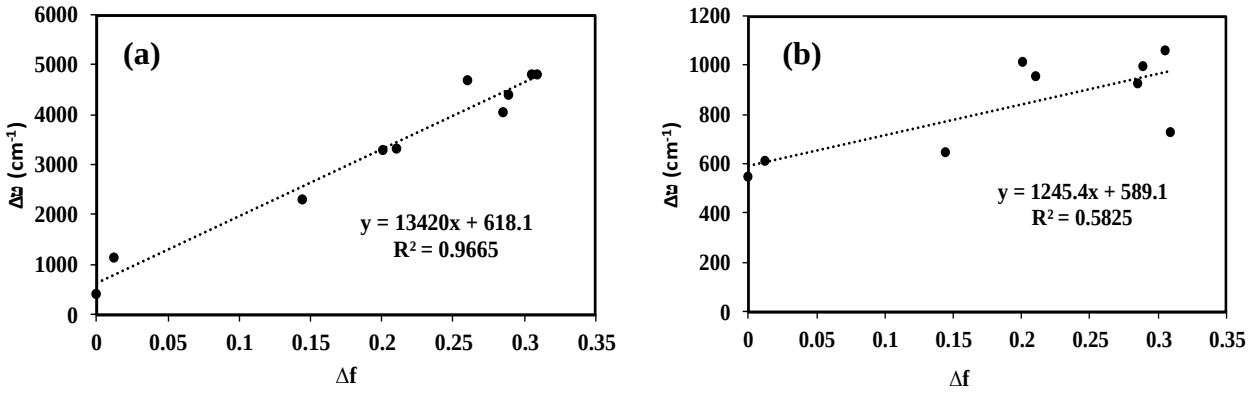
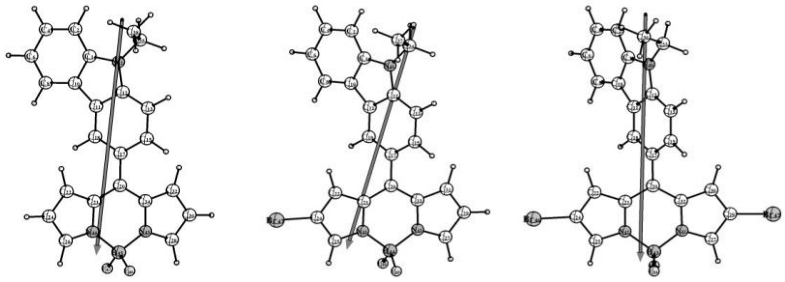


Figure S14. Lippert-Mataga plot: dependence of the Stokes shift on the solvent polarity function, Δf for (a) **C2** and (b) **C3**.



C1 **C2** **C3**

Figure S15. The direction of dipole moment in the optimized ground state geometry of **C1**, **C2**, and **C3**.

Twisted Intramolecular Charge Transfer

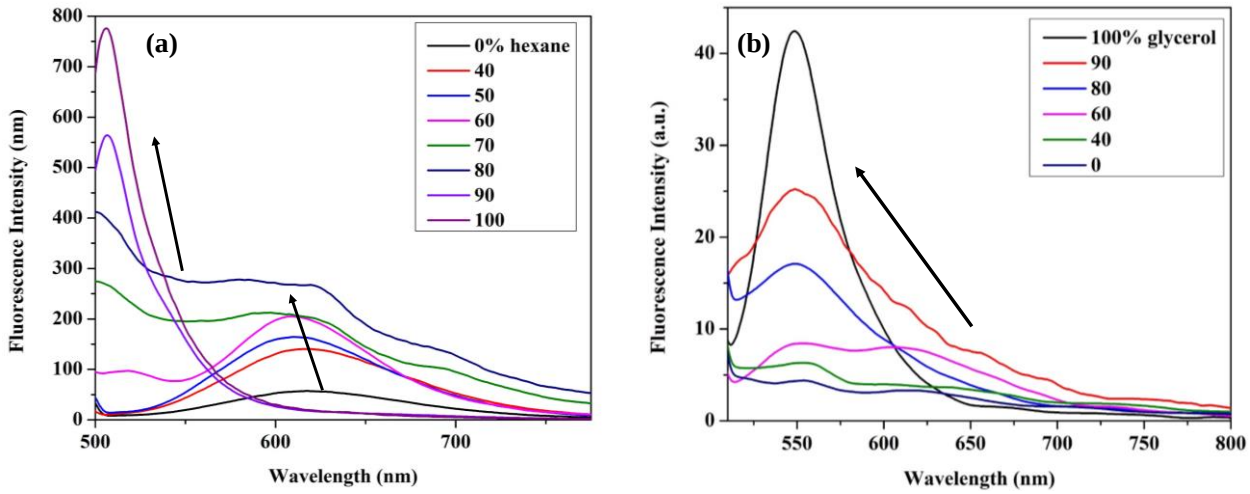


Figure S16. (a) Emission spectra of **C1** in the THF/hexane mixture with different hexane fractions (10^{-7} M, λ_{exc} = 480 nm); (b) Emission spectra of **C1** in the ethanol/glycerol mixture with different glycerol fractions (10^{-7} M, λ_{exc} = 480 nm).

Singlet Oxygen Generation: Chemical Quenching with DPBF

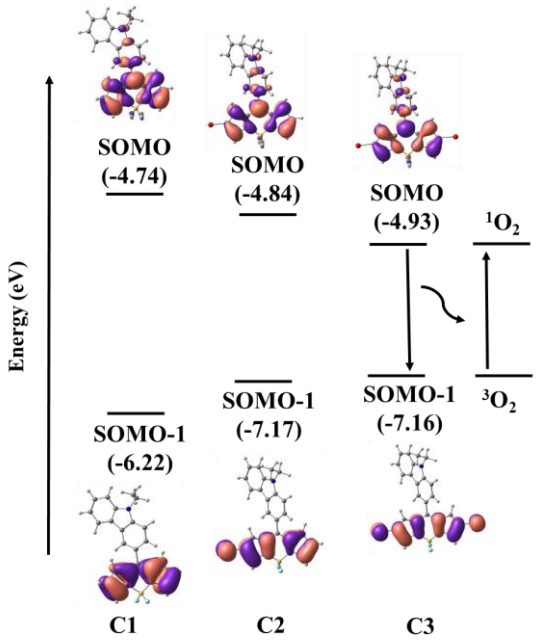


Figure S17. The singly occupied molecular orbitals and the energy gap between SOMO and SOMO-1 orbitals in *meso*-carbazole BODIPY are given. The mechanism of singlet oxygen generation is illustrated. Eigenvalues are given in eV. The surfaces are plotted at the iso-surface value of 0.03.

Aggregation-Induced Emission Studies

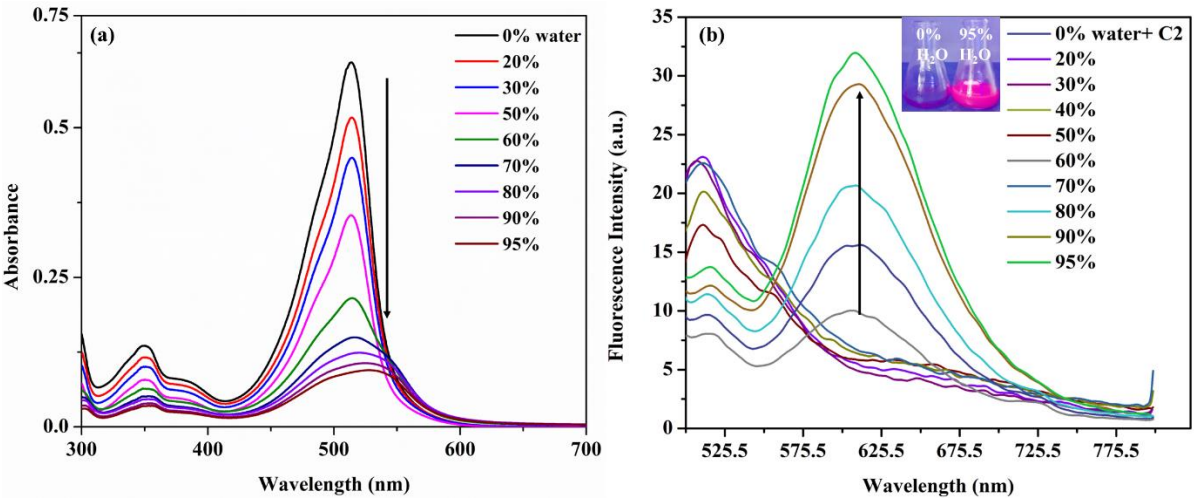


Figure S18. (a) Absorption spectra of **C2** in DMSO-H_2O mixtures with different water fractions (10^{-5} M); (b) Fluorescence spectra of **C2** in DMSO-H_2O mixtures with different water fractions (10^{-6} M, λ_{exc} = 480 nm) (Inset: photograph of **C2** in DMSO/H_2O mixture (f_w = 0% and 95%,), taken under 365 nm excitation of a UV lamp).

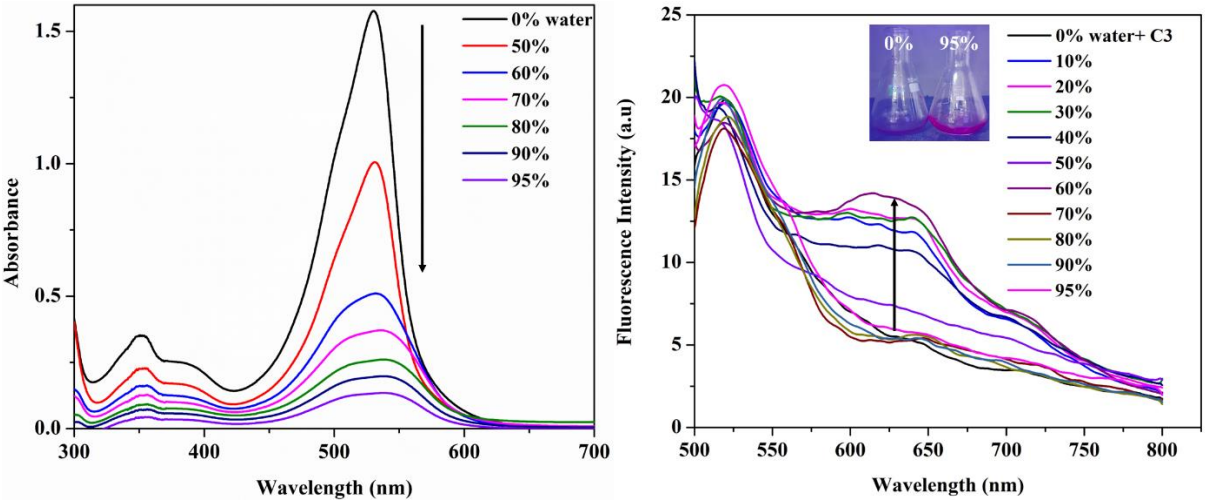
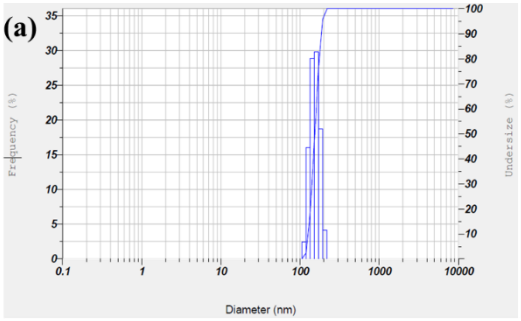


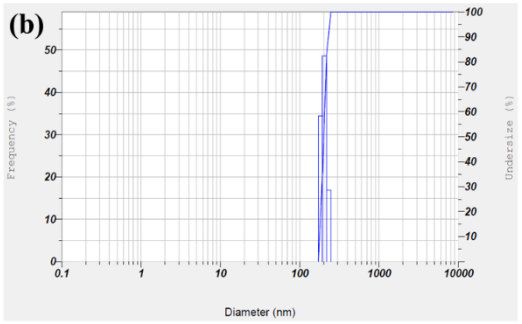
Figure S19. (a) Absorption spectra of **C3** in DMSO-H_2O mixtures with different water fractions (10^{-5} M); (b) Fluorescence spectra of **C3** in DMSO-H_2O mixtures with different water fractions (10^{-6} M, λ_{exc} = 480 nm) (Inset: photograph of **C3** in DMSO/H_2O mixture (f_w = 0% and 95%,), taken under 365 nm excitation of a UV lamp).

Table S9. Calculated Φ_f in the aggregated state and AIE factor of *meso*-carbazole substituted BODIPYs

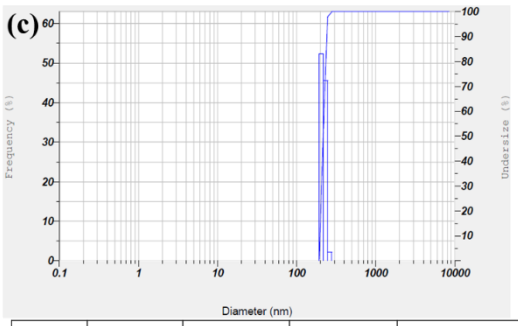
BODIPY	Φ_f in the aggregated state	α_{AIE}
C1	0.52	26
C2	0.21	21
C3	0.015	15



Peak No.	S.P.Area Ratio	Mean	S. D.	Mode
1	1.00	154.7 nm	21.8 nm	157.8 nm
2	--	-- nm	-- nm	-- nm
3	--	-- nm	-- nm	-- nm
Total	1.00	154.7 nm	21.8 nm	157.8 nm



Peak No.	S.P.Area Ratio	Mean	S. D.	Mode
1	1.00	202.0 nm	17.3 nm	201.2 nm
2	--	-- nm	-- nm	-- nm
3	--	-- nm	-- nm	-- nm
Total	1.00	202.0 nm	17.3 nm	201.2 nm



Peak No.	S.P.Area Ratio	Mean	S. D.	Mode
1	1.00	219.0 nm	14.7 nm	216.9 nm
2	--	-- nm	-- nm	-- nm
3	--	-- nm	-- nm	-- nm
Total	1.00	219.0 nm	14.7 nm	216.9 nm

Figure S20. DLS images of (a) **C1 (**2.88 ×10^{-5} M) and (b) **C2** (2.39 × 10^{-5} M) **(c) C3** (2.88 × 10^{-5} M) in 7:3 water-DMSO fraction.

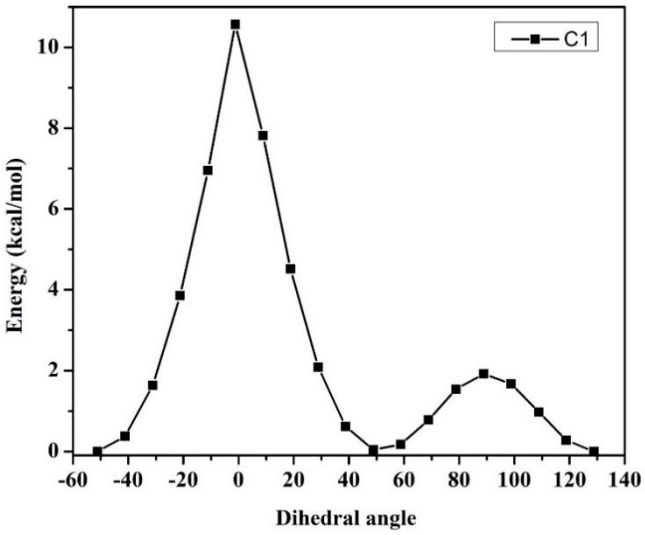


Figure S21. Plot between the dihedral angle of rotation between carbazole and BODIPY in **C1** vs energy (kcal/ mol) of rotation calculated at BP86/Def2-TZVPP level of theory.