Supplementary Information

Substituted diphenyl butadiynes: a computational study of geometries and electronic transitions using DFT/TD-DFT

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Table of Contents: 1. Optimized ground state geometry of the fluorophores (Fig. S1), 2. Mulliken charge analysis of **Me_2NMe_2N** (Fig. S2), **$PhMe_2N$** (Fig. S3), **Me_2NOMe** (Fig. S4), and **Me_2NCN** (Fig. S5), 3. Combined plot of Mulliken charge analysis of **$PhMe_2N$** and **Me_2NCN** (Fig. S6), 4. Correlation of C(Ph)–O(OMe) bond length with dielectric constant (Fig. S7), 5. UV-vis experimental absorption spectra of the fluorophores in cyclohexane (Fig. S8 and S9), 6. Variation of absorption wavelength with dielectric constant (Fig. S10 and S11), 7. Variation of HOMO and LUMO energy for different fluorophores (Fig. S12), 8. Orbital contributions ($S_0 \rightarrow S_1$) for the fluorophores (Table S1 and S2), 9. TDDFT potential energy curves (Fig. S13 and S14), 10. Correlation between experimental and TD-DFT absorption wavelength in DCM (Fig. S15), MeOH (Fig. S16), and CH_3CN (Fig. S17), 11. Correlation of vertical excitation energy with (a) twist angle, (b) pyramidalization, and (c) C(Ph)–N(NMe_2) bond length in **Me_2NOMe** (Fig. S18) and **Me_2NCN** (Fig. S19), 12. Optimized LE state geometry of the fluorophores (Fig. S20), 13. Geometrical parameters of ICT state of **$PhMe_2N$** (Fig. S21), 14. ICT emission energy of **PhCN** and **Me_2NCN** (Table S3), 15. HOMO and LUMO in ICT emissive state in CH_3CN (Fig. S22), 16. Magnitude of absorption and LE TDM (Table S4), 17. Cartesian co-ordinates of the optimized geometries.

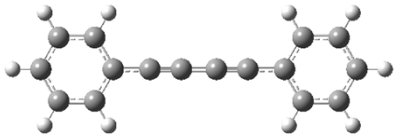
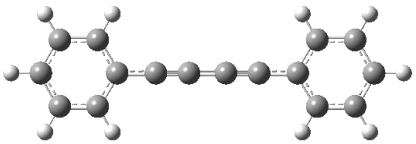
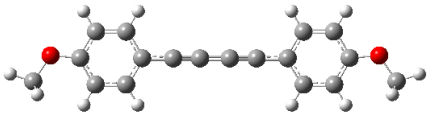
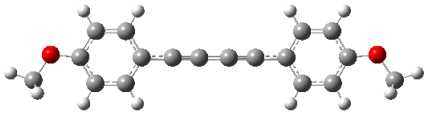
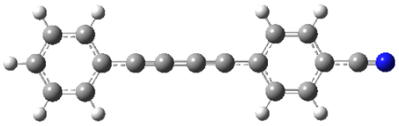
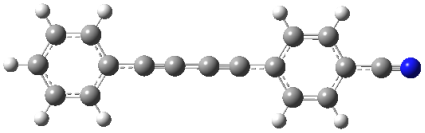
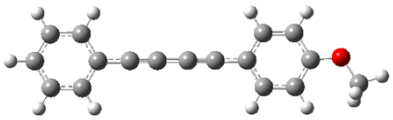
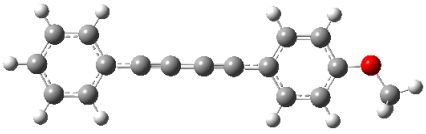
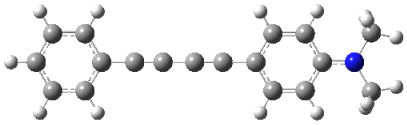
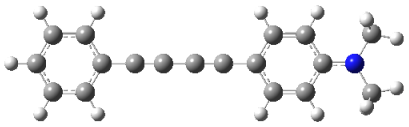
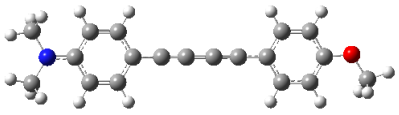
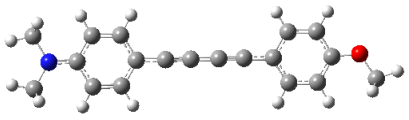
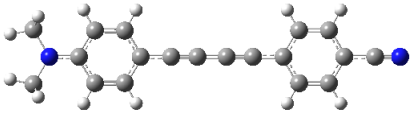
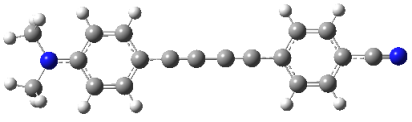
Molecules	Cyclohexane	CH_3CN
PhPh		
OMeOMe		
PhCN		
PhOMe		
$PhMe_2N$		
Me_2NOMe		
Me_2NCN		

Fig. S1 Optimized ground state geometry of the fluorophores using B3LYP/6-311G(d,p)

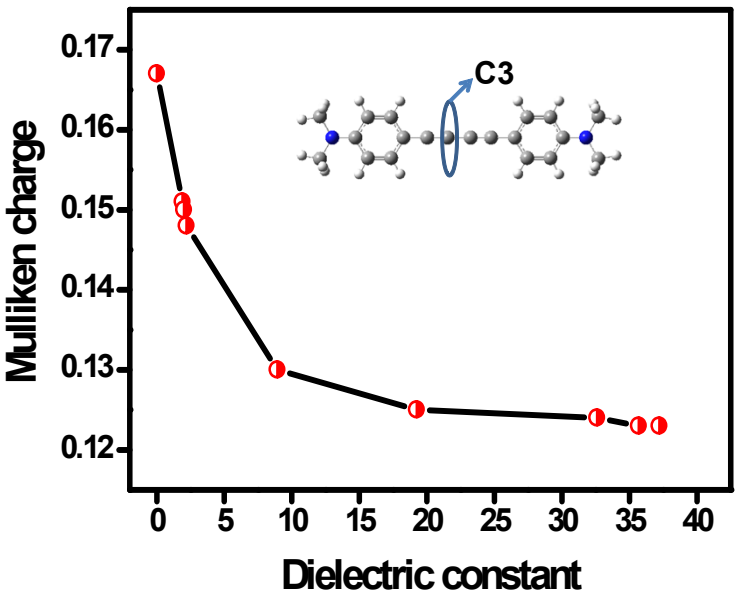


Fig. S2 Mulliken charge analysis of C3 of the derivative **Me_2NMe_2N** using B3LYP/6-311G(d,p)

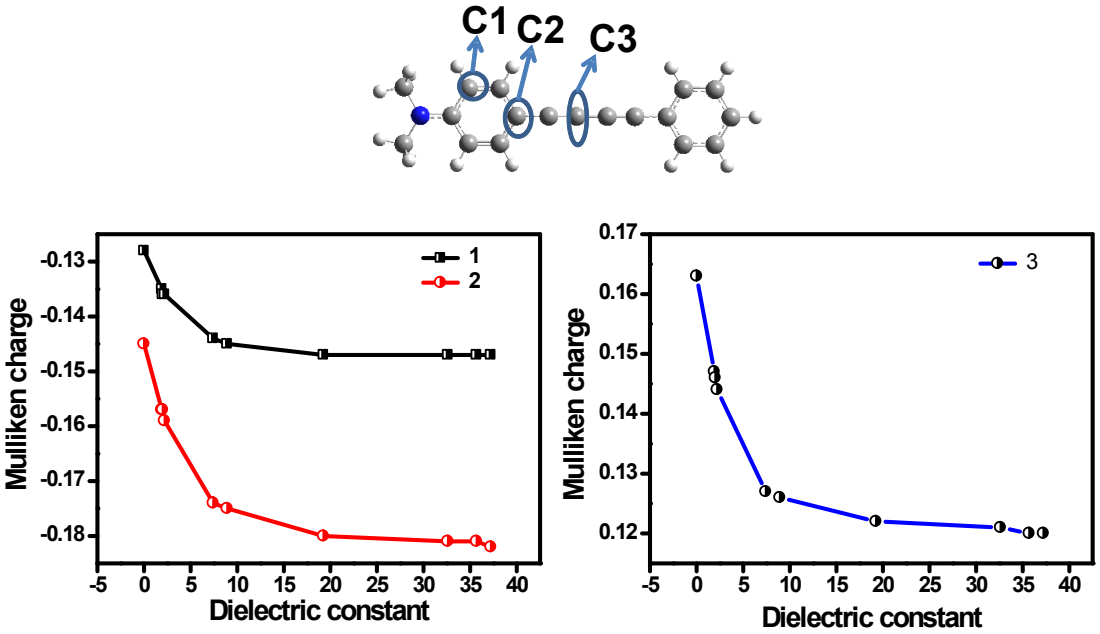


Fig. S3 Mulliken charge analysis of C1, C2, and C3 of the derivative **$PhMe_2N$** using B3LYP/6-311G(d,p)

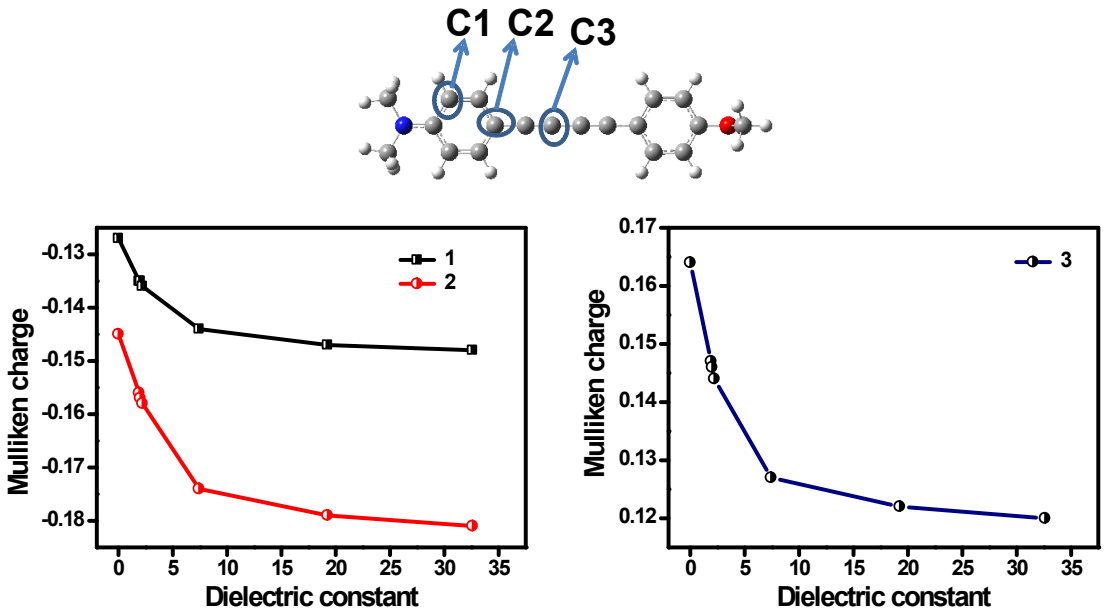


Fig. S4 Mulliken charge analysis of C1, C2, and C3 of the derivative **Me_2NOMe** using B3LYP/6-311G(d,p)

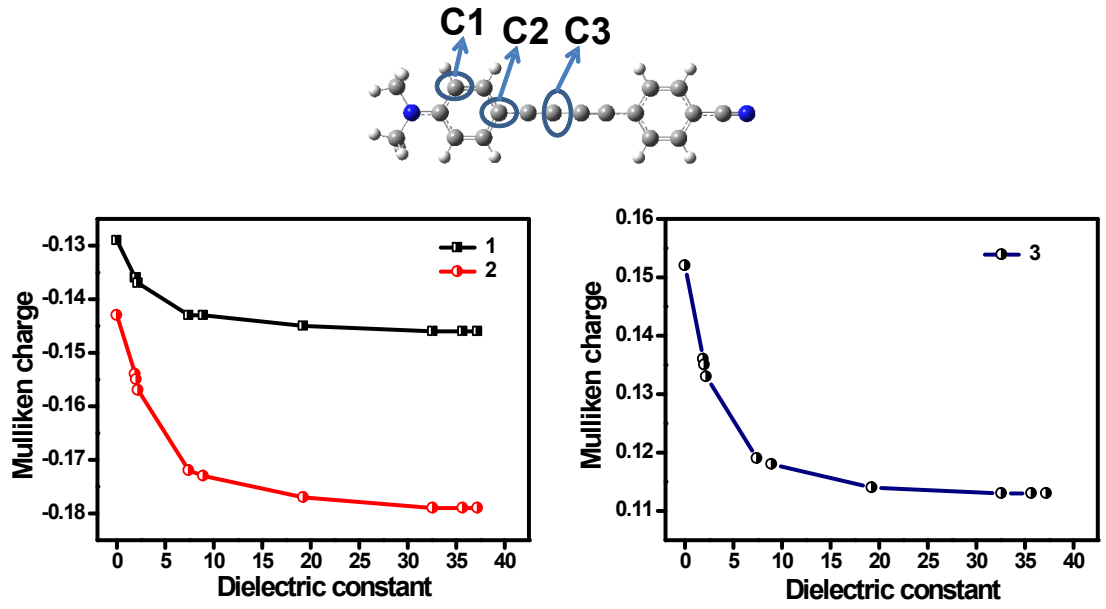


Fig. S5 Mulliken charge analysis of C1, C2, and C3 of the derivative **Me_2NCN** using B3LYP/6-311G(d,p)

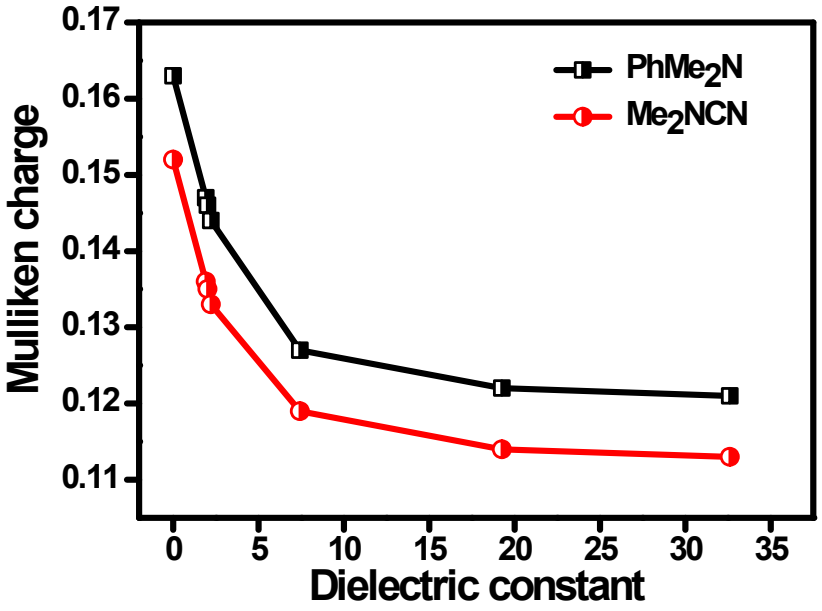


Fig. S6 Mulliken charge analysis of C3 of the derivative **$PhMe_2N$** and **Me_2NCN** using B3LYP/6-311G(d,p)

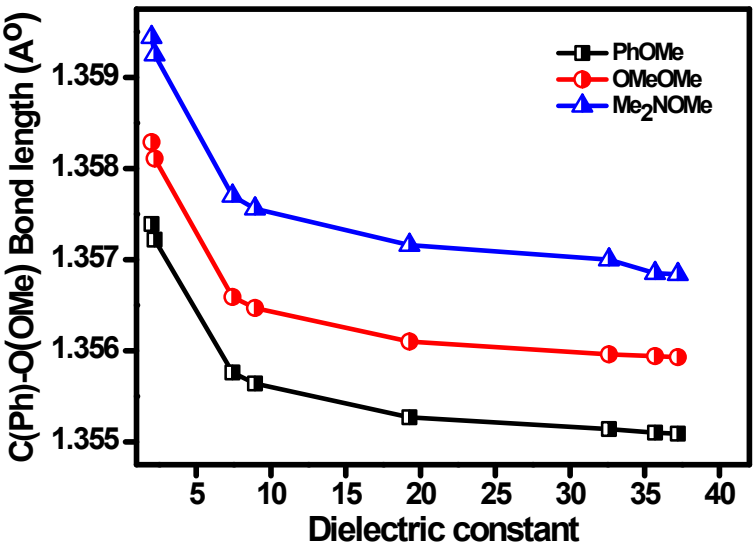


Fig. S7 Correlation of C(Ph)–O(OMe) bond length with dielectric constant at ground state B3LYP/6-311G(d,p) optimized geometry

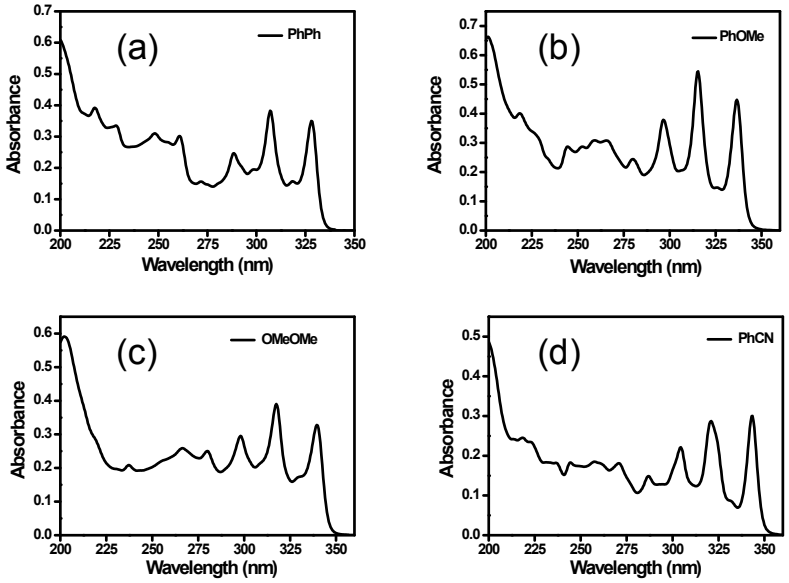


Fig. S8 UV-vis experimental absorption spectra of (a) **PhPh**, (b) **PhOMe**, (c) **OMeOMe**, and (d) **PhCN** in cyclohexane (concentration = 1 x 10^{-5} M) with high resolution (JASCO V-650, bandwidth = 0.5 nm)

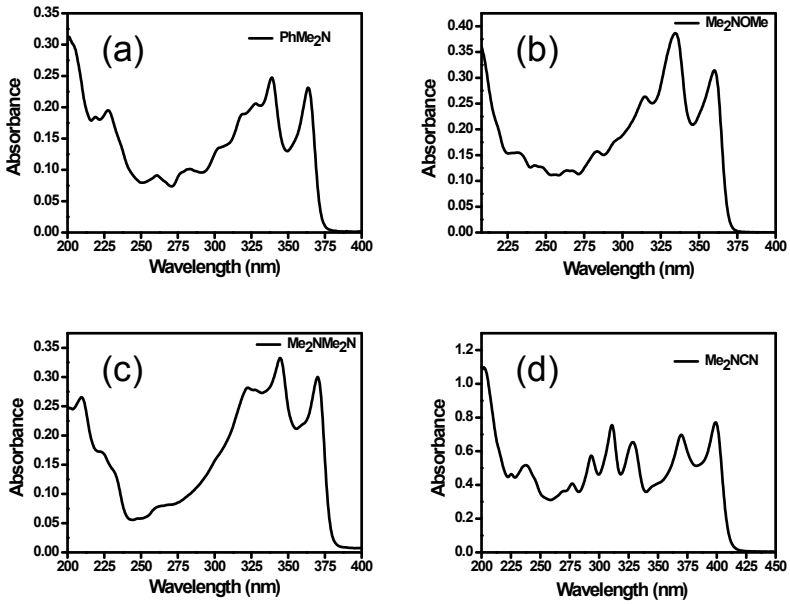


Fig. S9 UV-vis experimental absorption spectra of (a) **$PhMe_2N$**, (b) **Me_2NOMe**, (c) **Me_2NMe_2N**, and (d) **Me_2NCN** in cyclohexane (concentration = 1 x 10^{-5} M for a, b, c and concentration = 1.9 x 10^{-5} M for d) with high resolution (JASCO V-650, bandwidth = 0.5 nm)

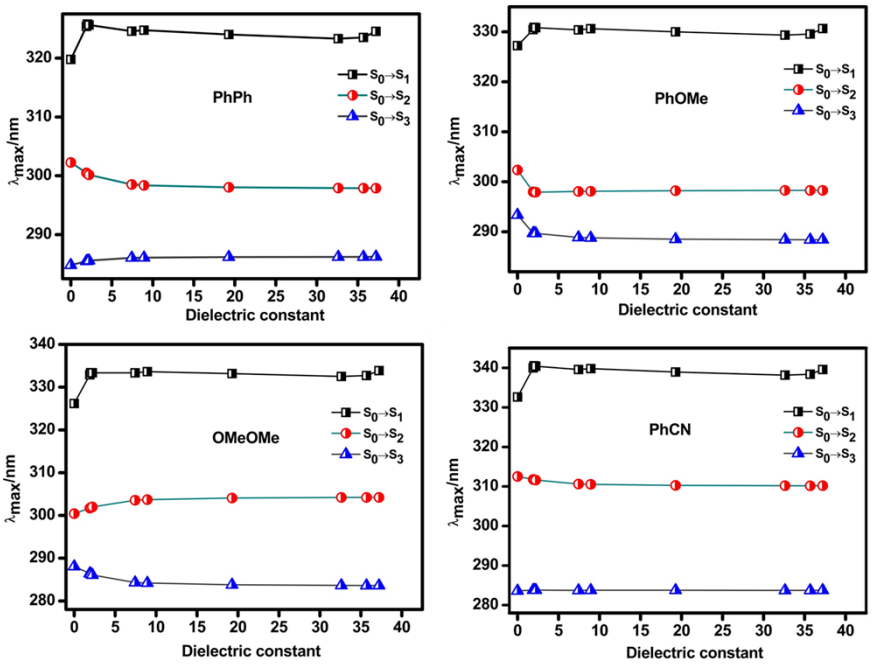


Fig. S10 Variation of absorption wavelength with dielectric constant for (a) **PhPh**, (b) **PhOMe**, (c) **OMeOMe**, and (d) **PhCN** using CAM-B3LYP/6-311+G(d,p)

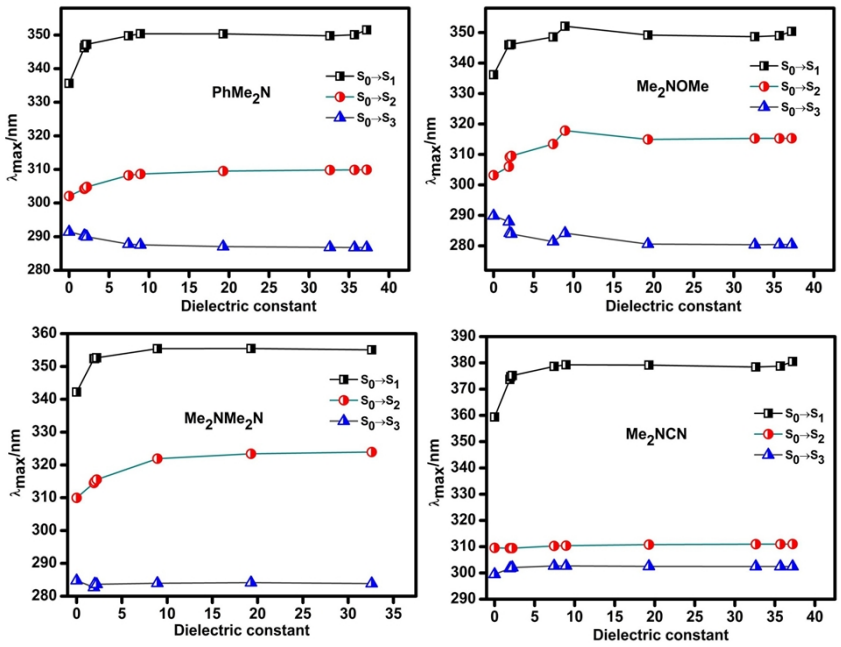


Fig. S11 Variation of absorption wavelength with dielectric constant for (a) **$PhMe_2N$**, (b) **Me_2NOMe**, (c) **Me_2NMe_2N**, and (d) **Me_2NCN** using CAM-B3LYP/6-311+G(d,p)

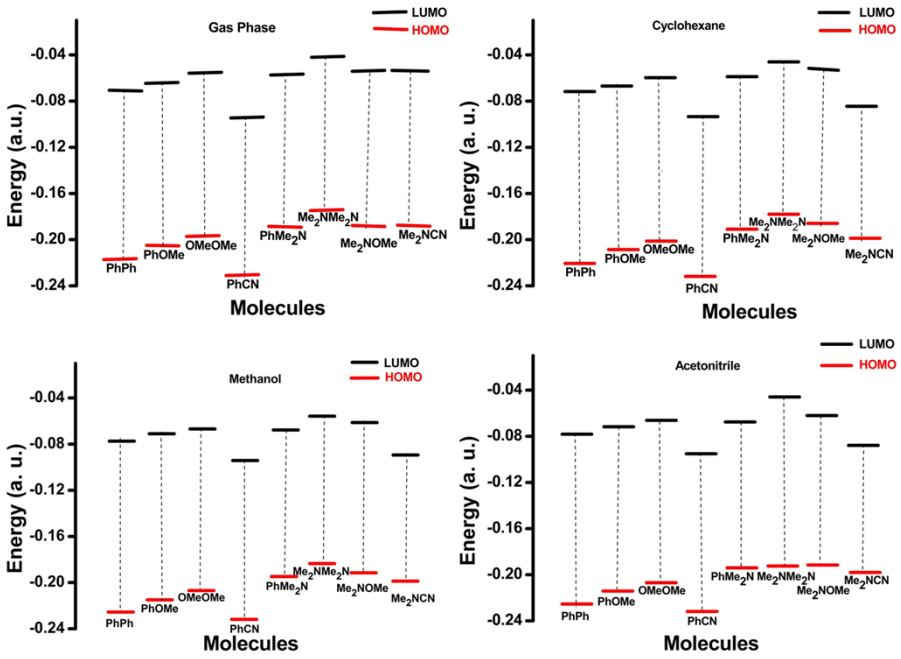


Fig. S12 Variation of HOMO and LUMO energy of different butadiynyl fluorophores in (a) gas phase, (b) cyclohexane, (c) methanol, and (d) CH_3CN using B3LYP/6-311G(d,p)

Table S1 % of orbital contributions ($S_0 \rightarrow S_1$) for the fluorophores in cyclohexane

Molecule	% of orbital contributions				
	BLYP/ 6-311G(d,p)	PBE/ 6-311G(d,p)	B3LYP/ 6-311G(d,p)	B98/ 6-311G(d,p)	PBE0/ 6-311G(d,p)
PhPh	H→L (95%) H-1→L+1 (5%)	H→L (95%) H-1→L+1 (5%)	H→L (93%) H-1→L+1 (7%)	H→L (93%) H-1→L+1 (7%)	H→L (93%) H-1→L+1 (7%)
OMeOMe	H→L (97%) H-2→L+3 (3%)	H→L (97%) H-2→L+3 (2%)	H→L (95%) H-2→L+3 (5%)	H→L (94%) H-2→L+3 (5%)	H→L (94%) H-2→L+3 (5%)
Me_2NMe_2N	H→L (97%)	H→L (97%)	H→L (97%) H-2→L+1 (2%)	H→L (96%) H-2→L+1 (3%)	H→L (96%) H-2→L+1 (3%)
PhCN	H→L (96%) H-1→L+3 (2%)	H→L (96%) H-1→L+3 (2%)	H→L (95%) H-1→L+3 (4%)	H→L (95%) H-1→L+3 (2%)	H→L (95%) H-1→L+3 (4%)
PhOMe	H→L (95%) H-1→L+2 (3%)	H→L (95%) H-1→L+2 (2%)	H→L (94%) H-1→L+2 (5%)	H→L (94%) H-1→L+1 (5%)	H→L (94%) H-1→L+1 (5%)
$PhMe_2N$	H→L (95%) H→L+4 (3%)	H→L (95%) H→L+4 (3%)	H→L (96%) H-2→L+1 (3%)	H→L (96%) H-2→L+1 (3%)	H→L (95%) H-2→L+1 (3%)
Me_2NOMe	H→L (95%)	H→L (95%) H→L+4 (2%)	H→L (96%) H-2→L+2 (3%)	H→L (96%) H-2→L+2 (3%)	H→L (95%) H-2→L+2 (3%)
Me_2NCN	H→L (96%) H→L+2 (2%)	H→L (96%) H→L+2 (2%)	H→L (98%)	H→L (98%)	H→L (97%)

Table S2 % of orbital contributions ($S_0 \rightarrow S_1$) for the fluorophores in cyclohexane

Molecule	% of orbital contributions				
	M06-2X/ 6-311G(d,p)	M05-2X/ 6-311G(d,p)	LC-BLYP/ 6-311G(d,p)	LC-PBE/ 6-311G(d,p)	CAM-B3LYP/ 6-311G(d,p)
PhPh	H→L (90%) H-1→L+2 (7%)	H→L (89%) H-1→L+1 (7%)	H→L (77%) H-1→L+2 (12%) H→L+7 (2%) H-2→L+1 (4%)	H→L (78%) H-1→L+2 (11%) H-2→L+1 (4%) H→L+7 (2%)	H→L (86%) H-1→L+2 (9%)
OMeOMe	H→L (90%) H-2→L+3 (5%)	H→L (90%) H-2→L+1 (5%)	H→L (78%) H-2→L+3 (10%) H-5→L (3%) H-1→L+4 (4%)	H→L (79%) H-2→L+3 (9%) H-5→L (3%) H-1→L+4 (4%)	H→L (87%) H-1→L+4 (2%) H-2→L+3 (7%)
Me_2NMe_2N	H→L (91%) H-1→L+4 (3%) H-2→L+2 (3%)	H→L (91%) H-1→L+4 (3%) H-2→L+1 (3%)	H→L (78%) H-1→L+4 (5%) H-1→L+1 (2%) H-2→L+1 (4%) H-3→L (4%)	H→L (79%) H-1→L+4 (5%) H-1→L+1 (2%) H-2→L+1 (4%) H-3→L (4%)	H→L (88%) H-1→L+4 (3%) H-2→L+1 (4%) H-3→L (2%)
PhCN	H→L (90%) H-1→L+3 (5%)	H→L (89%) H-1→L+3 (5%)	H→L (75%) H-1→L+3 (9%) H-3→L+1 (4%) H→L+1 (3%) H→L+7 (2%)	H→L (76%) H-1→L+3 (9%) H-3→L+1 (4%) H→L+1 (3%) H→L+5 (2%)	H→L (86%) H-1→L+3 (7%)

Molecule	% of orbital contributions				
	M06-2X/ 6-311G(d,p)	M05-2X/ 6-311G(d,p)	LC-BLYP/ 6-311G(d,p)	LC-PBE/ 6-311G(d,p)	CAM-B3LYP/ 6-311G(d,p)
PhOMe	H→L (89%) H-1→L+2 (6%)	H→L (89%) H-2→L+1 (6%)	H→L (76%) H-2→L+4 (10%) H-1→L+2 (2%) H-1→L (2%)	H→L (77%) H-2→L+3(10%) H-1→L+2 (2%) H-1→L (2%)	H→L (85%) H-2→L+2 (8%)
PhMe$_2$N	H→L (88%) H-1→L (4%) H-2→L+1 (4%)	H→L (87%) H-1→L (4%) H-2→L+1 (4%)	H→L (71%) H-1→L (8%) H-2→L+4 (8%) H-1→L+2 (3%) H→L+2 (5%)	H→L (71%) H-1→L (8%) H-1→L+2 (3%) H-2→L+3 (7%)	H→L (83%) H→L+4 (2%) H-1→L (6%) H-2→L+1 (5%)
Me$_2$NOMe	H→L (90%) H-2→L+2 (4%)	H→L (89%) H-1→L+4 (2%) H-1→L (2%) H-1→L+2 (4%)	H→L (75%) H-1→L+4 (5%) H-1→L (4%) H-2→L+3 (7%) H-5→L (2%)	H→L (76%) H-1→L+4 (5%) H-1→L (4%) H-2→L+3 (7%) H-5→L (2%)	H→L (85%) H-1→L+4 (2%) H-1→L (3%) H-2→L+2 (5%)
Me$_2$NCN	H→L (86%) H→L+2 (5%) H-1→L (6%) H-2→L+3 (2%)	H→L (84%) H→L+1 (5%) H-1→L (6%) H-2→L+3 (3%)	H→L (62%) H-1→L (14%) H→L+1 (12%) H-2→L+3 (6%)	H→L (62%) H-1→L (14%) H→L+1 (12%) H-2→L+3 (5%)	H→L (80%) H-1→L (8%) H-2→L+3 (4%) H→L+1 (6%)

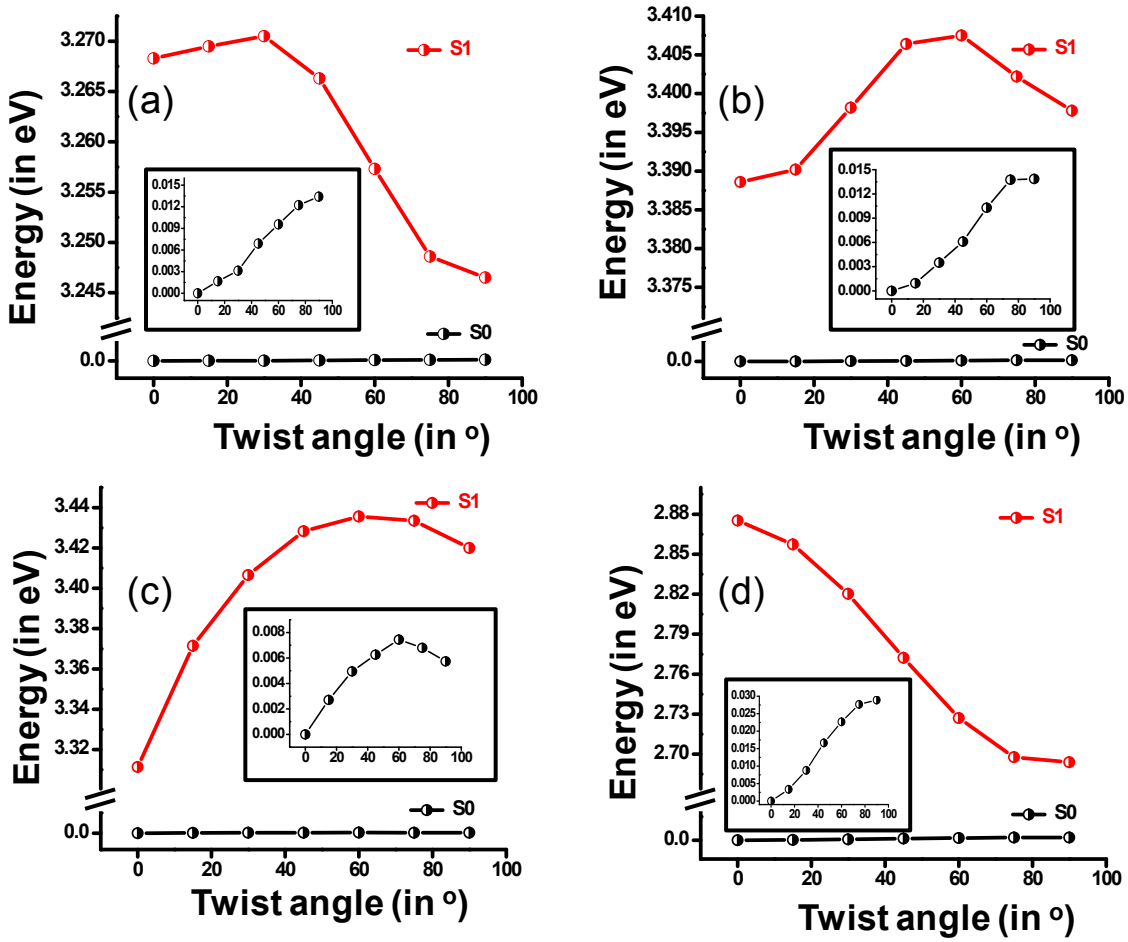


Fig. S13 TDDFT potential energy curves (energy relative to the minimum of the ground state) of the ground and 1st excited singlet state of (a) **PhMe$_2$N**, (b) **PhCN**, (c) **Me$_2$NOMe**, and (d) **Me$_2$NCN** in cyclohexane as a function of twist angle of the phenyl ring around the butadiyne moiety using PBE0/6-311+G(d,p) (expanded energy scale of S_0 is in inset)

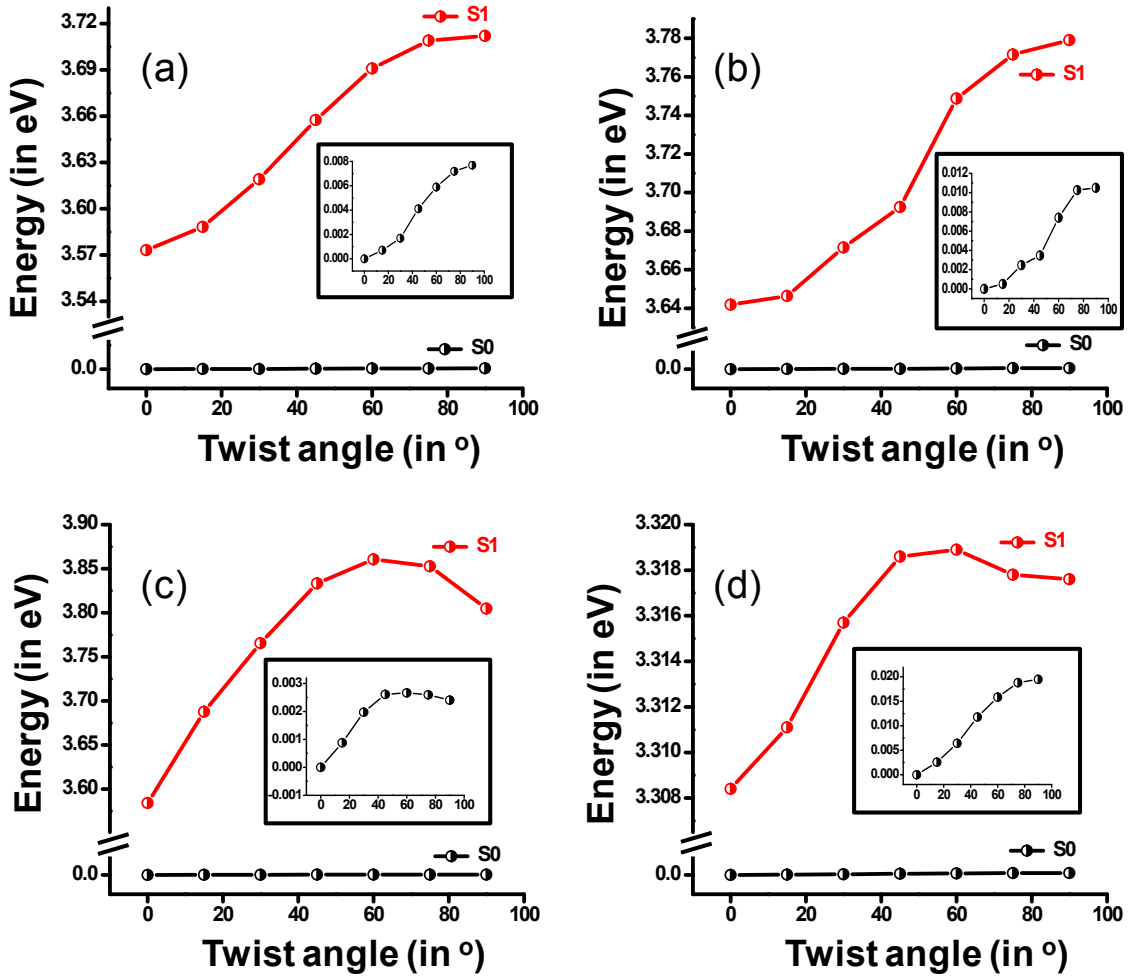


Fig. S14 TDDFT potential energy curves (energy relative to the minimum of the ground state) of the ground and 1st excited singlet state of (a) **PhMe$_2$N**, (b) **PhCN**, (c) **Me$_2$NOMe**, and (d) **Me$_2$NCN** in cyclohexane as a function of twist angle of the phenyl ring around the butadiyne moiety using CAM-B3LYP/6-311+G(d,p) (expanded energy scale of S_0 is in inset)

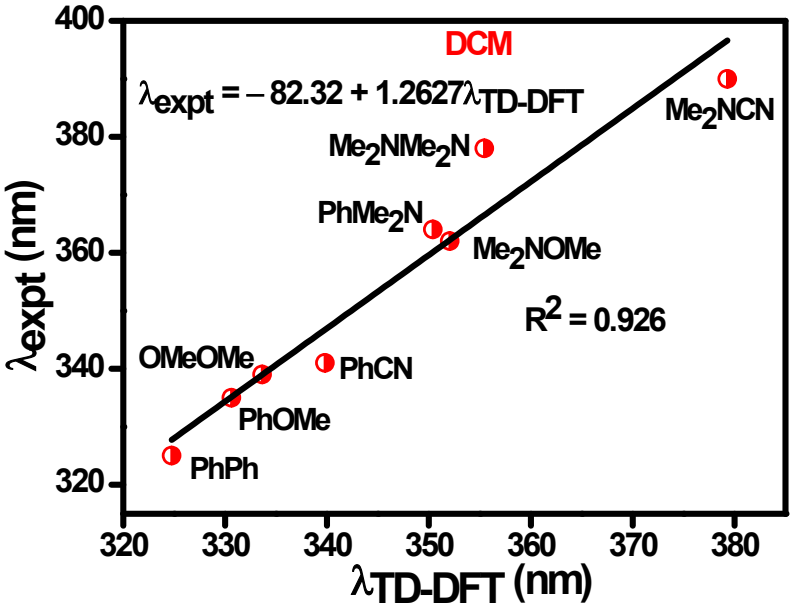


Fig. S15 Correlation between experimental (ref. 1) and TD-DFT absorption wavelength in DCM using CAM-B3LYP/6-311+G(d,p) level of theory

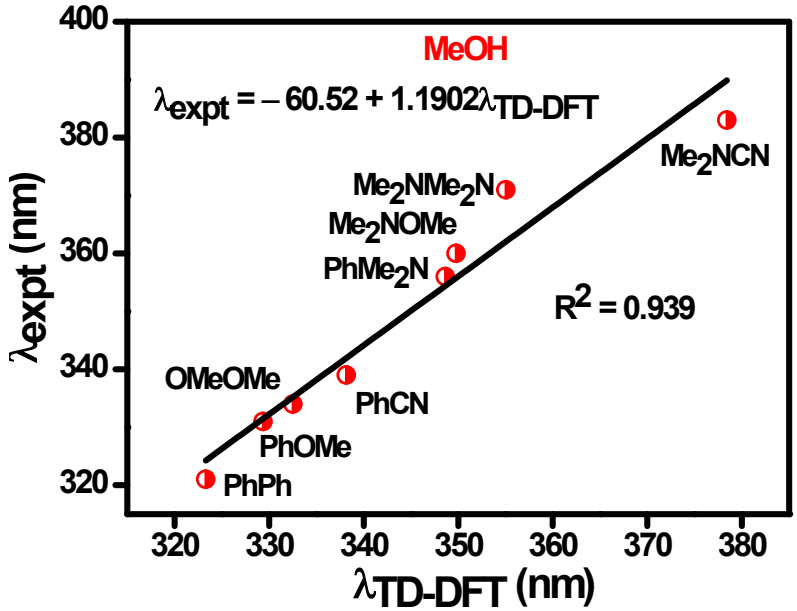


Fig. S16 Correlation between experimental (ref. 1) and TD-DFT absorption wavelength in MeOH using CAM-B3LYP/6-311+G(d,p) level of theor

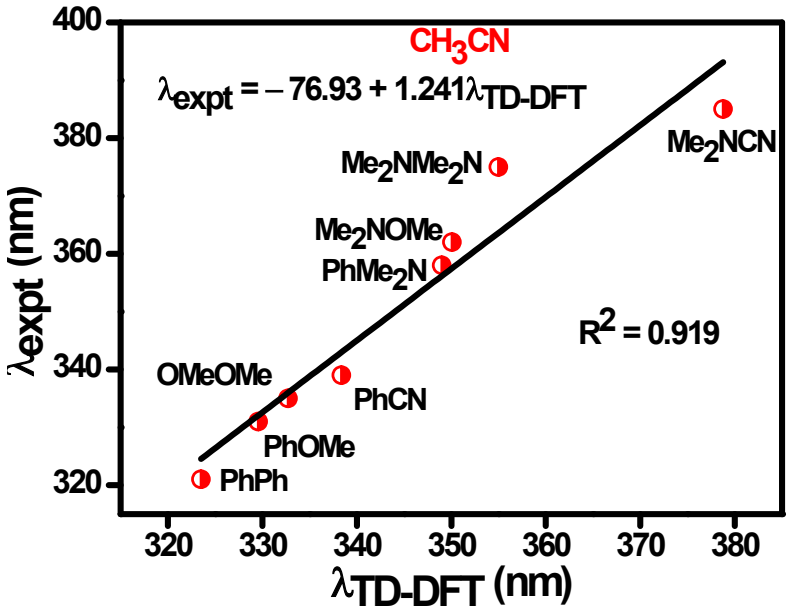


Fig. S17 Correlation between experimental (ref. 1) and TD-DFT absorption wavelength in CH_3CN using CAM-B3LYP/6-311+G(d,p) level of theory

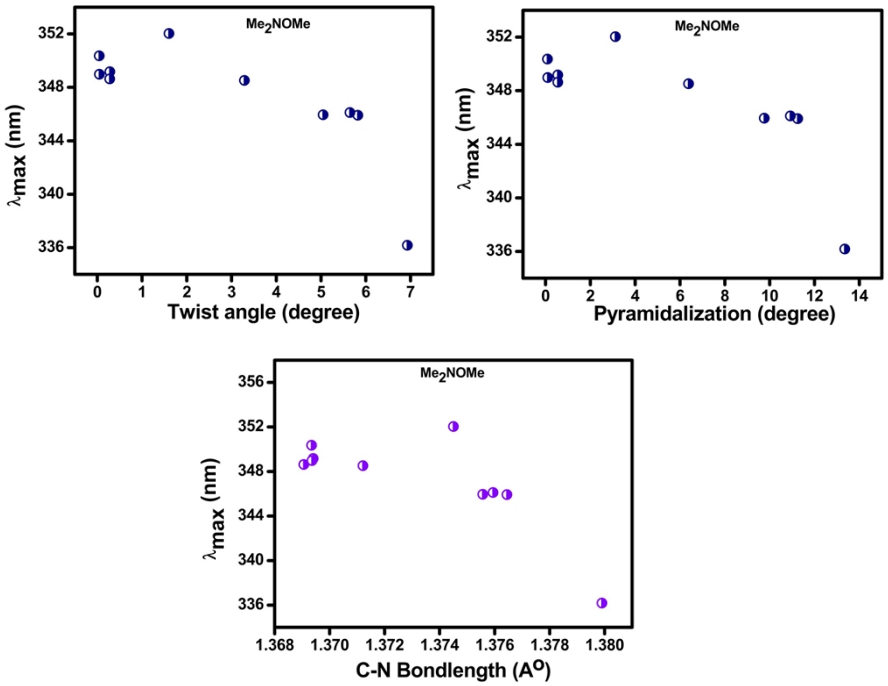


Fig. S18 Correlation between vertical excitation energy and (a) twist angle, (b) pyramidalization, and (c) C(Ph)–N(NMe_2) bond length in **Me_2NOMe**

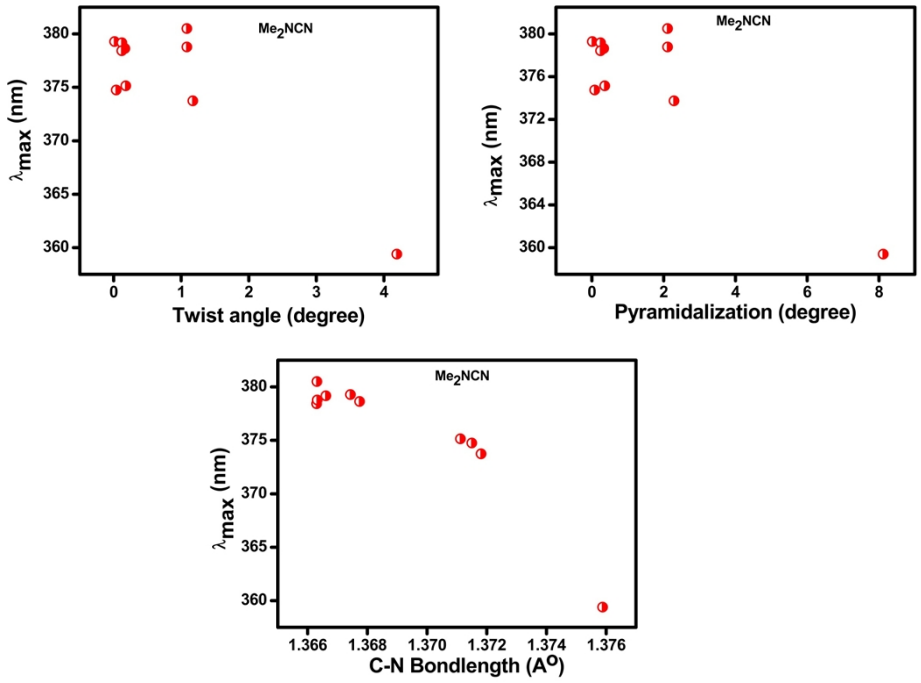


Fig. S19 Correlation between vertical excitation energy and (a) twist angle, (b) pyramidalization of NMe_2, and (c) C(Ph)–N(NMe_2) bond length in **Me_2NCN**

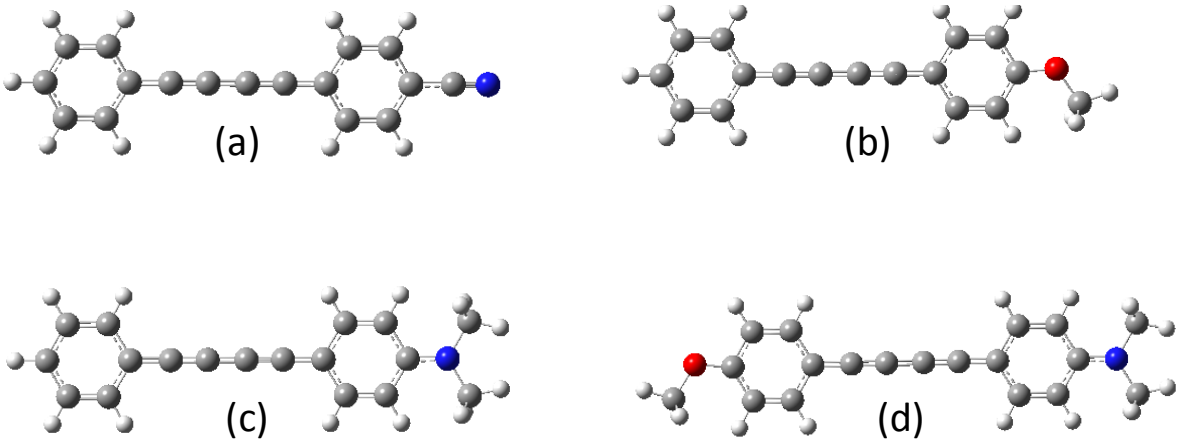


Fig. S20 Optimized LE state geometry of the fluorophores (a) **PhCN**, (b) **PhOMe**, (c) **PhMe_2N**, and (d) **Me_2NOMe** in CH_3CN using B3LYP/6-311G(d,p) level of theory

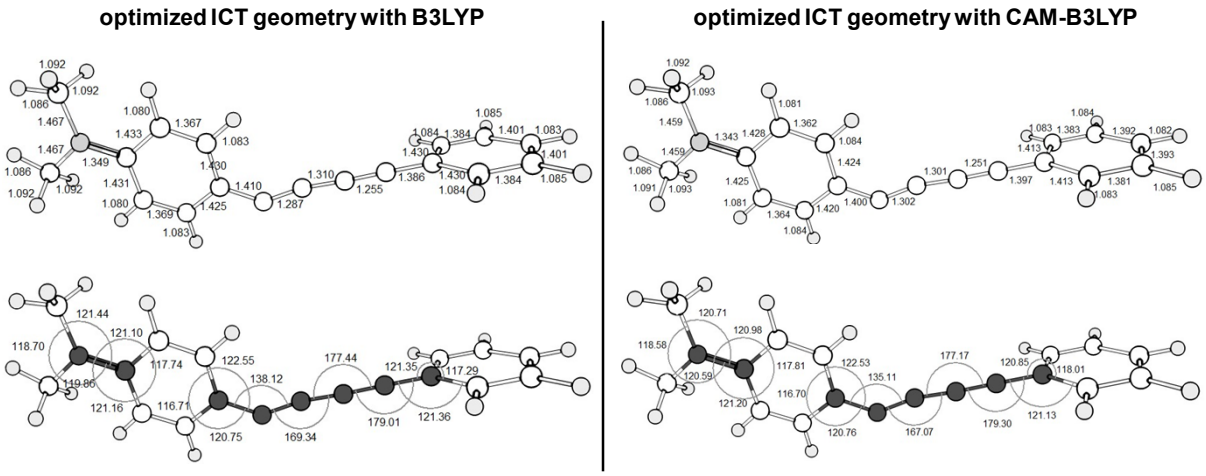


Fig. S21 Geometrical parameters of the optimized ICT state geometry of **PhMe$_2$N**

Table S3 ICT emission energy of **PhCN** and **Me$_2$NCN** using different functionals and 6-311+G(d,p) basis set

Molecules	ICT emission energies (in eV) in CH_3CN					
	Expt.[a]	B3LYP	PBE0	M052X	LC-BLYP	CAM-B3LYP
PhCN	2.62	2.67	2.75	2.78	3.20	3.01
Me$_2$NCN	2.05	2.03	2.15	2.52	3.04	2.67

[a]Ref: 1

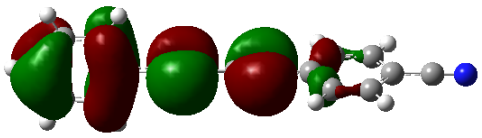
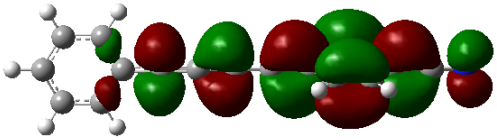
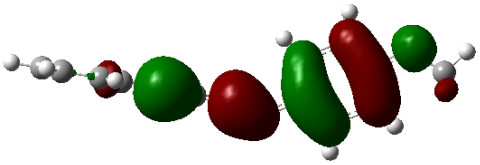
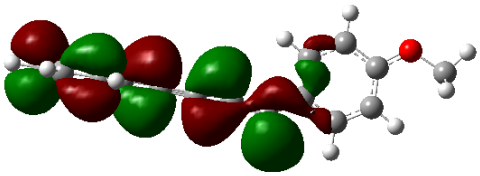
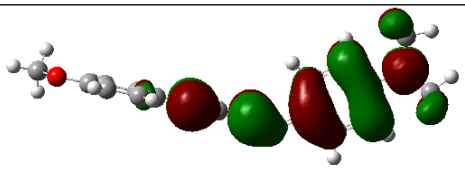
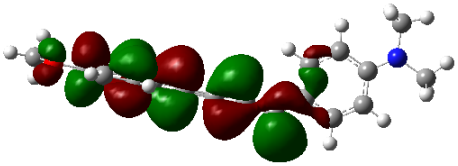
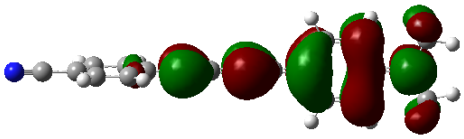
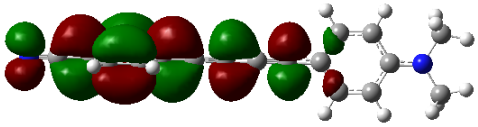
Molecules	HOMO	LUMO
PhCN		
PhOMe		
Me_2NOMe		
Me_2NCN		

Fig. S22 HOMO and LUMO of **PhCN, PhOMe, Me_2NOMe, and Me_2NCN** in ICT emissive state in CH_3CN

Table S4 Absorption and LE TDM vectors using CAM-B3LYP/6-311+G(d,p)

Molecules	Absorption TDM				LE TDM			
	Magnitude (Debye)	Vector			Magnitude (Debye)	Vector		
		x	y	z		x	y	z
PhCN	7.12	7.12	0	0	7.97	0	-7.97	0
PhOMe	2.38	-1.53	-1.82	0	2.98	-2.35	-1.84	0
$PhMe_2N$	5.17	5.17	0	0	6.38	6.38	0	0

Cartesian co-ordinates of the optimized ground state geometry of the fluorophores in acetonitrile (B3LYP/6-311G(d,p))

Optimized ground state geometry of PhPh

6	-5.419539000	1.207897000	-0.000870000
6	-4.029818000	1.214109000	-0.000880000
6	-3.315668000	-0.000021000	0.000000000
6	-4.029881000	-1.214112000	0.000883000
6	-5.419603000	-1.207828000	0.000878000
6	-6.118388000	0.000052000	0.000006000
1	-5.959139000	2.147822000	-0.001553000
1	-3.485881000	2.150801000	-0.001565000
1	-3.485995000	-2.150834000	0.001565000
1	-5.959251000	-2.147725000	0.001564000
6	-1.895127000	-0.000056000	-0.000003000
6	-0.678536000	-0.000084000	-0.000007000
6	0.678536000	-0.000043000	-0.000012000
6	1.895127000	-0.000047000	-0.000015000
6	3.315668000	-0.000015000	-0.000006000
6	4.029824000	1.214111000	0.000880000

6	4.029876000	-1.214111000	-0.000883000
6	5.419545000	1.207892000	0.000881000
1	3.485892000	2.150806000	0.001561000
6	5.419597000	-1.207833000	-0.000868000
1	3.485984000	-2.150830000	-0.001570000
6	6.118388000	0.000045000	0.000010000
1	5.959149000	2.147815000	0.001568000
1	5.959241000	-2.147732000	-0.001549000
1	7.202123000	0.000068000	0.000017000
1	-7.202123000	0.000081000	0.000008000

Optimized ground state geometry of PhOMe

6	-4.408263000	-1.019594000	0.001029000
6	-3.018711000	-1.050527000	0.001203000
6	-2.262919000	0.134597000	0.000006000
6	-2.952651000	1.367045000	-0.001364000
6	-4.333572000	1.403307000	-0.001526000
6	-5.076546000	0.211485000	-0.000341000
1	-4.956379000	-1.951540000	0.001958000
1	-2.508734000	-2.006208000	0.002272000

1	-2.389727000	2.292456000	-0.002300000
1	-4.866556000	2.346351000	-0.002582000
6	-0.845903000	0.095494000	0.000150000
6	0.371212000	0.063425000	0.000266000
6	1.727660000	0.029749000	0.000389000
6	2.944271000	-0.000098000	0.000465000
6	4.364449000	-0.033169000	0.000190000
6	5.051374000	-1.263059000	-0.001403000
6	5.107232000	1.163846000	0.001533000
6	6.440954000	-1.288699000	-0.001632000
1	4.486432000	-2.187291000	-0.002443000
6	6.496492000	1.125770000	0.001273000
1	4.585350000	2.113057000	0.002776000
6	7.167865000	-0.097551000	-0.000305000
1	6.958562000	-2.240984000	-0.002860000
1	7.057274000	2.053288000	0.002316000
8	-6.423876000	0.356392000	-0.000657000
6	-7.243233000	-0.816825000	0.000673000
1	-7.067387000	-1.419741000	0.895913000

1	-8.269881000	-0.457558000	0.000362000
1	-7.067521000	-1.421668000	-0.893295000
1	8.251323000	-0.122484000	-0.000497000

Optimized ground state geometry of OMeOMe

6	-5.412534000	1.355126000	0.000166000
6	-4.030888000	1.348221000	0.000126000
6	-3.314316000	0.131181000	-0.000041000
6	-4.045236000	-1.069358000	-0.000157000
6	-5.435509000	-1.067949000	-0.000110000
6	-6.130117000	0.148136000	0.000051000
1	-5.965202000	2.286821000	0.000289000
1	-3.488203000	2.285680000	0.000215000
1	-3.515402000	-2.014213000	-0.000291000
1	-5.963454000	-2.011482000	-0.000196000
6	-1.896258000	0.123261000	-0.000082000
6	-0.678516000	0.120442000	-0.000100000
6	0.678512000	0.120405000	-0.000103000
6	1.896255000	0.123198000	-0.000096000
6	3.314313000	0.131138000	-0.000049000

6	4.030865000	1.348189000	-0.000144000
6	4.045251000	-1.069389000	0.000075000
6	5.412511000	1.355118000	-0.000108000
1	3.488165000	2.285639000	-0.000244000
6	5.435524000	-1.067957000	0.000106000
1	3.515432000	-2.014252000	0.000155000
6	6.130114000	0.148139000	0.000016000
1	5.965165000	2.286822000	-0.000179000
1	5.963483000	-2.011481000	0.000192000
8	-7.481049000	0.264512000	0.000118000
6	-8.274592000	-0.925904000	0.000026000
1	-8.086037000	-1.526193000	0.894553000
1	-9.308908000	-0.589199000	0.000050000
1	-8.086049000	-1.526055000	-0.894595000
8	7.481045000	0.264539000	0.000056000
6	8.274613000	-0.925861000	0.000127000
1	9.308922000	-0.589134000	0.000168000
1	8.086046000	-1.526060000	0.894710000
1	8.086109000	-1.526108000	-0.894437000

Optimized ground state geometry of PhCN

6	-4.573048000	-1.216230000	0.000049000
6	-3.188350000	-1.215078000	0.000066000
6	-2.474738000	0.000098000	0.000015000
6	-3.188481000	1.215197000	-0.000054000
6	-4.573179000	1.216200000	-0.000070000
6	-5.274386000	-0.000053000	-0.000017000
1	-5.115676000	-2.152856000	0.000088000
1	-2.646958000	-2.152269000	0.000118000
1	-2.647190000	2.152447000	-0.000094000
1	-5.115908000	2.152767000	-0.000122000
6	-1.056964000	0.000176000	0.000029000
6	0.159343000	0.000213000	0.000048000
6	1.515045000	0.000144000	0.000077000
6	2.731618000	0.000069000	0.000099000
6	4.151262000	0.000007000	0.000035000
6	4.864197000	-1.214855000	-0.000053000
6	4.864305000	1.214805000	0.000067000

6	6.253673000	-1.208450000	-0.000106000
1	4.319797000	-2.151189000	-0.000077000
6	6.253780000	1.208277000	0.000013000
1	4.319988000	2.151187000	0.000136000
6	6.951807000	-0.000117000	-0.000074000
1	6.793682000	-2.148028000	-0.000173000
1	6.793872000	2.147807000	0.000039000
1	8.035521000	-0.000165000	-0.000117000
6	-6.703142000	-0.000131000	-0.000032000
7	-7.859083000	-0.000191000	-0.000049000

Optimized ground state geometry of $PhMe_2N$

6	-6.930602000	-1.207115000	-0.001312000
6	-5.540756000	-1.213357000	-0.000543000
6	-4.824229000	-0.000006000	0.001205000
6	-5.540686000	1.213387000	0.002188000
6	-6.930532000	1.207228000	0.001390000
6	-7.630630000	0.000077000	-0.000365000
1	-7.469612000	-2.147551000	-0.002690000
1	-4.997714000	-2.150692000	-0.001331000

1	-4.997589000	2.150689000	0.003531000
1	-7.469488000	2.147695000	0.002130000
6	-3.403914000	-0.000048000	0.001748000
6	-2.186102000	-0.000065000	0.001854000
6	-0.829986000	-0.000086000	0.001504000
6	0.389493000	-0.000125000	0.000615000
6	1.802853000	-0.000093000	-0.001284000
6	2.535731000	-1.205444000	-0.000648000
6	2.535666000	1.205299000	-0.002643000
6	3.917329000	-1.211251000	-0.003377000
1	2.002670000	-2.149122000	0.003031000
6	3.917262000	1.211177000	-0.005388000
1	2.002553000	2.148952000	-0.000567000
6	4.657932000	-0.000019000	-0.009325000
1	4.430347000	-2.162453000	-0.000652000
1	4.430238000	2.162407000	-0.004352000
7	6.026148000	0.000048000	-0.019640000
6	6.763014000	1.257534000	0.009856000
1	6.555895000	1.830880000	0.920974000

1	7.829017000	1.044501000	-0.020498000
1	6.519534000	1.886983000	-0.852716000
6	6.763208000	-1.257293000	0.011086000
1	6.518789000	-1.888132000	-0.850189000
1	7.829146000	-1.044173000	-0.020916000
1	6.557252000	-1.829229000	0.923366000
1	-8.714375000	0.000110000	-0.001000000

Optimized ground state geometry of Me_2NMe_2N

6	5.431005000	0.895820000	-0.814641000
6	4.048464000	0.890253000	-0.810297000
6	3.314785000	0.000402000	0.000929000
6	4.049289000	-0.889138000	0.811748000
6	5.431834000	-0.893882000	0.815573000
6	6.172316000	0.001455000	0.000624000
1	5.942471000	1.599415000	-1.456338000
1	3.515459000	1.587391000	-1.446565000
1	3.516936000	-1.586922000	1.447855000
1	5.943979000	-1.597650000	1.456536000
6	1.898508000	-0.000073000	0.001126000

6	0.678563000	-0.000454000	0.001284000
6	-0.678571000	-0.000848000	0.001439000
6	-1.898516000	-0.001184000	0.001540000
6	-3.314795000	-0.001531000	0.001690000
6	-4.048762000	-0.891242000	-0.809426000
6	-4.049008000	0.888288000	0.812467000
6	-5.431308000	-0.896601000	-0.813507000
1	-3.515986000	-1.588305000	-1.445969000
6	-5.431551000	0.893244000	0.816544000
1	-3.516428000	1.586285000	1.448149000
6	-6.172319000	-0.002431000	0.002235000
1	-5.942991000	-1.599869000	-1.455389000
1	-5.943481000	1.597546000	1.457089000
7	-7.541714000	-0.004009000	0.003878000
6	-8.278009000	0.937117000	0.837913000
1	-8.048303000	1.976633000	0.577642000
1	-9.344462000	0.781344000	0.692212000
1	-8.057134000	0.795017000	1.901781000
6	-8.277990000	-0.929380000	-0.847572000

1	-8.040051000	-1.972457000	-0.611554000
1	-9.344334000	-0.784412000	-0.690347000
1	-8.065415000	-0.762765000	-1.909926000
7	7.541698000	0.002445000	0.001053000
6	8.278421000	-0.934467000	0.839422000
1	9.344769000	-0.782269000	0.689242000
1	8.061103000	-0.785209000	1.903156000
1	8.045594000	-1.974951000	0.586363000
6	8.277632000	0.932798000	-0.845257000
1	9.344063000	0.785514000	-0.690823000
1	8.063231000	0.772981000	-1.908200000
1	8.041171000	1.974746000	-0.602441000

Optimized ground state geometry of Me_2NOMe

6	5.917679000	-1.031783000	-0.000161000
6	4.527032000	-1.049760000	-0.000199000
6	3.780094000	0.141216000	0.000013000
6	4.483590000	1.366100000	0.000264000
6	5.865599000	1.389375000	0.000300000
6	6.598608000	0.191896000	0.000091000

1	6.455334000	-1.970999000	-0.000331000
1	4.009632000	-2.002618000	-0.000397000
1	3.930733000	2.298756000	0.000430000
1	6.406254000	2.329305000	0.000492000
6	2.362056000	0.115328000	-0.000021000
6	1.143930000	0.093713000	-0.000049000
6	-0.212505000	0.069483000	-0.000083000
6	-1.431714000	0.046309000	-0.000115000
6	-2.845654000	0.017138000	-0.000156000
6	-3.553599000	-1.202814000	-0.000024000
6	-3.605117000	1.205696000	-0.000307000
6	-4.935379000	-1.238157000	-0.000058000
1	-3.001475000	-2.136640000	0.000126000
6	-4.987278000	1.182005000	-0.000341000
1	-3.093441000	2.162286000	-0.000378000
6	-5.702626000	-0.043956000	-0.000267000
1	-5.425654000	-2.202395000	0.000066000
1	-5.518682000	2.124249000	-0.000435000
7	-7.071662000	-0.073717000	-0.000451000

6	-7.833826000	1.167270000	0.000285000
1	-7.621978000	1.775036000	-0.886231000
1	-8.895999000	0.934965000	-0.000089000
1	-7.622289000	1.773950000	0.887648000
6	-7.778504000	-1.346946000	0.000634000
1	-7.540551000	-1.943724000	0.888076000
1	-8.849757000	-1.161386000	0.000258000
1	-7.540266000	-1.945248000	-0.885677000
8	7.948955000	0.324599000	0.000150000
6	8.755050000	-0.854627000	-0.000034000
1	9.785206000	-0.506272000	0.000065000
1	8.574120000	-1.457633000	0.893868000
1	8.574183000	-1.457314000	-0.894163000

Optimized ground state geometry of Me_2NCN

6	-6.095372000	-1.215754000	0.000130000
6	-4.711156000	-1.214849000	0.000945000
6	-3.994228000	-0.000038000	0.001273000
6	-4.711094000	1.214811000	0.000822000
6	-6.095310000	1.215789000	0.000010000

6	-6.798475000	0.000036000	-0.000355000
1	-6.637607000	-2.152769000	-0.000150000
1	-4.170610000	-2.152639000	0.001296000
1	-4.170499000	2.152573000	0.001072000
1	-6.637497000	2.152831000	-0.000365000
6	-2.578505000	-0.000078000	0.001890000
6	-1.360193000	-0.000097000	0.002117000
6	-0.006886000	-0.000102000	0.002028000
6	1.213377000	-0.000031000	0.001478000
6	2.623875000	-0.000013000	-0.000046000
6	3.356395000	-1.206655000	-0.000935000
6	3.356376000	1.206641000	0.000118000
6	4.736868000	-1.212311000	-0.003132000
1	2.822681000	-2.149862000	0.000740000
6	4.736850000	1.212324000	-0.002065000
1	2.822647000	2.149837000	0.002735000
6	5.477426000	0.000016000	-0.006254000
1	5.250408000	-2.163122000	-0.002395000
1	5.250375000	2.163145000	-0.000186000

7	6.843728000	0.000025000	-0.013675000
6	7.581724000	1.257837000	0.004862000
1	7.372167000	1.838778000	0.910136000
1	8.647490000	1.043619000	-0.020358000
1	7.340392000	1.878720000	-0.864384000
6	7.581734000	-1.257763000	0.006563000
1	7.343839000	-1.878110000	-0.864058000
1	8.647574000	-1.043448000	-0.014199000
1	7.368693000	-1.839303000	0.910596000
6	-8.226348000	0.000075000	-0.001248000
7	-9.382643000	0.000077000	-0.001995000

Cartesian co-ordinates of the optimized LE state geometry of the fluorophores in acetonitrile (B3LYP/6-311G(d,p))

Optimized LE state geometry of PhOMe

6	-4.395416000	-1.031390000	-0.002880000
6	-3.017365000	-1.067517000	-0.051484000
6	-2.238573000	0.137360000	-0.062543000
6	-2.953901000	1.384559000	-0.029036000
6	-4.324814000	1.409576000	0.019559000

6	-5.069834000	0.207256000	0.034665000
1	-4.948229000	-1.960990000	0.004379000
1	-2.504423000	-2.021084000	-0.080676000
1	-2.392526000	2.310444000	-0.040344000
1	-4.866352000	2.347897000	0.048738000
6	-0.863331000	0.101865000	-0.103057000
6	0.389586000	0.067833000	-0.111197000
6	1.703409000	0.034277000	-0.103149000
6	2.956557000	0.002389000	-0.087013000
6	4.333993000	-0.031692000	-0.026395000
6	5.047055000	-1.278795000	-0.003286000
6	5.107606000	1.178757000	0.011110000
6	6.427330000	-1.296864000	0.061392000
1	4.483083000	-2.203784000	-0.036487000
6	6.487075000	1.128874000	0.075759000
1	4.589844000	2.130431000	-0.008230000
6	7.164648000	-0.101451000	0.098884000
1	6.946788000	-2.249005000	0.080731000
1	7.052745000	2.054260000	0.104915000

8	-6.408829000	0.351535000	0.083367000
6	-7.242995000	-0.814416000	0.086373000
1	-7.045707000	-1.434161000	0.964978000
1	-8.264246000	-0.441682000	0.123140000
1	-7.094331000	-1.400145000	-0.825721000
1	8.247800000	-0.128184000	0.151426000

Optimized LE state geometry of PhCN

6	1.215752000	4.573336000	0.000000000
6	1.214932000	3.188637000	0.000000000
6	-0.000074000	2.474737000	0.000000000
6	-1.215343000	3.188188000	0.000000000
6	-1.216677000	4.572886000	0.000000000
6	-0.000592000	5.274386000	0.000000000
1	2.152250000	5.116184000	0.000000000
1	2.152255000	2.647477000	0.000000000
1	-2.152466000	2.646680000	0.000000000
1	-2.153375000	5.115387000	0.000000000
6	0.000191000	1.056965000	0.000000000
6	0.000367000	-0.159345000	0.000000000

6	0.000399000	-1.515043000	0.000000000
6	0.000431000	-2.731618000	0.000000000
6	0.000431000	-4.151265000	0.000000000
6	1.215263000	-4.864247000	0.000000000
6	-1.214401000	-4.864247000	0.000000000
6	1.208793000	-6.253724000	0.000000000
1	2.151620000	-4.319890000	0.000000000
6	-1.207932000	-6.253724000	0.000000000
1	-2.150759000	-4.319891000	0.000000000
6	0.000431000	-6.951803000	0.000000000
1	2.148348000	-6.793773000	0.000000000
1	-2.147486000	-6.793774000	0.000000000
1	0.000431000	-8.035517000	0.000000000
6	-0.000856000	6.703139000	0.000000000
7	-0.001071000	7.859081000	0.000000000

Optimized LE state geometry of $PhMe_2N$

6	6.923132000	1.211477000	-0.003567000
6	5.541969000	1.226804000	0.000828000
6	4.795690000	0.000011000	0.000857000

6	5.541976000	-1.226777000	-0.001423000
6	6.923138000	-1.211443000	-0.005863000
6	7.634668000	0.000019000	-0.006934000
1	7.463630000	2.152381000	-0.003827000
1	5.003229000	2.167205000	0.002863000
1	5.003240000	-2.167180000	-0.001162000
1	7.463640000	-2.152344000	-0.007848000
6	3.413219000	0.000008000	0.005238000
6	2.164970000	-0.000006000	0.006407000
6	0.841740000	-0.000009000	0.007525000
6	-0.404938000	-0.000107000	0.007565000
6	-1.787584000	-0.000075000	0.004409000
6	-2.538324000	1.219931000	0.002804000
6	-2.538377000	-1.220047000	0.003917000
6	-3.910899000	1.219115000	-0.002567000
1	-2.004207000	2.161986000	0.005672000
6	-3.910953000	-1.219168000	-0.001562000
1	-2.004302000	-2.162125000	0.007627000
6	-4.652634000	-0.000009000	-0.007483000

1	-4.429142000	2.167445000	-0.000798000
1	-4.429232000	-2.167475000	0.000864000
7	-6.016616000	0.000041000	-0.020332000
6	-6.760184000	-1.255995000	0.004446000
1	-6.551573000	-1.825900000	0.916858000
1	-7.824419000	-1.037782000	-0.029784000
1	-6.508212000	-1.881038000	-0.858471000
6	-6.760062000	1.256147000	0.002281000
1	-6.507021000	1.880178000	-0.862071000
1	-7.824318000	1.038041000	-0.032948000
1	-6.552391000	1.827020000	0.914301000
1	8.718111000	0.000022000	-0.010226000

Optimized LE state geometry of Me_2NCN

6	-6.095334000	-1.215744000	-0.000416000
6	-4.711119000	-1.214832000	-0.000408000
6	-3.994196000	-0.000009000	0.000016000
6	-4.711066000	1.214841000	0.000432000
6	-6.095279000	1.215809000	0.000425000
6	-6.798442000	0.000047000	0.000001000

1	-6.637580000	-2.152750000	-0.000743000
1	-4.170556000	-2.152610000	-0.000730000
1	-4.170462000	2.152595000	0.000760000
1	-6.637488000	2.152837000	0.000746000
6	-2.578480000	-0.000041000	0.000024000
6	-1.360168000	-0.000105000	0.000031000
6	-0.006859000	-0.000120000	0.000038000
6	1.213407000	-0.000277000	0.000039000
6	2.623901000	-0.000164000	-0.000017000
6	3.356490000	-1.206782000	0.000210000
6	3.356317000	1.206555000	-0.000242000
6	4.736961000	-1.212362000	0.000157000
1	2.822815000	-2.150010000	0.000432000
6	4.736785000	1.212326000	-0.000298000
1	2.822504000	2.149705000	-0.000324000
6	5.477411000	0.000033000	-0.000209000
1	5.250614000	-2.163117000	0.000338000
1	5.250307000	2.163150000	-0.000409000
7	6.843667000	0.000120000	-0.000455000

6	7.581518000	1.258137000	-0.000143000
1	7.356497000	1.858799000	0.887972000
1	8.647504000	1.043602000	-0.001009000
1	7.355314000	1.859751000	-0.887274000
6	7.581670000	-1.257805000	0.000559000
1	7.355752000	-1.859843000	-0.886367000
1	8.647632000	-1.043151000	-0.000140000
1	7.356489000	-1.858097000	0.888875000
6	-8.226314000	0.000080000	-0.000007000
7	-9.382605000	0.000113000	-0.000014000

Cartesian co-ordinates of the optimized ICT state geometry of the fluorophores in acetonitrile (B3LYP/6-311G(d,p))

Optimized ICT state geometry of PhOMe

6	-4.630551000	0.943075000	-0.000315000
6	-3.351198000	1.451436000	-0.000506000
6	-2.204956000	0.606569000	-0.000292000
6	-2.428918000	-0.808314000	0.000056000
6	-3.695683000	-1.325194000	0.000177000
6	-4.817212000	-0.456768000	0.000105000

1	-5.477841000	1.613466000	-0.000487000
1	-3.193050000	2.522670000	-0.000828000
1	-1.569205000	-1.467049000	0.000151000
1	-3.877329000	-2.392774000	0.000440000
6	-0.914546000	1.169205000	-0.000500000
6	0.303714000	0.719476000	-0.000405000
6	1.591582000	0.530346000	-0.000124000
6	2.826217000	0.284229000	-0.000079000
6	4.190921000	0.046273000	0.000011000
6	4.918852000	-0.080149000	1.221825000
6	4.918820000	-0.081280000	-1.221689000
6	6.283295000	-0.315796000	1.205619000
1	4.390925000	0.011858000	2.163166000
6	6.283267000	-0.316927000	-1.205299000
1	4.390877000	0.009845000	-2.163106000
6	6.984662000	-0.437215000	0.000204000
1	6.811336000	-0.406464000	2.149101000
1	6.811283000	-0.408469000	-2.148709000
8	-6.004643000	-1.058599000	0.000424000

6	-7.214664000	-0.275499000	0.000428000
1	-7.270391000	0.343380000	-0.896749000
1	-8.022999000	-1.001216000	0.000881000
1	-7.269978000	0.344045000	0.897169000
1	8.051913000	-0.621311000	0.000276000

Optimized ICT state geometry of PhCN

6	4.559262000	-1.112359000	-0.502660000
6	3.188669000	-1.122266000	-0.506648000
6	2.442918000	-0.000008000	-0.000040000
6	3.188629000	1.122258000	0.506605000
6	4.559222000	1.112370000	0.502686000
6	5.288002000	0.000010000	0.000031000
1	5.098298000	-1.969294000	-0.889565000
1	2.653889000	-1.980110000	-0.893837000
1	2.653818000	1.980096000	0.893769000
1	5.098228000	1.969311000	0.889617000
6	1.071603000	-0.000018000	-0.000074000
6	-0.187774000	-0.000031000	-0.000104000
6	-1.496384000	-0.000017000	-0.000131000

6	-2.750401000	0.000005000	-0.000187000
6	-4.137151000	0.000007000	-0.000071000
6	-4.862713000	-0.508654000	1.118672000
6	-4.862901000	0.508662000	-1.118693000
6	-6.242485000	-0.505841000	1.110552000
1	-4.310212000	-0.893310000	1.965968000
6	-6.242672000	0.505838000	-1.110345000
1	-4.310542000	0.893320000	-1.966082000
6	-6.933067000	-0.000004000	0.000161000
1	-6.793181000	-0.892100000	1.958843000
1	-6.793512000	0.892091000	-1.958546000
1	-8.016413000	-0.000008000	0.000250000
6	6.698450000	0.000019000	0.000066000
7	7.861769000	0.000027000	0.000095000

Optimized ICT state geometry of $PhMe_2N$

6	-6.687093000	0.428596000	1.205513000
6	-5.333874000	0.137161000	1.221211000
6	-4.606803000	-0.021117000	0.000185000
6	-5.333976000	0.136002000	-1.220910000

6	-6.687192000	0.427470000	-1.205365000
6	-7.385210000	0.578339000	0.000030000
1	-7.210682000	0.541719000	2.149406000
1	-4.810908000	0.024601000	2.163495000
1	-4.811096000	0.022545000	-2.163132000
1	-7.210860000	0.539709000	-2.149318000
6	-3.252441000	-0.314547000	0.000306000
6	-2.030781000	-0.601307000	0.000438000
6	-0.743806000	-0.843268000	0.000470000
6	0.455261000	-1.310987000	0.000513000
6	1.775047000	-0.815761000	0.000031000
6	2.887349000	-1.706437000	0.000044000
6	2.071920000	0.583321000	-0.000502000
6	4.180772000	-1.256746000	-0.000418000
1	2.686731000	-2.770889000	0.000383000
6	3.356657000	1.051583000	-0.000968000
1	1.244964000	1.283260000	-0.000428000
6	4.466142000	0.145382000	-0.000938000
1	4.988619000	-1.973396000	-0.000550000

1	3.530209000	2.117806000	-0.001181000
7	5.736568000	0.599125000	-0.001397000
6	6.036189000	2.034834000	-0.003072000
1	5.628564000	2.519092000	0.887176000
1	7.114669000	2.157962000	0.010311000
1	5.606550000	2.512510000	-0.886440000
6	6.852024000	-0.353234000	-0.000214000
1	6.807329000	-0.992862000	-0.884643000
1	7.780667000	0.208806000	0.017468000
1	6.822121000	-0.986823000	0.889132000
1	-8.443973000	0.806380000	-0.000038000

Optimized ICT state geometry of Me_2NCN

6	6.097852000	-0.049978000	1.215252000
6	4.712794000	-0.050084000	1.212906000
6	3.998177000	-0.000564000	-0.000538000
6	4.713805000	0.049394000	-1.213364000
6	6.098866000	0.050126000	-1.214519000
6	6.799576000	0.000294000	0.000668000
1	6.640429000	-0.088044000	2.151174000

1	4.170830000	-0.088294000	2.149056000
1	4.172624000	0.087296000	-2.149981000
1	6.642224000	0.088555000	-2.149973000
6	2.578584000	-0.000780000	-0.001109000
6	1.361336000	-0.000818000	-0.001455000
6	0.005519000	-0.000730000	-0.001709000
6	-1.213736000	-0.000585000	-0.001640000
6	-2.627431000	-0.000337000	-0.001328000
6	-3.358877000	1.204824000	0.038327000
6	-3.359360000	-1.205236000	-0.039984000
6	-4.740394000	1.210820000	0.039602000
1	-2.825437000	2.147706000	0.069673000
6	-4.740880000	-1.210729000	-0.039622000
1	-2.826304000	-2.148317000	-0.071880000
6	-5.481245000	0.000182000	0.000396000
1	-5.252826000	2.161659000	0.073712000
1	-5.253703000	-2.161387000	-0.072937000
7	-6.848872000	0.000435000	0.001220000
6	-7.586707000	-1.256795000	-0.018344000

1	-7.325349000	-1.913983000	0.841873000
1	-8.652185000	-1.042581000	0.020006000
1	-7.387796000	-1.831373000	-0.930142000
6	-7.586218000	1.257958000	0.020680000
1	-7.325062000	1.914737000	-0.839916000
1	-8.651797000	1.044134000	-0.017007000
1	-7.386612000	1.832787000	0.932161000
6	8.228714000	0.000746000	0.001289000
7	9.400114000	0.001116000	0.001799000

Optimized ICT state geometry of $PhMe_2N$ using CAM-B3LYP/6-311G(d,p)

6	6.643623000	0.535583000	-1.155694000
6	5.294914000	0.232693000	-1.188372000
6	4.586842000	-0.016486000	0.009340000
6	5.302371000	0.037190000	1.226784000
6	6.649255000	0.344197000	1.235689000
6	7.337421000	0.590390000	0.049973000
1	7.164726000	0.726998000	-2.086239000
1	4.767426000	0.190169000	-2.133112000
1	4.780820000	-0.161035000	2.155267000

1	7.174393000	0.383419000	2.183767000
6	3.223199000	-0.319964000	-0.014355000
6	2.005534000	-0.606383000	-0.038686000
6	0.727624000	-0.844472000	-0.084468000
6	-0.466834000	-1.362289000	-0.104176000
6	-1.770173000	-0.851228000	-0.078158000
6	-2.891306000	-1.721903000	-0.063167000
6	-2.044787000	0.545955000	-0.064448000
6	-4.172327000	-1.255273000	-0.020108000
1	-2.707105000	-2.789780000	-0.079764000
6	-3.316393000	1.032275000	-0.027990000
1	-1.206402000	1.232110000	-0.084327000
6	-4.433664000	0.144789000	0.015736000
1	-4.992233000	-1.959242000	-0.007637000
1	-3.474528000	2.101216000	-0.022907000
7	-5.689471000	0.616800000	0.078999000
6	-5.947441000	2.053048000	0.065816000
1	-5.594582000	2.507494000	-0.863843000
1	-7.018283000	2.217004000	0.138829000

1	-5.473461000	2.539460000	0.920475000
6	-6.827030000	-0.296770000	0.074921000
1	-6.777359000	-0.988936000	0.916385000
1	-7.741707000	0.282515000	0.164125000
1	-6.873612000	-0.871864000	-0.853469000
1	8.393246000	0.824768000	0.067624000

Reference:

1. A. K. Pati, M. Mohapatra, P. Ghosh, S. J. Gharpure and A. K. Mishra, *J. Phys. Chem. A* **2013,** *117*, 6548-6560.