Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Long-Living Optical Gain Induced by Solvent Viscosity in a Push-Pull Molecule

Marta M. Mróz[†], *Sara Benedini*[§], *Alessandra Forni*[#,*], *Chiara Botta*[‡], *Dario Pasini*[§], *Elena Cariati*[Δ], *Tersilla Virgili*[†,*]

[†]IFN-CNR, Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo Da Vinci, 32, 20132 Milano, Italy

[‡]ISMAC –CNR and UdR INSTM di Milano, Via Corti 12, 20133 Milano, Italy

[#]ISTM - CNR, c/o Dipartimento di Chimica, Università degli Studi di Milano and UdR INSTM di Milano, Via Golgi 19, 20133 Milano, Italy

[§]Department of Chemistry and INSTM Research Unit, University of Pavia, Viale Taramelli, 10, 27100 Pavia, Italy.

[Δ]Università degli Studi di Milano, Dipartimento di Chimica and UdR INSTM di Milano, via Golgi 19, 20133 Milano, Italy

E.mail: * tersilla.virgili@polimi.it , aforni@istm.cnr.it

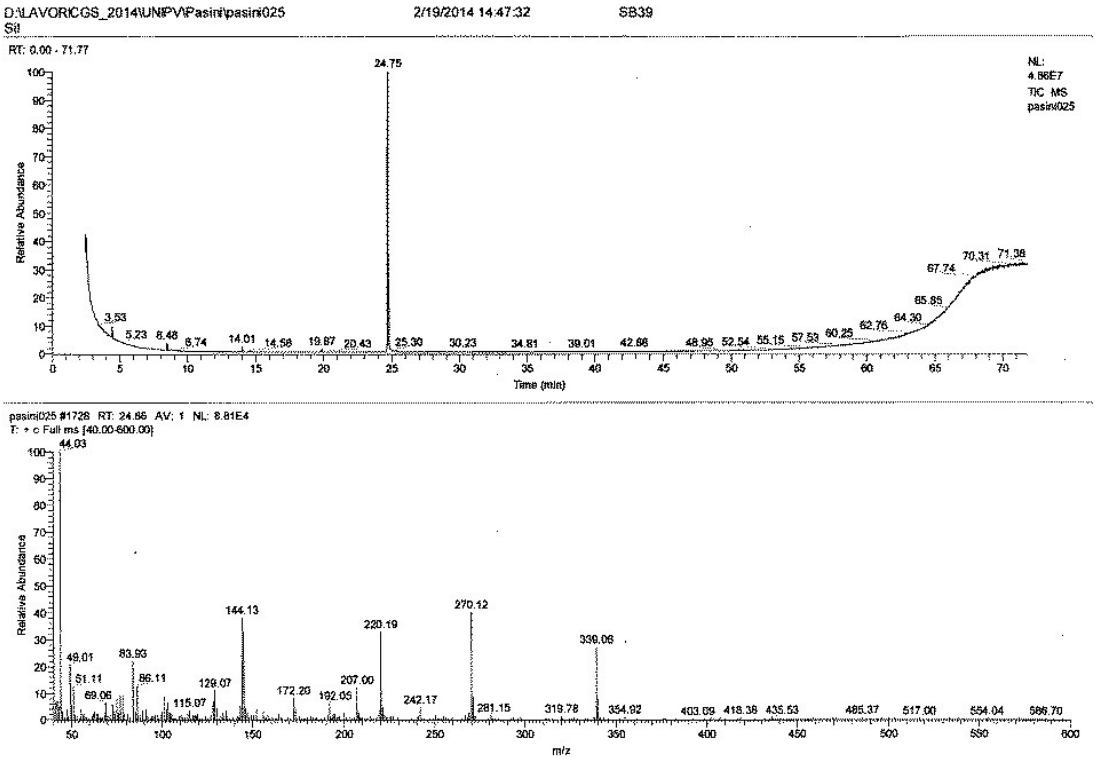

Fig S1: GC/MS compound **1**.

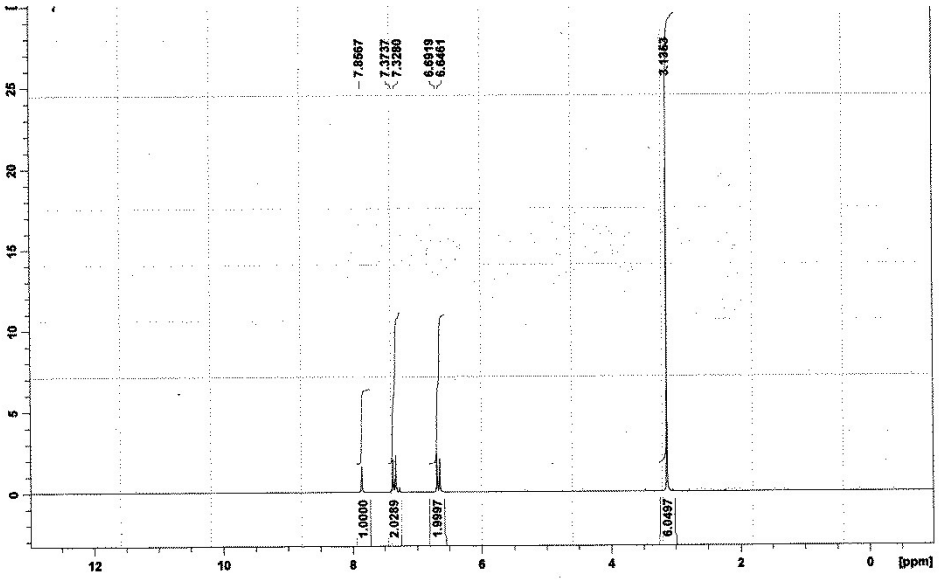

Fig S2: ^{1}H NMR of compound **1** (200 MHz, $CDCl_3$)

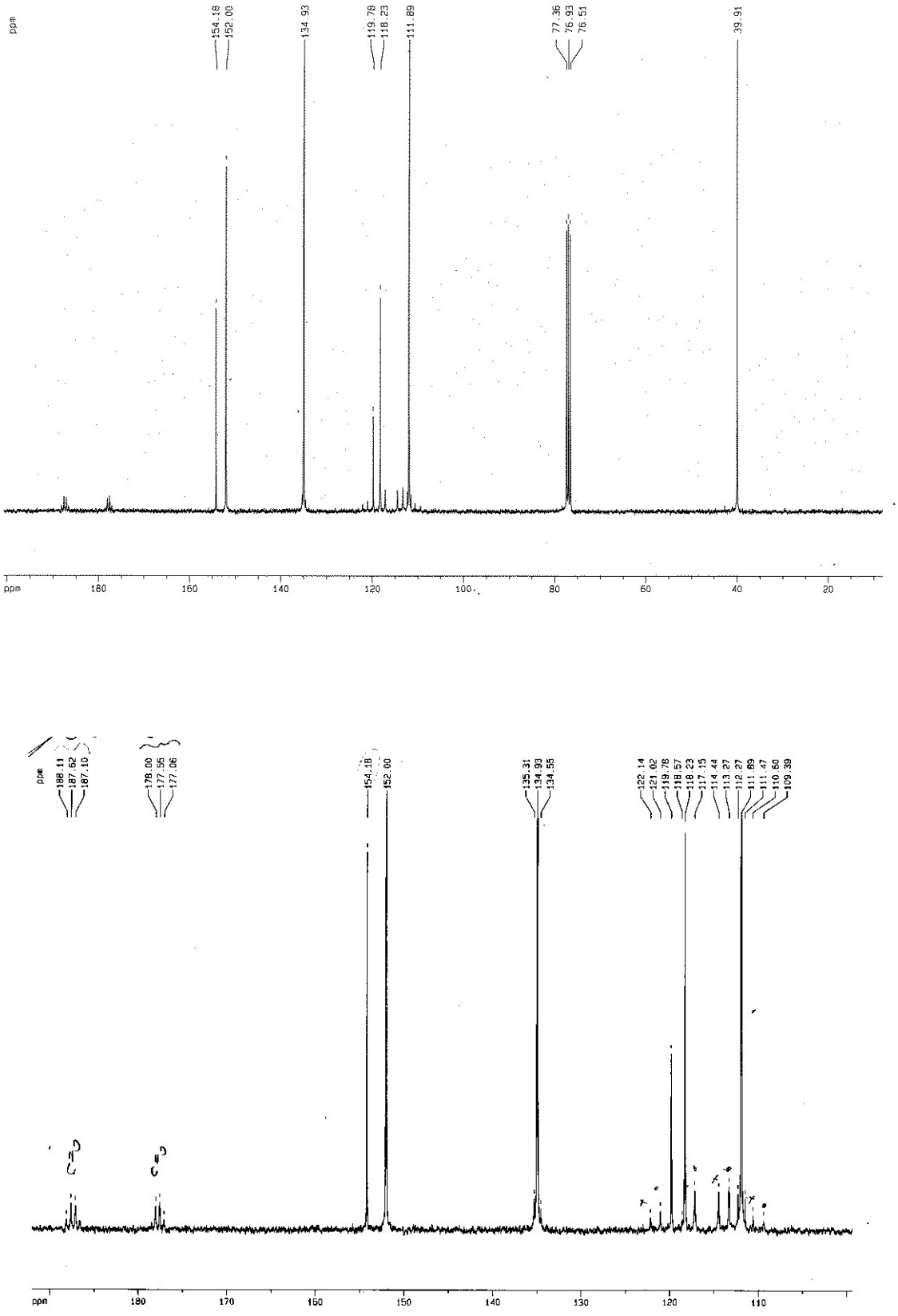

Fig S3: ^{13}C NMR of compound **1** (300 MHz, $CDCl_3$)

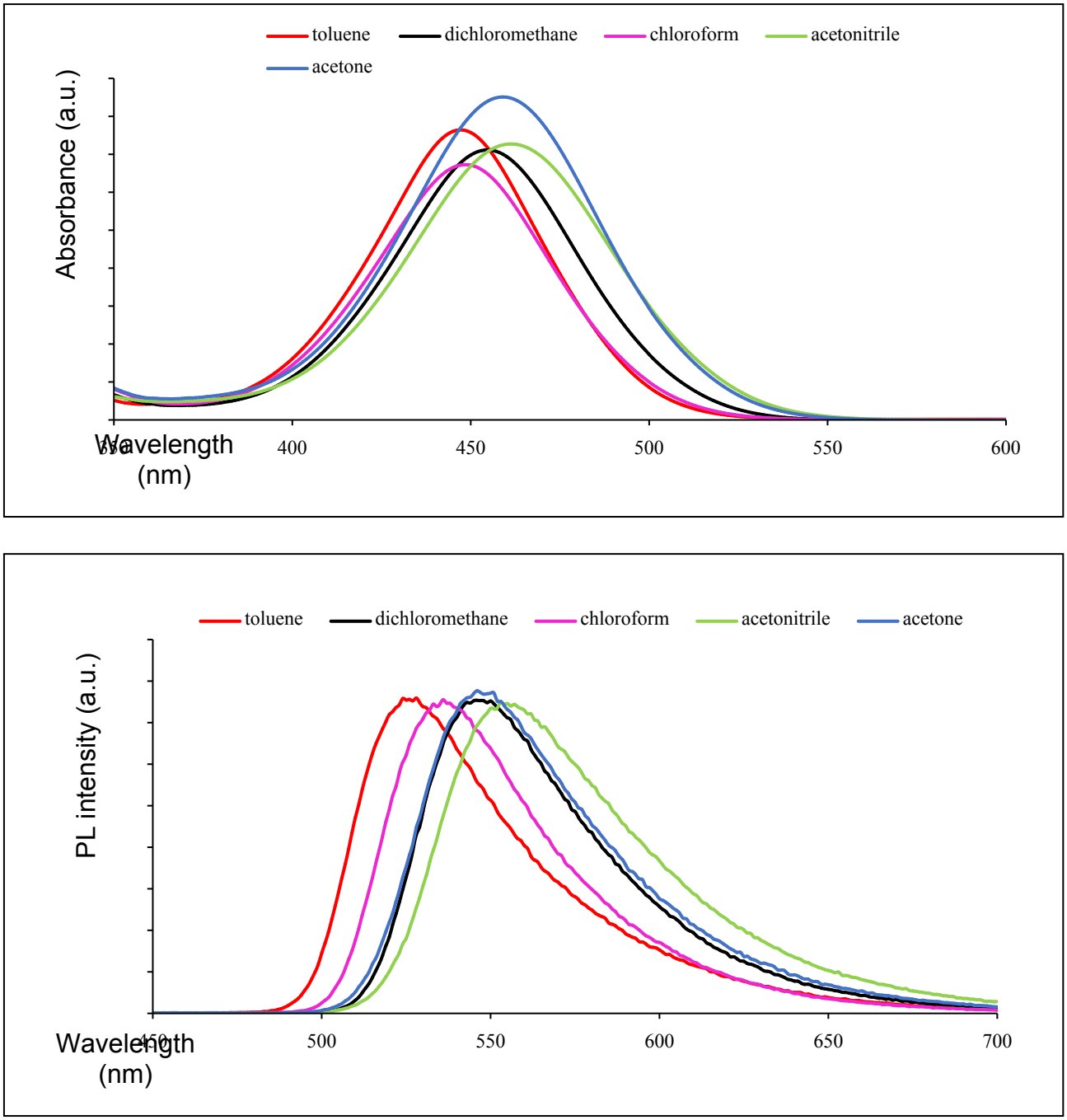

Fig.S4 Absorption (top figure) and emission (bottom figure) spectra in non-viscous solvents.

Table S1. Optical properties of the solutions with solvent parameters (where n is the refractive index, ε the solvent polarizability, and Δf the solvent orientation polarizability)

	Abs (nm)	Em (nm)	Stokes shift (eV)	n	ε	Δf
n-hexane	420	484	0,390	1,375	1,900	0,001
toluene	447	522	0,399	1,497	2,400	0,015
chloroform	449	536	0,448	1,448	4,800	0,147
dichloromethane	455	543	0,442	1,420	9,100	0,220
PEG[a]	455	527	0,372	1,466	12,400	0,225
acetone	459	546	0,430	1,359	21,000	0,285
DEG[b]	464	543	0,389	1,447	31,690	0,266
acetonitrile	461	553	0,447	1,342	36,200	0,306

[a]polyethylene glycol with molecular weight of 400; [b]diethylene glycol.

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

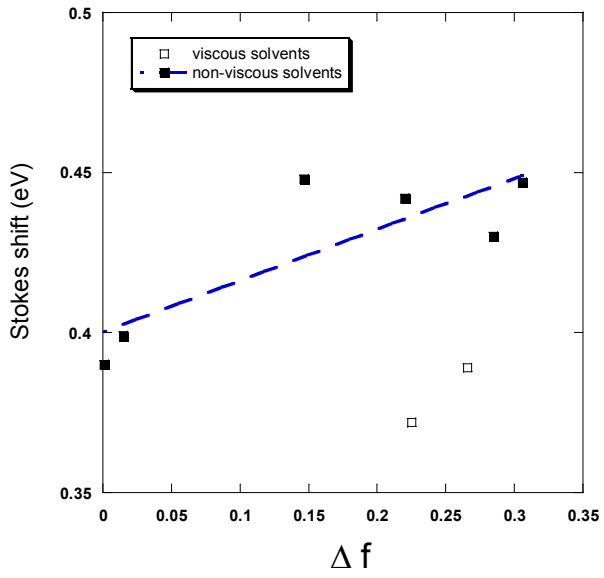

Fig.S5 Plot of the Stokes shifts as a function of the orientation polarizability Δf with the linear fit for non-viscous solvents.

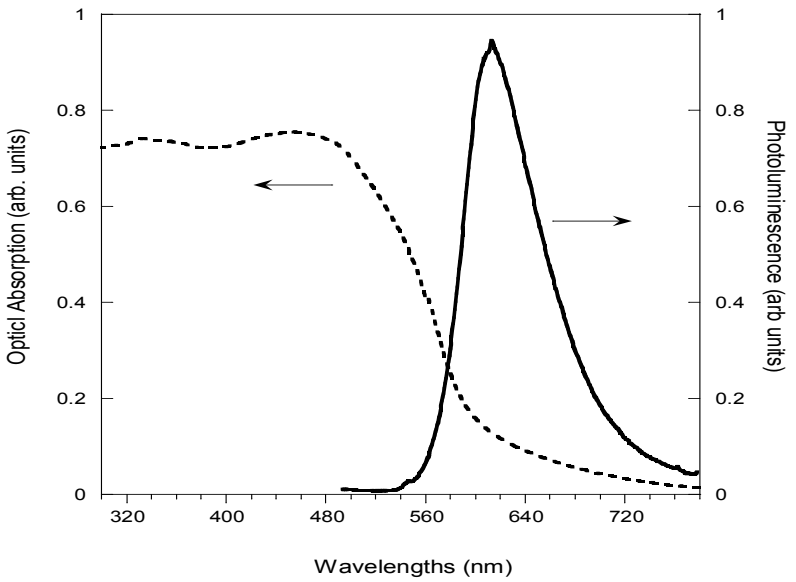

Fig.S6 Absorption (dotted line) and emission (solid line) of solid state **1** .

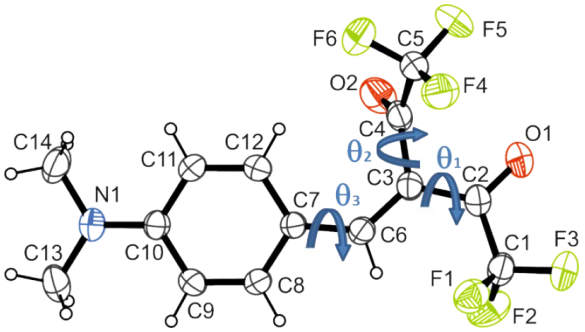

Fig.S7. Ortep drawing of 1 with thermal ellipsoids at the 30% probability level.

Table S2. Selected geometrical parameters (distances in Å, angles in degrees) for **1** as obtained by X-ray analysis and CAM-B3LYP/6-311++G(d,p) geometry optimization in different solvents.

	O1–C2	O2–C4	C2–C3	C3–C4	C3–C6	C6–C7	C10–N1	θ_1	θ_2	θ_3
X-ray	1.218(3)	1.200(3)	1.442(3)	1.490(3)	1.367(3)	1.425(3)	1.347(2)	170(1)	-60(1)	-6(1)
n-hexane	1.209	1.199	1.457	1.489	1.365	1.434	1.356	172.4	-54.3	5.6
toluene	1.210	1.199	1.455	1.489	1.366	1.432	1.355	172.6	-54.4	0.6
chloroform	1.212	1.201	1.452	1.485	1.371	1.427	1.351	170.9	-50.0	-1.0
dichloromethane	1.213	1.202	1.450	1.483	1.374	1.424	1.349	170.3	-48.4	-2.1
acetone	1.214	1.202	1.449	1.482	1.376	1.422	1.348	170.0	-47.6	-2.6
acetonitrile (ACN)	1.214	1.202	1.448	1.482	1.376	1.422	1.347	169.9	-47.4	-2.9

Table S3. Thermal analysis on GS, LE and TICT states from PCM-(TD)-CAM-B3LYP/6-311++G(d,p) calculations in ACN.

GS:

```
E =   SCF Done:  E(RCAM-B3LYP) =  -1344.24702684
      Zero-point correction=                           0.237289 (Hartree/Particle)
      Thermal correction to Energy=                    0.258889
      Thermal correction to Enthalpy=                  0.259833
      Thermal correction to Gibbs Free Energy=         0.183441
      Sum of electronic and zero-point Energies=          -1344.009738
      Sum of electronic and thermal Energies=             -1343.988138
      Sum of electronic and thermal Enthalpies=           -1343.987194
G =   Sum of electronic and thermal Free Energies=        -1344.063586
```

LE:

```
E =   Total Energy, E(TD-HF/TD-KS) =  -1344.15147533
      Zero-point correction=                           0.234531 (Hartree/Particle)
      Thermal correction to Energy=                    0.256522
      Thermal correction to Enthalpy=                  0.257466
      Thermal correction to Gibbs Free Energy=         0.180513
      Sum of electronic and zero-point Energies=          -1343.916945
      Sum of electronic and thermal Energies=             -1343.894954
      Sum of electronic and thermal Enthalpies=           -1343.894009
G =   Sum of electronic and thermal Free Energies=        -1343.970963
```

TICT:

```
E =   Total Energy, E(TD-HF/TD-KS) =  -1344.15370939
      Zero-point correction=                           0.235276 (Hartree/Particle)
      Thermal correction to Energy=                    0.256208
      Thermal correction to Enthalpy=                  0.257153
      Thermal correction to Gibbs Free Energy=         0.183331
      Sum of electronic and zero-point Energies=          -1343.918433
      Sum of electronic and thermal Energies=             -1343.897501
      Sum of electronic and thermal Enthalpies=           -1343.896557
G =   Sum of electronic and thermal Free Energies=        -1343.970379
```

$\Delta(E_{LE}-E_{GS})$ = 0.09555151 a.u. = 2.600 eV

$\Delta(E_{TICT}-E_{GS})$ = 0.09331745 a.u. = 2.539 eV

$\Delta(E_{LE}-E_{TICT})$ = 0.00223406 a.u. = 0.0608 eV

$\Delta(G_{LE}-G_{GS})$ = 0.092623 a.u. = 2.520 eV

$\Delta(G_{TICT}-G_{GS})$ = 0.093207 a.u. = 2.536 eV

$\Delta(G_{LE}-G_{TICT})$ = -0.000584 a.u. = -0.0159 eV

where $G = E + E_t + E_r + E_v + E_e + E_{zero\text{-}point} + k_bT - TS_{tot}$
and $S_{tot} = S_t + S_r + S_v + S_{el}$

Table S4. PCM-(TD)-CAM-B3LYP/6-311++G(d,p) optimized coordinates of 1 in ACN.

GS:

F	2.30737700	-2.47290800	1.26396600
F	2.30909100	-2.97740400	-0.84516800
F	4.15893800	-2.49988600	0.15794000
F	2.80980900	1.69931300	1.38709500
F	3.31224800	2.84724600	-0.38352300
F	1.53914300	3.32072700	0.75136600
O	3.71661600	-0.07467600	-0.57428900
O	0.78998000	1.94093300	-1.43658300
N	-5.31499000	-0.00593800	0.09010400
C	2.87193000	-2.17974400	0.08115500
C	2.70270800	-0.67950900	-0.28992000
C	1.38810900	-0.07260500	-0.30320300
C	1.42599200	1.38208000	-0.58281100
C	2.30572200	2.30956500	0.31129900
C	0.23659700	-0.81576600	-0.17827500
H	0.40689100	-1.87931800	-0.06015400
C	-1.15103300	-0.50930300	-0.13599000
C	-2.03378900	-1.60916800	-0.01741800
H	-1.61748500	-2.60959200	0.02027500
C	-3.39243600	-1.46395500	0.05350700
H	-4.01044700	-2.34466500	0.14117900
C	-3.98010400	-0.17314400	0.02098500
C	-3.10063200	0.94071400	-0.08516100
H	-3.50058300	1.94328200	-0.10803000
C	-1.74621900	0.77397800	-0.16527500
H	-1.13895700	1.66076000	-0.25303400
C	-6.19742400	-1.15998100	0.19833700
H	-6.08438700	-1.82706500	-0.65966800
H	-7.22676600	-0.81550100	0.22761200
H	-5.99987600	-1.72735900	1.11137900
C	-5.89909100	1.32897000	0.06916900
H	-5.55324700	1.92807600	0.91510300
H	-6.97945300	1.24104200	0.13483800
H	-5.65495700	1.85524800	-0.85674200

LE:

F	2.19889000	-2.27771400	1.44817300
F	2.61549000	-2.99679300	-0.55499400
F	4.21778500	-2.25957200	0.68884500
F	2.79310900	1.94044500	1.10118800
F	3.05924200	2.78597100	-0.88030400
F	1.42695800	3.43267700	0.36718500
O	3.75488900	-0.02198400	-0.52212000
O	0.23595400	1.74800100	-1.22492300
N	-5.19609000	-0.00111000	0.20696100
C	2.94487700	-2.05878000	0.35541200
C	2.74826700	-0.62768300	-0.21595500
C	1.38984300	-0.12523200	-0.37132100
C	1.19864100	1.29809500	-0.61295900
C	2.14335800	2.35594100	0.00433500
C	0.29510700	-1.00323100	-0.47118400
H	0.50073100	-2.03903400	-0.71425900
C	-1.08438900	-0.69355600	-0.28911600
C	-2.06394100	-1.58166800	-0.82002500
H	-1.73041100	-2.44850100	-1.37794200

C	-3.39908300	-1.36624200	-0.66033200
H	-4.09949700	-2.06542600	-1.09223900
C	-3.87772400	-0.23049600	0.07033600
C	-2.90620500	0.63868800	0.64275100
H	-3.22136200	1.49070300	1.22639000
C	-1.57034400	0.41761400	0.46997200
H	-0.86961700	1.08053900	0.95518100
C	-6.17969500	-0.90147500	-0.38314200
H	-6.04618500	-0.97181200	-1.46482500
H	-7.17385200	-0.51425600	-0.18448800
H	-6.10527200	-1.90287900	0.04844600
C	-5.67259000	1.14704500	0.96680400
H	-5.35051900	1.08783900	2.00968000
H	-6.75730200	1.16270800	0.94023400
H	-5.30082300	2.08051100	0.53715100

TICT:

F	2.63267000	-2.36303700	1.26256600
F	2.75833100	-2.80707000	-0.85742400
F	4.48687600	-2.07573500	0.20370800
F	2.87259600	2.19840800	1.04560200
F	2.61591100	2.76772300	-1.03798100
F	1.28698100	3.52739600	0.47057300
O	3.70471400	0.23788500	-0.56480900
O	-0.22564800	1.60175700	-0.18714800
N	-5.16692600	-0.13580500	0.06034400
C	3.16397900	-1.94886300	0.10052800
C	2.77854400	-0.47821600	-0.24522600
C	1.37868200	-0.10451100	-0.17071500
C	0.97105500	1.26253700	-0.12615600
C	1.95702600	2.42796000	0.08707600
C	0.36719500	-1.08581600	-0.18434100
H	0.62307100	-2.13317300	-0.26622500
C	-1.05374200	-0.78054800	-0.12290700
C	-1.73775100	-0.70235600	1.12456000
H	-1.16169400	-0.80276700	2.03536500
C	-3.07638900	-0.49010300	1.19620700
H	-3.55232200	-0.42203400	2.16219000
C	-3.85675900	-0.35746500	0.00103100
C	-3.18341900	-0.47583000	-1.25880300
H	-3.74224900	-0.40174600	-2.17883900
C	-1.84279100	-0.67896300	-1.30583300
H	-1.34647800	-0.76115000	-2.26411000
C	-5.85418300	-0.02073200	1.34822700
H	-5.75219200	-0.94163000	1.92258500
H	-6.90796700	0.15928000	1.16720000
H	-5.45239300	0.81266400	1.92469300
C	-5.96526700	-0.00163700	-1.15983800
H	-5.60621500	0.83141400	-1.76431300
H	-6.99646800	0.18986700	-0.88399300
H	-5.92650200	-0.91913500	-1.74756100