Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Twisted intramolecular charge transfer in a carbazole-based chromophore. The stable [(4-*N*-carbazolyl)-2,3,5,6-tetrachlorophenyl]bis(2,3,5,6-tetrachlorophenyl)methyl radical

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SUPPLEMENTARY MATERIAL

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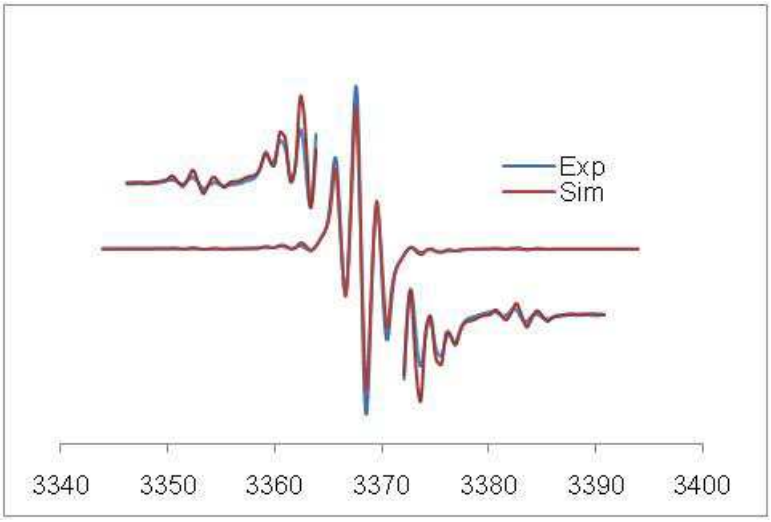

Figure S1. EPR spectrum of CH_2Cl_2 solution (~10^{-3} M) of **1** at 298 K. The extensions show a more detailed ^{13}C couplings.

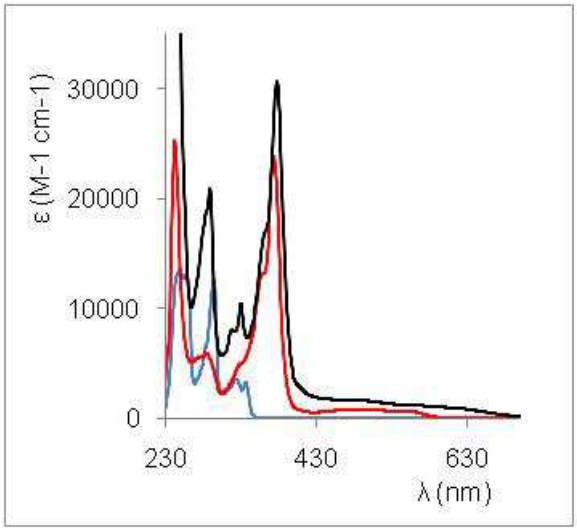

Figure S2. UV-vis spectra of **1** (black), DTM (red) and carbazole (blue) in THF.

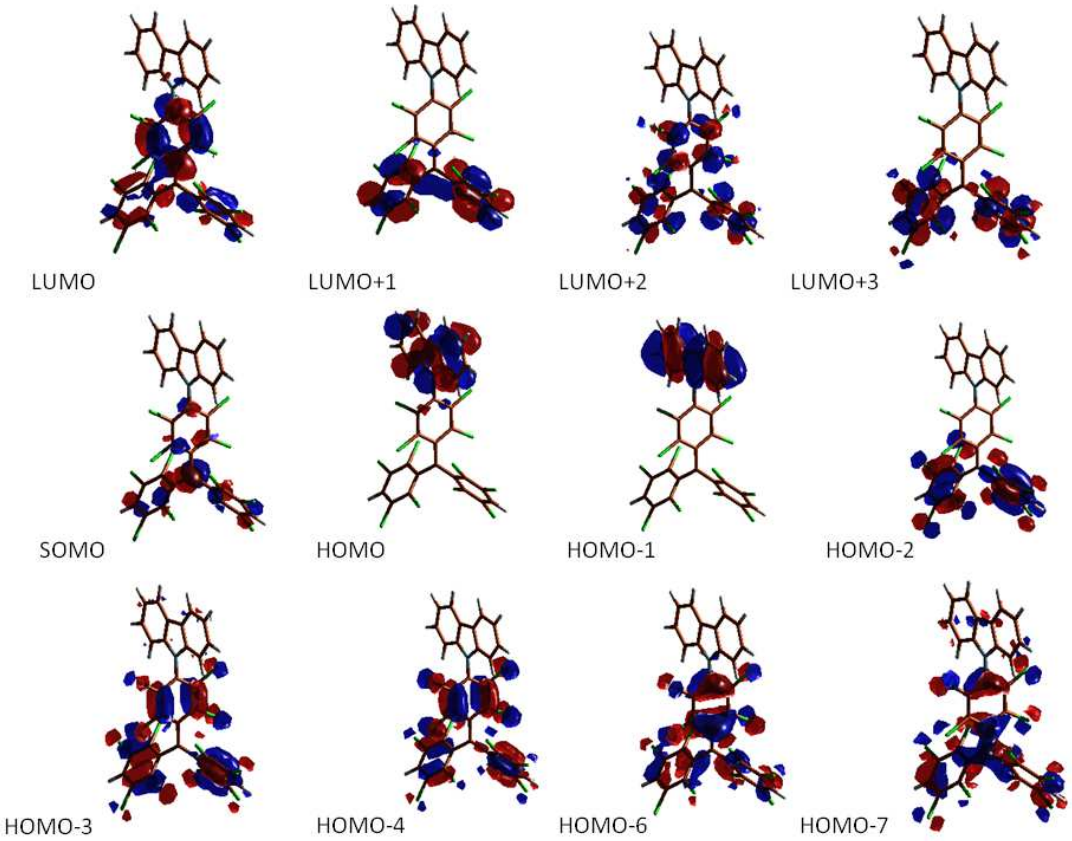

Figure S3. Electronic features of the most relevant molecular orbitals involved in the electronic spectra. A contour value of 0.08 a.u. have been employed for this draw.

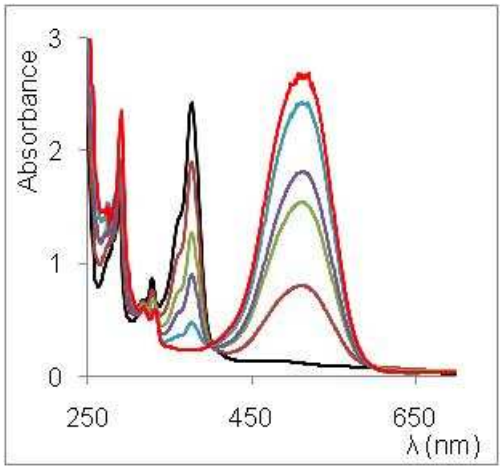

Figure S4. UV-VIS spectra of **1** in THF with different amounts of aqueous solution of TBAH.

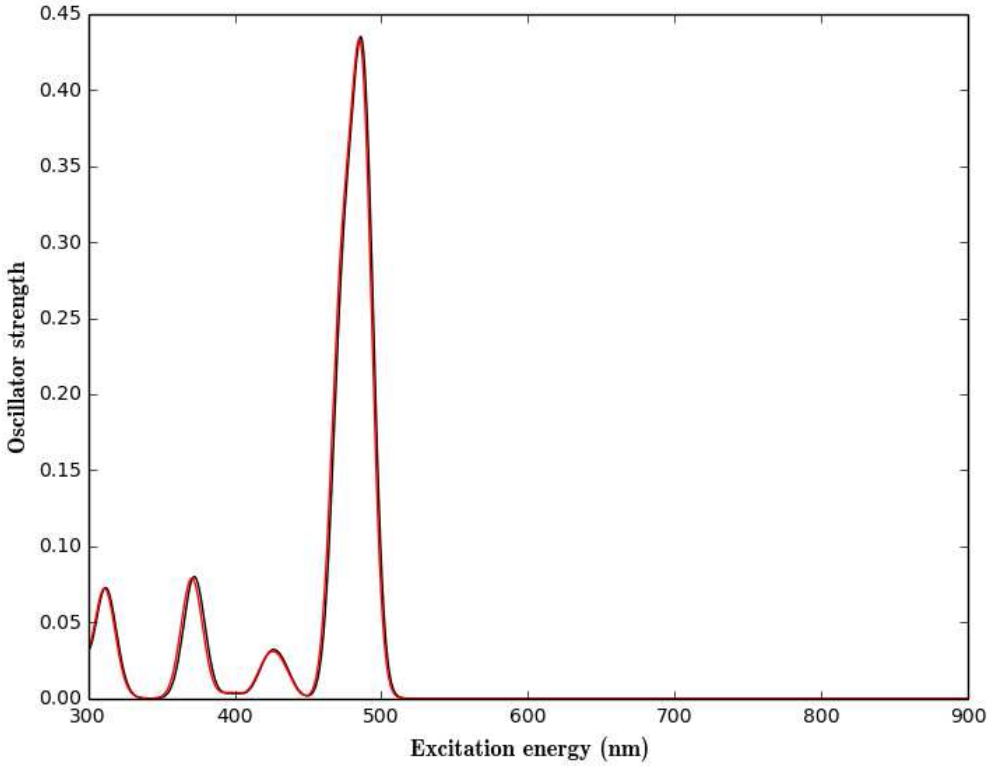

Figure S5. Calculated electronic spectra of anion **1**$^{-}$ in CH_2Cl_2 (black) and DMF (red). Both lines are overlapped.

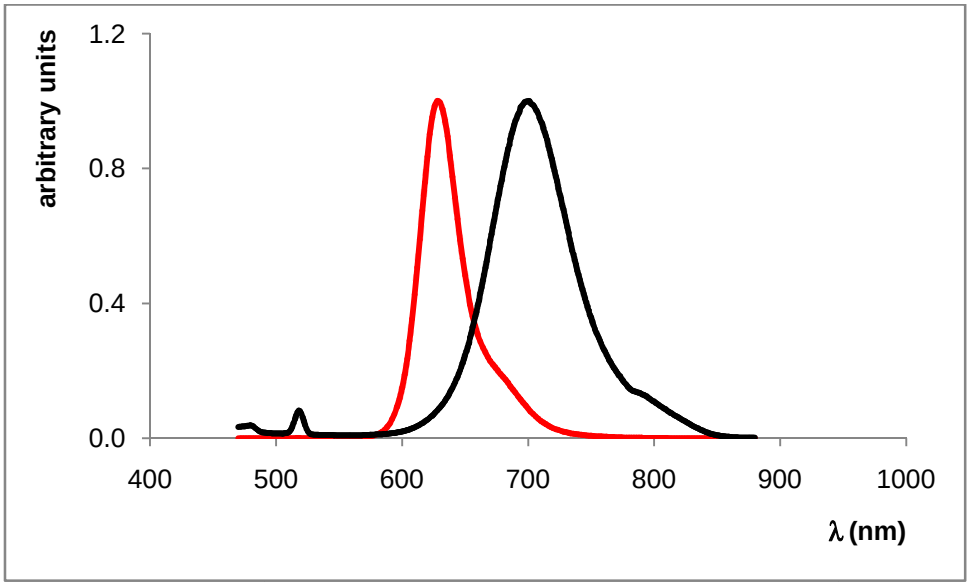

Figure S6. Normalized emission spectra of cyclohexane solutions (10^{-4} M) of radical adducts, **1** (black) and czTTM (red).

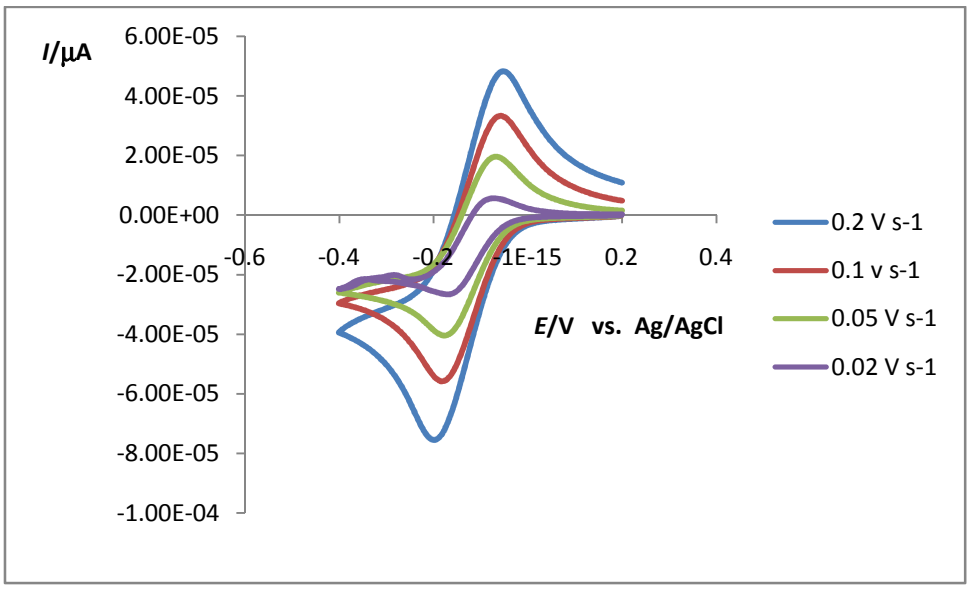

Figure S7. Cyclic voltammograms for the reduction of **1** (~10^{-3} M) in CH_2Cl_2 with 0.1 M TBAP on Pt at 25 ºC at different scan rates, vs. Ag/AgCl. The initial and final potential was 0.2 V; the reverse potential was -0.4 V.

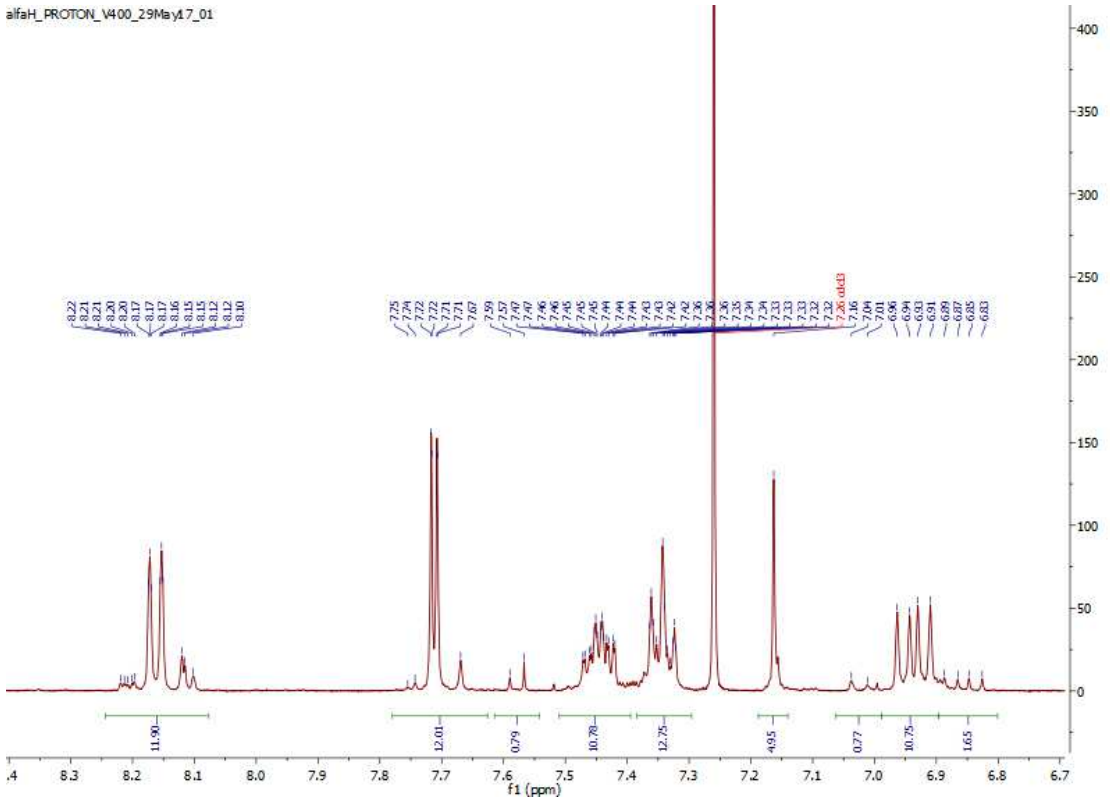

Figure S8. ^{1}H NMR spectrum (400 MHz; $CDCl_3$) of [4-(N-carbazolyl)-2,3,5,6-tetrachlorophenyl]bis(2,3,5,6-tetrachlorophenyl)methane (**1H**)

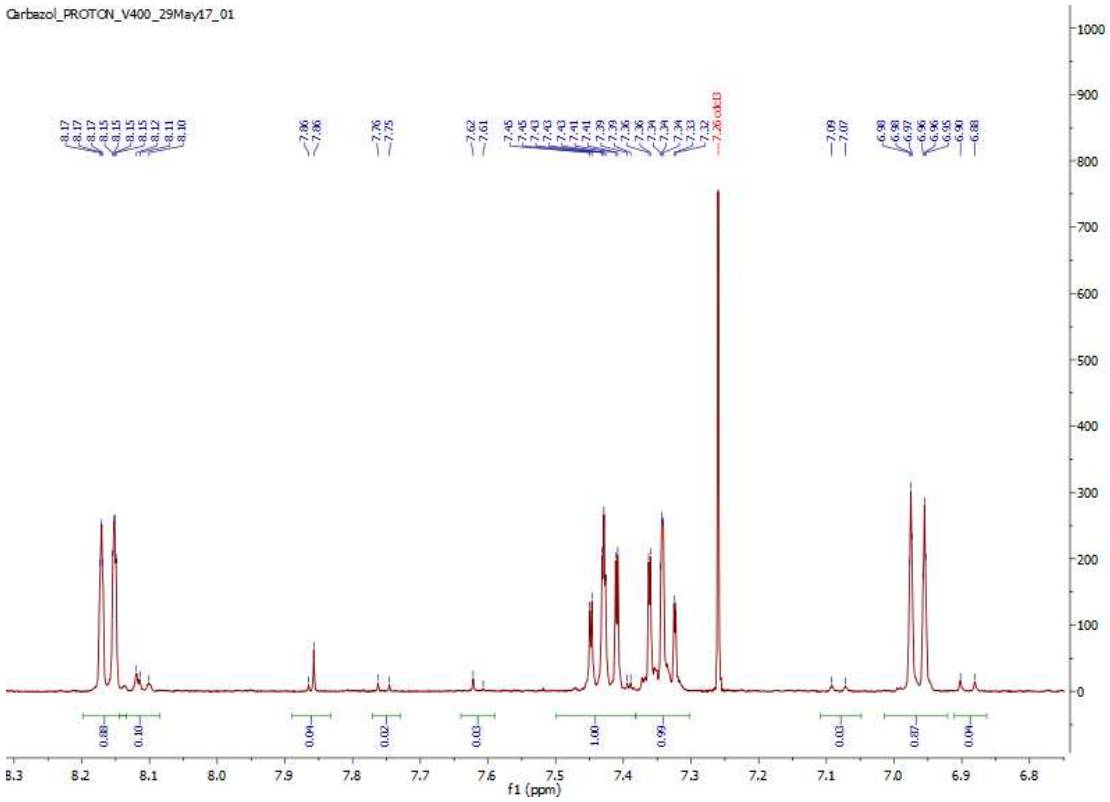

Figure S9. ^{1}H NMR spectrum (400 MHz; $CDCl_3$) of N-pentachlorophenylcarbazole

Table S1. Intramolecular charge transfer band in the visible spectrum of **1** in different solvents (dipole moment measured in debyes).

Solvent	Dipole moment (D)	λ(ε) nm(M^{-1} $cm Å^{-1}$)
Cyclohexane	0.0	640(1350)
Toluene	0.31	633(1000)
Chloroform	1.08	612(980)
Dichloromethane	1.60	600(950)
Tetrahydrofuran	1.63	609(980)
Ethyl acetate	1.78	607(710)
Acetone	2.88	598(950)

Table S2. Optimized Cartesian coordinates (in Å) of radical adduct **1** obtained at B3LYP/6-31+G(2df,2p) level of theory. The B3LYP absolute energy is -6764.50812 hartree

C	-6.987839	-2.808435	1.161790
C	-5.638229	-3.165802	1.307937
C	-4.614902	-2.293044	0.945538
C	-4.980375	-1.051529	0.430419
C	-6.334892	-0.670055	0.275130
C	-7.342012	-1.564595	0.648197
N	-4.166176	-0.000097	0.000031
C	-4.980296	1.051378	-0.430402
C	-6.334842	0.669965	-0.275217
C	-7.341892	1.564553	-0.648358
C	-6.987624	2.808379	-1.161918
C	-5.637987	3.165686	-1.307958
C	-4.614727	2.292880	-0.945485
C	-2.041239	0.618747	1.035316
C	-0.642292	0.618605	1.034987
C	0.099428	-0.000034	0.000056
C	-0.642252	-0.618730	-1.034852
C	-2.041203	-0.618967	-1.035182
C	-2.758451	-0.000123	0.000061
C	1.578664	0.000051	-0.000001
C	4.062178	2.568463	1.323996
C	3.720861	3.697521	0.591295
C	2.689233	3.629320	-0.335529
C	1.997445	2.432096	-0.541577
C	2.315224	1.265624	0.200047
C	3.369119	1.367674	1.143920
C	2.315245	-1.265547	-0.200065
C	3.368874	-1.367734	-1.144190
C	4.061886	-2.568573	-1.324234
C	3.720746	-3.697512	-0.591279
C	2.689361	-3.629155	0.335803
C	1.997680	-2.431873	0.541865
Cl	3.768009	0.032438	2.177101
Cl	0.807279	2.384255	-1.803471
Cl	3.767655	-0.032741	-2.177752
Cl	0.807866	-2.383750	1.804070
Cl	0.170908	-1.305896	-2.404869
Cl	0.170794	1.306143	2.404864
Cl	2.314965	-5.065211	1.237550
Cl	5.350420	-2.713390	-2.479306
Cl	2.314680	5.065514	-1.236993
Cl	5.351012	2.713055	2.478755
Cl	-2.927332	1.345702	2.330787
Cl	-2.927235	-1.345785	-2.330772
H	-7.760154	-3.510396	1.453811
H	-5.384467	-4.139776	1.710553
H	-3.575380	-2.575044	1.060975
H	-8.386092	-1.293023	0.539873
H	-8.385994	1.293028	-0.540114
H	-7.759885	3.510377	-1.453994
H	-5.384150	4.139651	-1.710551
H	-3.575184	2.574832	-1.060845
H	4.256005	4.624509	0.741180
H	4.255824	-4.624535	-0.741179