Investigation on the key features of D-π-A type novel chalcone derivative for opto-electronic applications

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Table S1 Calculated bond lengths [Å] and bond angles [°] of 2,4,5-TMBC optimized molecule at DFT/B3LYP using 6-31G* basis set.

Bond lengths			Bond Angles			Dihedral angle		
	B3LYP	HF		B3LYP	HF		B3LYP	HF
Br1-C10	1.911	1.897	Br1-C10-C11	119.455	119.399	O4-O3-O2-Br1	-12.614	-43.441
C10-C11	1.395	1.385	Br1-C10-C8	119.318	119.382	O5-O4-O3-O2	2.151	3.956
C11-H12	1.084	1.073	C15-C16-O2	119.039	119.223	C6-O2-Br1-O3	2.307	-8.828
C11-C13	1.391	1.381	C17-C16-O2	121.984	122.077	H7-C6-O2-Br1	175.406	173.632
C13-H14	1.085	1.073	C21-C22-O3	116.627	117.168	C8-C6-O2-Br1	2.586	3.971
C13-C15	1.404	1.392	C23-C22-O3	122.753	122.514	H9-C8-C6-O2	172.934	169.258
C10-C8	1.393	1.381	C23-C25-O4	124.550	124.232	C10-C8-C6-O2	-6.919	-10.647
C8-H9	1.085	1.073	C26-C25-O4	115.566	115.862	C11-C10-C8-C6	0.576	0.704
C8-C6	1.395	1.386	C27-C26-O5	125.679	125.504	H12-C11-C10-C8	179.768	179.756
C6-H7	1.085	1.074	C25-C26-O5	115.472	115.844	C13-C11-C10-C8	-0.098	-0.005
C6-C15	1.403	1.389	C22-O3-C29	119.334	120.875	H14-C13-C11-C10	179.285	179.137
C15-C16	1.507	1.505	C25-O4-C33	118.553	120.222	C15-C6-O2-Br1	-14.927	-21.183
C16-O2	1.232	1.201	C26-O5-C37	117.695	119.248	C16-O2-Br1-C10	-0.854	-1.013
C16-C17	1.475	1.481	C15-C16-C17	118.972	118.693	C17-C6-O2-Br1	-179.012	-178.927
C17-H18	1.085	1.073	C16-C17-C19	120.141	119.971	H18-C17-C16-O2	174.213	169.465
C17-C19	1.354	1.333	C17-C19-C21	127.896	127.178	C19-C17-C16-O2	-4.447	-10.184
C19-H20	1.086	1.073	C19-C21-C22	119.744	119.844	H20-C19-C17-C16	-0.991	-2.189
C19-C21	1.451	1.466	C8-C6-C15	120.995	120.847	C21- C19-C17-C16	178.995	178.348
C21-C22	1.413	1.388	C6-C15-C16	123.996	123.233	C22-O3-O2-Br1	-11.663	-41.652
C22-O3	1.363	1.348	C6-C15-C13	118.506	118.837	C23-C22- O3-O2	-178.246	-176.596
O3-C29	1.418	1.400	C15-C13-C11	121.225	120.928	H24-C23-C22-O3	0.085	0.192
C29-H30	1.091	1.079	C13-C11-C10	118.953	119.065	C25-O4-O3-O2	2.177	4.303
C29-H31	1.098	1.085	C11-C10-C8	121.227	121.219	C26-O5-O4-O3	0.041	0.432
C29-H32	1.098	1.085	C21-C22-C23	120.620	120.315	C27-C26-O5-O4	-179.940	-179.771
C22-C23	1.403	1.397	C22-C23-C25	120.530	120.633	H28-C27-C26-O5	0.119	0.903
C23-H24	1.081	1.069	C23-C25-C26	119.884	119.905	C29-O3-O2-Br1	171.915	148.958
C23-C25	1.394	1.379	C25-C26-C27	118.849	118.650	H30-C29-O3-O2	-3.638	-10.083
C25-O4	1.356	1.339	C26-C27-C21	122.558	122.538	H31-C29-O3-O2	-122.283	-128.636
						H32-C29-O3-O2	115.035	108.604

O4-C33	1.419	1.399	C27-C21-C22	117.558	117.955	C33-O4-O3-O2	-177.803	-175.299
C33-H34	1.091	1.079	C18-C17-C19	121.324	121.816	H34-C33-O4-O3	179.986	179.955
C33-H35	1.098	1.085	C27-C21-C19	122.698	122.196	H35-C33-O4-O3	61.244	61.253
C33-H36	1.098	1.085	C17-C19-H20	116.008	116.978	H36-C33-O4-O3	-61.275	-61.354
C25-C26	1.420	1.409	C21-C19-H20	116.097	115.842	C37-O5-O4-O3	-174.407	-171.055
C26-O5	1.365	1.351	C22-C21-C19	119.744	119.844	H38-C37-O5-O4	-5.603	-8.680
O5-C37	1.417	1.396	C22-C23-H24	119.996	119.862	H39-C37-O5-O4	-124.400	-127.417
C37-H38	1.091	1.080	C25-C23-H24	119.474	119.505	H40-C37-O5-O4	113.216	110.107
C37-H39	1.099	1.086	C21-C27-H28	118.183	118.149			
C37-H40	1.099	1.086	C15-C13-H14	118.039	118.841			

Table S2 B3LYP and HF calculated along with experimental IR and Raman frequencies with their appropriate assignments for 2,4,5-TMBC.

Calculated (B3LYP)	Calculated (HF)	Exp.	Calculated (B3LYP)	Calculated (HF)	Exp.	Assignments
IR (cm^{-1})	IR (cm^{-1})	IR (cm^{-1})	Raman (cm^{-1})	Raman (cm^{-1})	Raman (cm^{-1})	
---	---	---	3133	---	3133	υ_{asy}(CH)
3070	3075	3081	3103	3075	3083	υ_{asy}(CH)
3018	3046	---	3041	3053	3033,3021	υ_{asy}(CH)
2988	2975	2998	---	---	2998	υ_{asy}(CH)
---	---	2952	2965	---	2952	υ_{asy}(CH)
2929	---	2927	2910	2925	2933	υ_{sym}(CH)
2855	2867	2852	---	2867	2844	υ_{sym}(CH)
---	1739	1735	---	1739	---	υ(CO)
---	---	1654	1664	---	1652	υ(CO)
1603	1617	1610	---	1617	1610	υ_{ring1}(C-C)
---	1585	1587	1572	1582	1575	$\upsilon_{ring1+2}$(C-H)
1522	1532	1560	1557	1532	1560	υ_{ring2}(C-C)
1499	1485	1511	---	---	---	$\delta_{in}(CCH_{ring1})$, υ_{ring1}(C-C)
1455	1558	1470	1472	1475	1482	$\delta_{asym}(CH_3)$
1418	1403	1442	1395	1403	1455	υ_{ring1}(C-C)
1381	1346	1398	1357	1346	1394	$\delta_{sym}(CH_3)$
1344	1317	1324	1318	---	1358	$\delta_{asym}(CH_3)$
1306	1303	1295	1295	1303	1290	υ_{ring2}(C-C)
1248	1275	1276	1280	1276	1278	υ_{ring2}(C-C)
---	1239,1203	1205	1218	1239,1206	1204	$\delta_{in}(CCH_{ring2})$, υ_{ring1}(C-C)
1177	1189	1172	1188	1155	1188	$\delta_{in}(CCH_{ring1})$, υ_{ring1}(C-C)
1144,1122	1125	1128	1126	1125	1128	$\delta_{in}(CCH_{ring2})$, υ_{ring2}(C-C)
1085	---	1070	1090	1067	1070	υ_{ring2}(C-C)
1055	1053	1029	1050	1053	1027	υ_{ring1}(C-C)
1010	1011	1006	1021	1012	1004	$\delta_{oop}(CH_{ring1})$
980	982	990	988	996	989	$\delta_{oop}(CH_{ring1})$
944	889	904	---	890	908	$\delta_{oop}(CH_{ring2})$
862	846	856	849	846	858	$\rho(CH_3)$,$\delta_{oop}(CH_{ring1,2})$
796	817,753	831	826	817	830	δ_{asym}(ring2), υ_{ring2}(C-C)
---	732	742	734	753,732	746	δ_{asym}(ring1)
707	667,646	647	668	689	703	δ_{puck}(ring1,2)
603	625	626	526	617	537	$\delta_{asymdef}$(ring1)
506	525	538	488	525	500	ρ(C-O),τ_{asym}(ring2)
470	465	475	456	489	456	τ_{asym}(ring1)
448	417	437	445	453	437	τ_{asym}(ring1), $\tau_{asymdef}$(ring1)

Note: Types of vibration: υ_{sym}, υ_{asym}, symmetric and asymmetric stretching; δ_{sym}, δ_{asym}, $\delta_{asymdef}$, symmetric, asymmetric and asymmetric' deformation; δ_{in}, δ_{oop}, in plane and out of plane bending; ρ, rocking; τ, torsion, τ_{asym}, $\tau_{asymdef}$, asymmetric and asymmetric' deformation; δ_{puck}, Puckring.

Table S3 Absorption wavelength (λ_{ab}), excitation energies E(eV), oscillator strengths (f_0), and major contributions for transitions in 2,4,5-TMBC calculated at different levels of theory.

Method	λ_{exc}	E(eV)	f_0	Major contribution
B3LYP	*400.00*	*3.103*	*0.5196*	*H→L (69.4%)*
HF	*270.00*	*4.596*	*0.0967*	*H→L (57.3%)*
CAM-B3LYP	*336.00*	*3.693*	*0.2560*	*H→L (56%)*
Wb97xd	*333.00*	*3.727*	*0.3128*	*H→L (60%)*
LC-BLYP	*298.17*	*4.158*	*0.8655*	*H→L (61.4%)*

Table S4

(1) Calculated values of polarizability, hyperpolarizability and dipole moment along their individual tensor components of 2,4,5TMBC molecule at HF/6-31G* level of theory.

Polarizability and dipole moment			*Hyperpolarizability*		
Components	*a. u.*	*esu (×10^{-24})*	*Component*	*a. u.*	*esu (×10^{-30})*
α_{xx}	*353.725*	*52.41*	β_{xxx}	*-1327.340*	*-11.469*
α_{xy}	*7.925*	*1.174*	β_{xxy}	*864.122*	*7.466*
α_{yy}	*207.569*	*30.755*	β_{xyy}	*-4.889*	*-0.042*
α_{xz}	*-13.308*	*-1.972*	β_{yyy}	*-32.415*	*-0.28*
α_{yz}	*14.004*	*2.075*	β_{xxz}	*198.234*	*1.713*
α_{zz}	*110.977*	*16.443*	β_{xyz}	*-47.106*	*-0.407*
α_{tot}	*224.090*	*33.203*	β_{yyz}	*7.625*	*0.066*
$\Delta\alpha$	*212.933*	*31.549*	β_{xzz}	*16.078*	*0.138*
μ_x	*2.017*	*5.127D*	β_{yzz}	*10.226*	*0.088*
μ_y	*-0.454*	*-1.153D*	β_{zzz}	*-21.805*	*-0.188*
μ_z	*-0.339*	*-0.861D*	β_0	*955.185*	*8.254*
μ_{tot}	*2.095*	*5.325D*	β_{tot}	*1591.976*	*13.756*

(2) Calculated values of polarizability, hyperpolarizability and dipole moment along their individual tensor components of 2,4,5TMBC molecule at CAM-B3LYP/6-31G* level of theory.

Polarizability and dipole moment			*Hyperpolarizability*		
Components	*a. u.*	*esu (×10^{-24})*	*Component*	*a. u.*	*esu (×10^{-30})*
α_{xx}	*409.436*	*29.34*	β_{xxx}	*-3222.768*	*-38.565*
α_{xy}	*3.213*	*4.30*	β_{xxy}	*1571.185*	*19.132*
α_{yy}	*229.257*	*36.75*	β_{xyy}	*-121.449*	*-1.668*
α_{xz}	*-14.205*	*8.00*	β_{yyy}	*22.265*	*0.311*
α_{yz}	*12.659*	*-4.74*	β_{xxz}	*343.390*	*0.833*
α_{zz}	*109.941*	*32.90*	β_{xyz}	*-59.111*	*-0.176*
α_{tot}	*315.177*	*46.699*	β_{yyz}	*18.545*	*0.019*
$\Delta\alpha$	*267.443*	*39.626*	β_{xzz}	*21.202*	*0.338*
μ_x	*2.038*	*5.181D*	β_{yzz}	*10.940*	*0.072*
μ_y	*-0.535*	*-1.360D*	β_{zzz}	*-21.134*	*-0.044*
μ_z	*-0.307*	*-0.780D*	β_0	*1467.657*	*12.682*
μ_{tot}	*2.343*	*5.413D*	β_{tot}	*2446.095*	*21.137*

(3) Calculated values of polarizability, hyperpolarizability and dipole moment along their individual tensor components of 2,4,5TMBC molecule at wb97xd/6-31G* level of theory.

Polarizability and dipole moment			*Hyperpolarizability*		
Components	*a. u.*	*esu (×10^{-24})*	*Component*	*a. u.*	*esu (×10^{-30})*
α_{xx}	*409.567*	*29.34*	β_{xxx}	*-3087.331*	*-26.677*
α_{xy}	*3.507*	*4.30*	β_{xxy}	*1508.303*	*13.033*
α_{yy}	*230.091*	*36.75*	β_{xyy}	*-113.387*	*-0.979*
α_{xz}	*-14.142*	*8.00*	β_{yyy}	*19.599*	*0.169*
α_{yz}	*12.731*	*-4.74*	β_{xxz}	*334.937*	*2.894*
α_{zz}	*110.999*	*32.90*	β_{xyz}	*-59.535*	*-0.514*
α_{tot}	*250.219*	*37.074*	β_{yyz}	*16.435*	*0.142*
$\Delta\alpha$	*261.474*	*38.572*	β_{xzz}	*23.591*	*0.204*
μ_x	*2.058*	*5.231D*	β_{yzz}	*13.436*	*0.116*
μ_y	*-0.531*	*-1.350D*	β_{zzz}	*-20.959*	*-0.181*
μ_z	*-0.307*	*-0.781D*	β_0	*1504.749*	*13.046*
μ_{tot}	*2.147*	*5.458D*	β_{tot}	*2507.915*	*21.671*

(4) Calculated values of polarizability, hyperpolarizability and dipole moment along their individual tensor components of 2,4,5TMBC molecule at LC-BLYP/6-31G* level of theory.

Polarizability and dipole moment	*Hyperpolarizability*

Components	*a. u.*	*esu ($\times 10^{-24}$)*	*Component*	*a. u.*	*esu ($\times 10^{-30}$)*
α_{xx}	*375.555*	*55.645*	β_{xxx}	*-2410.545*	-20.829
α_{xy}	*5.003*	*0.741*	β_{xxy}	*1178.572*	10.184
α_{yy}	*223.814*	*33.162*	β_{xyy}	*-65.291*	-0.564
α_{xz}	*-7.517*	*-1.114*	β_{yyy}	*-3.654*	-0.032
α_{yz}	*8.556*	*1.267*	β_{xxz}	*139.133*	1.202
α_{zz}	*98.464*	*14.589*	β_{xyz}	*-25.159*	-0.217
α_{tot}	*232.611*	*34.465*	β_{yyz}	*6.696*	0.058
$\Delta\alpha$	*240.683*	*35.661*	β_{xzz}	*19.828*	0.171
μ_x	*1.926*	*4.894D*	β_{yzz}	*9.841*	0.085
μ_y	*-0.474*	*-1.204D*	β_{zzz}	*-10.256*	-0.088
μ_z	*-0.153*	*-0.390D*	β_0	*1158.324*	10.009
μ_{tot}	*1.989*	*5.055D*	β_{tot}	*1930.539*	16.682

Table S5 Thermodynamic parameters of 2,4,5-TMBC molecule at 298K and 1PA

Methods	E (Thermal) (KCal/Mol)	C_V (Cal/Mol-Kelvin)	S (Cal/Mol-Kelvin)
B3LYP	210.965	82.303	166.366
HF	224.853	77.052	162.218
CAM-B3LYP	213.504	81.120	165.539
Wb97xd	212.936	81.114	163.505
LC-BLYP	216.803	79.654	163.643

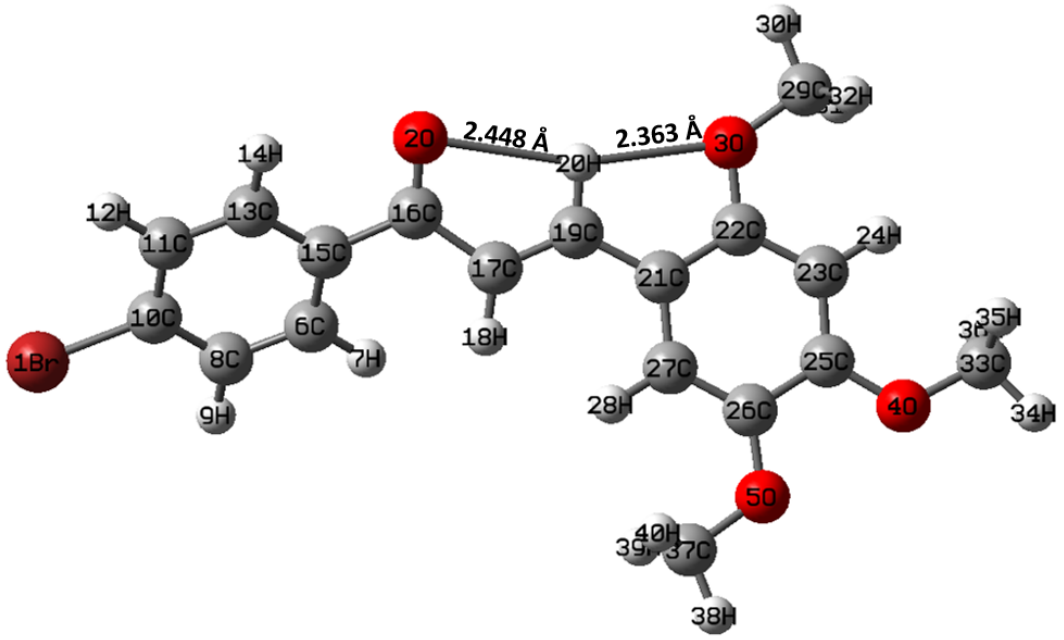

Fig. S1 (b) Optimized molecular geometry of 2,4,5TMBC molecule at HF using 6-31G* basis set

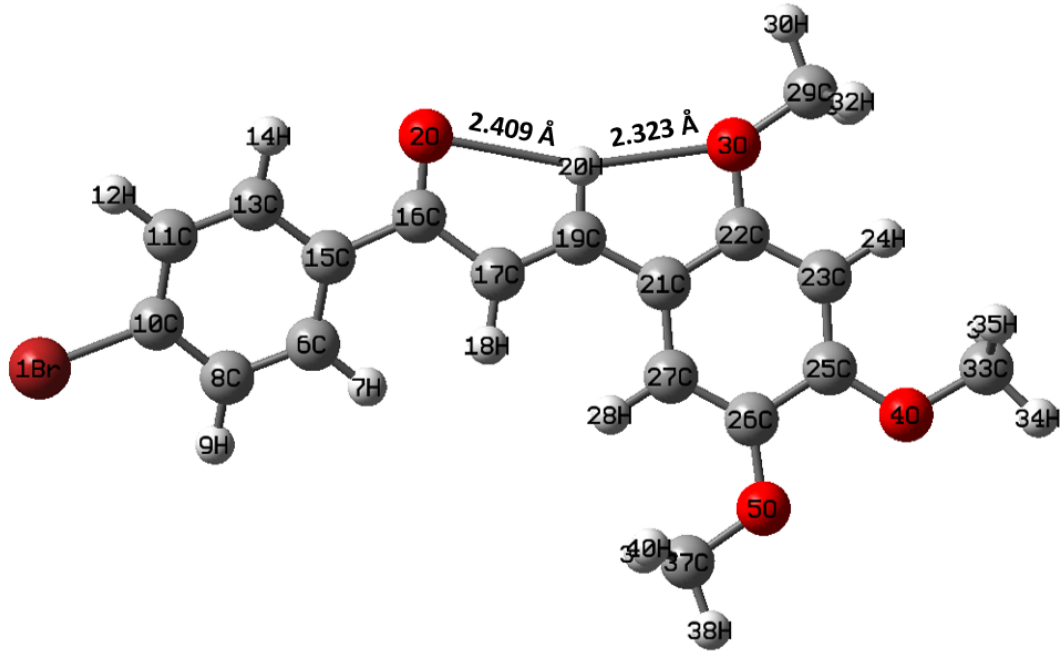

Fig. S1 (c) Optimized molecular geometry of 2,4,5TMBC molecule at CAM-B3LYP using 6-31G* basis set

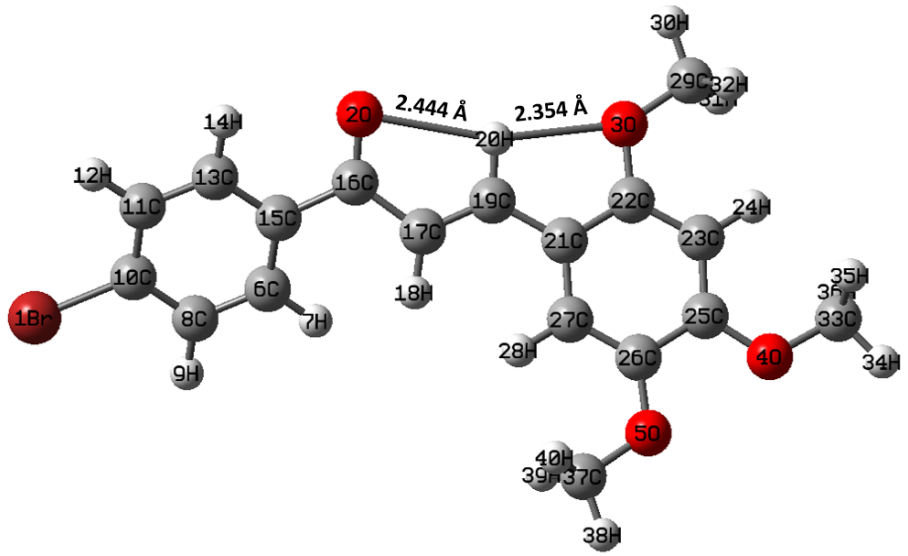

Fig. S1 (d) Optimized molecular geometry of 2,4,5TMBC molecule at wb97xd using 6-31G* basis set

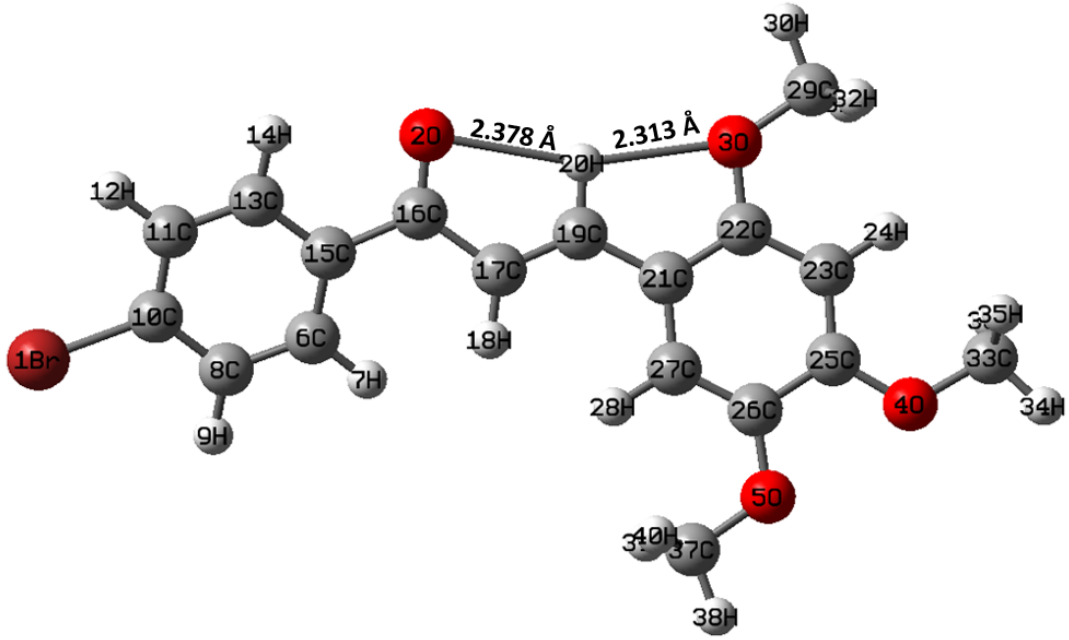

Fig. S1 (e) Optimized molecular geometry of 2,4,5TMBC molecule at LC-BLYP using 6-31G* basis set

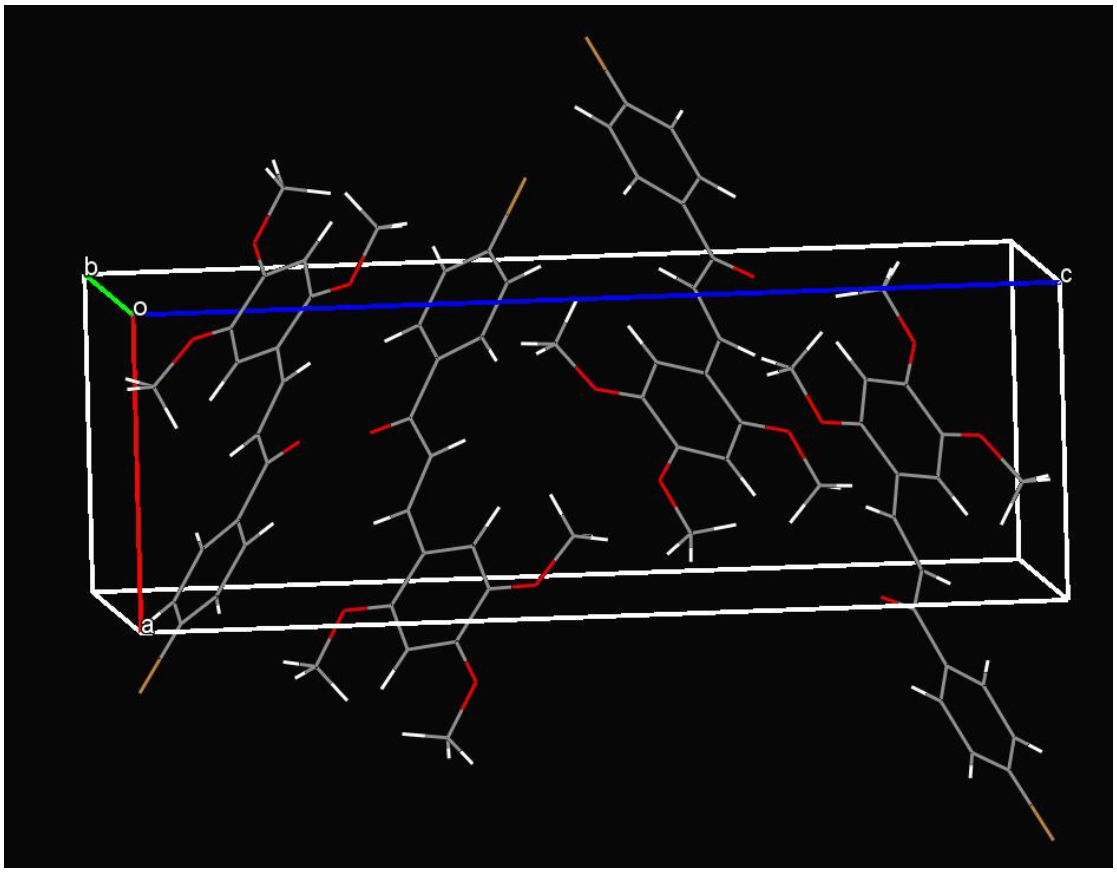

Fig. S2. Optimized geometry of 2,4,5-TMBC applying Periodic boundary conditions (PBC) at PBE/DNP level of theory.

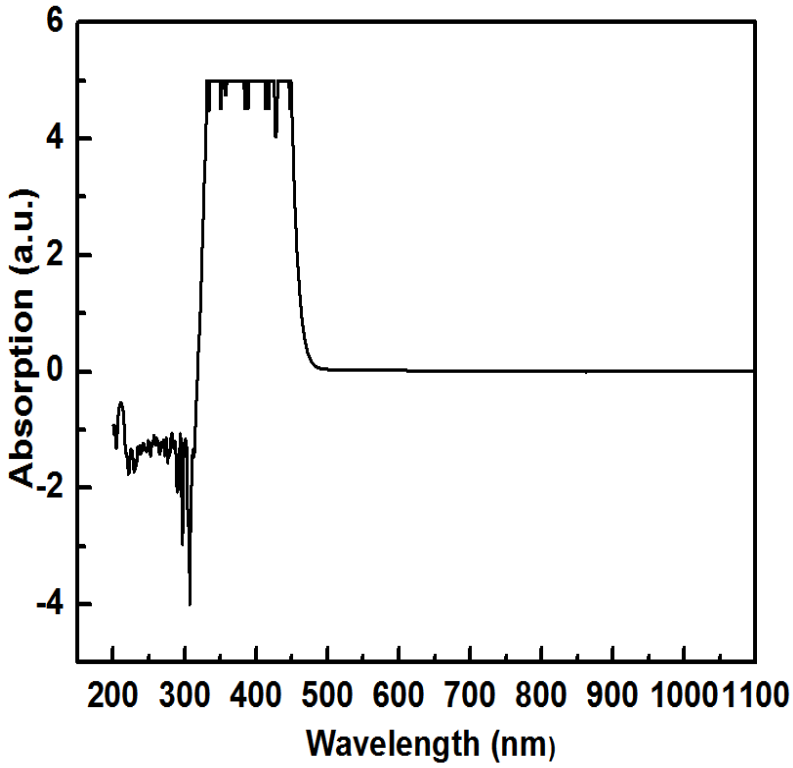

Fig. S3 Experimentally recorded UV-VIS-NIR spectra of 2,4,5-TMBC crystal molecule

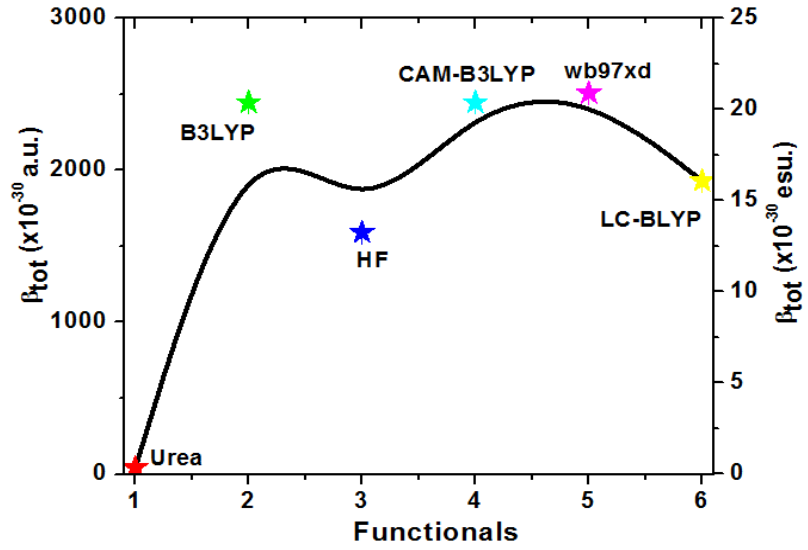

Fig. S4. Variation of hyperpolarizability values calculated at different levels of theory.

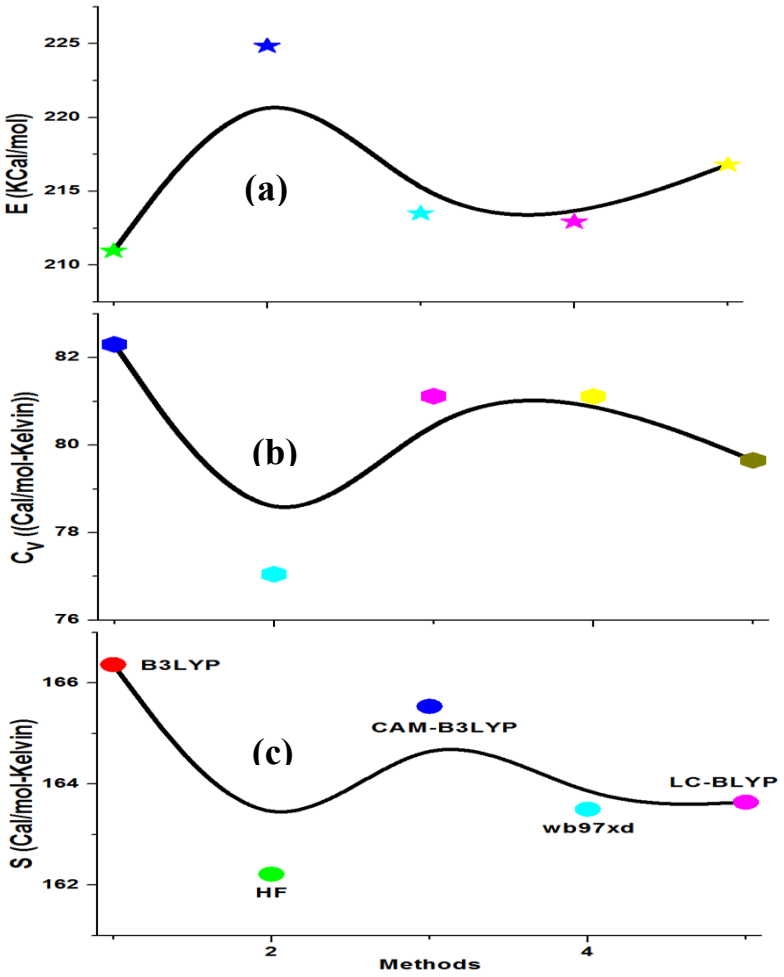

Fig. S5. Variation of thermodynamic parameters calculated at different levels of theory at 298K.

GCRD parameters of 2,4,5-TMBC molecule are computed as follows:

For absolute hardness (η) an approximation was developed earlier [1-3] as given below:

$$\eta = \frac{I - A}{2}$$

where I is the vertical ionization energy and A is vertical electron affinity.

As per Koopman's theorem [4] connected within the framework of HF self-consistent field molecular orbital theory the ionization energy and electron affinity can be stated through HOMO and LUMO orbital energies:

$I = E_{HOMO}$

$A = E_{LUMO}$

Values of I and A of 2,4,5-TMBC are given in Table 2. As it is known that the higher HOMO energy relates to the more responsive molecule in the reactions with electrophiles, while lower LUMO energy is vital for molecular reactions with nucleophiles [5].

Hence, the hardness of any materials is communicates to the gap between the HOMO and LUMO orbitals. It evidently specifies that if the HOMO-LUMO energy gap is larger than molecule will be harder [3]. Therefore, the hardness (η):

$$\eta = \frac{1}{2}(E_{LUMO} - E_{HOMO})$$

Chemical potential is calculated by:

$$\mu = -\left(\frac{I + A}{2}\right)$$

Softness is calculated by:

$$S = \frac{I}{2\eta}$$

Electronegativity is calculated by:

$$\chi = \left(\frac{I + A}{2}\right)$$

Electrophilic index is calculated by:

$$\omega = \frac{\mu^2}{2\eta}$$

where I [E_{HOMO} = (5.306)] is the ionization potential and A [E_{LUMO}= (1.932)] is the electron affinity of the molecule.

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