Supporting information

C-H···S Interaction Exhibits all the Characteristics of Conventional Hydrogen Bonds

*Sanat Ghosh,[≠] Pragya Chopra,[‡] and Sanjay Wategaonkar**

Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Mumbai 400 005, India.

≠ Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense de Madrid, 28040 Madrid, Spain.

‡ Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany.

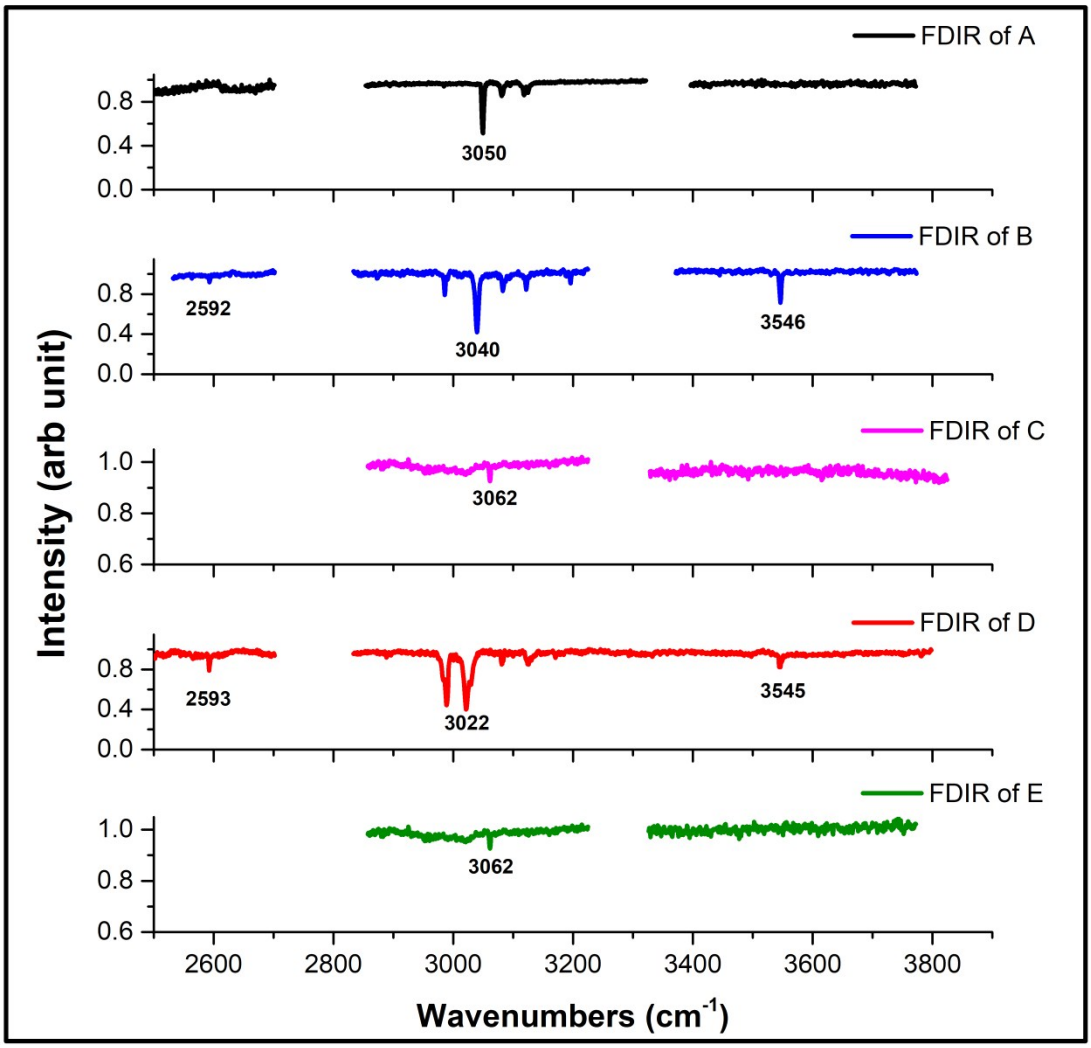

Fig. S1 FDIR spectra of the LIF transitions A, B, C, D, and E in the C-H, S-H and O-H frequency region. FDIR spectra of A, C, and E did not show any O-H transition. FDIR spectra of B and D showed both O-H transition and S-H transition, i.e., they are mixed clusters of TCNB with H_2O and H_2S. FDIR spectrum of A did not show any S-H transition because its intrinsic IR transition probability in H_2S is very low. FDIR spectra of C and E in the S-H region were not recorded.

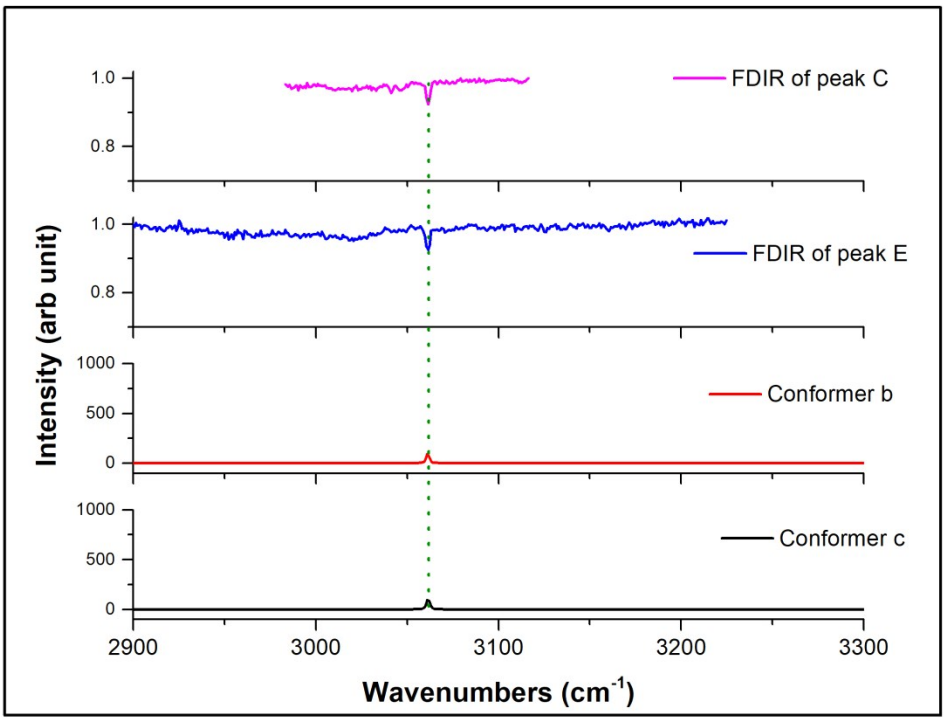

Fig. S2 Comparison of the FDIR spectra of C and E transitions with the computed IR spectra of the conformer 'b' and 'c' computed at the *cp*-MP2/aug-cc-pVDZ level.

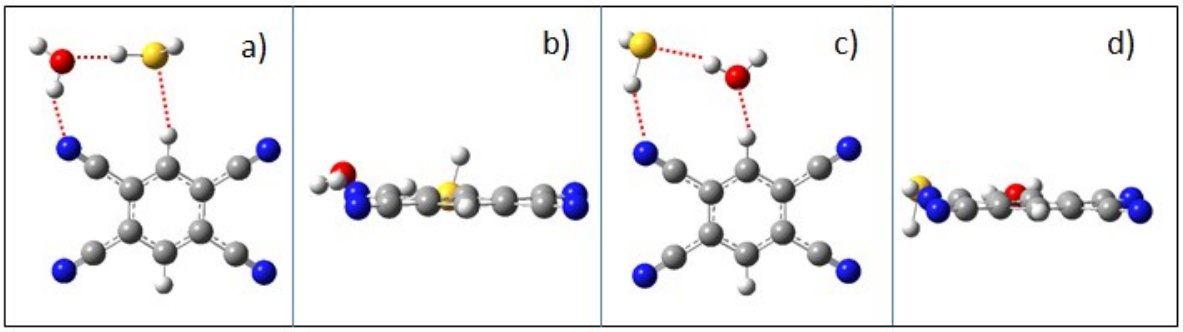

Fig. S3 Structures of the mixed clusters of TCNB with H_2O and H_2S. Figure 'a' and 'b' are the top view and side view of the conformer 'SO' and Figure 'c' and 'd' are the top view and side view of the conformer 'OS'.

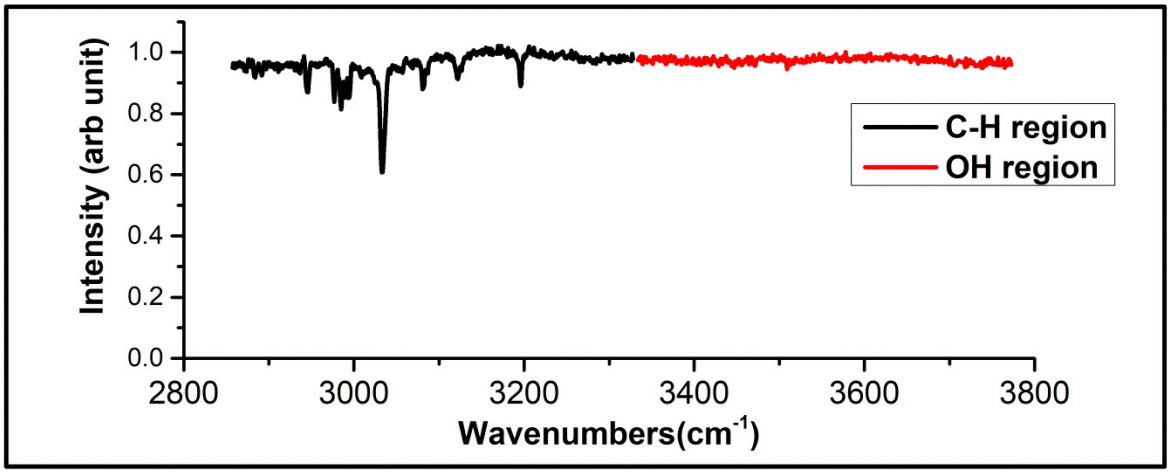

Fig. S4 FDIR spectrum of LIF transition F, extended to the O-H frequency region to confirm the absence of mixed cluster.

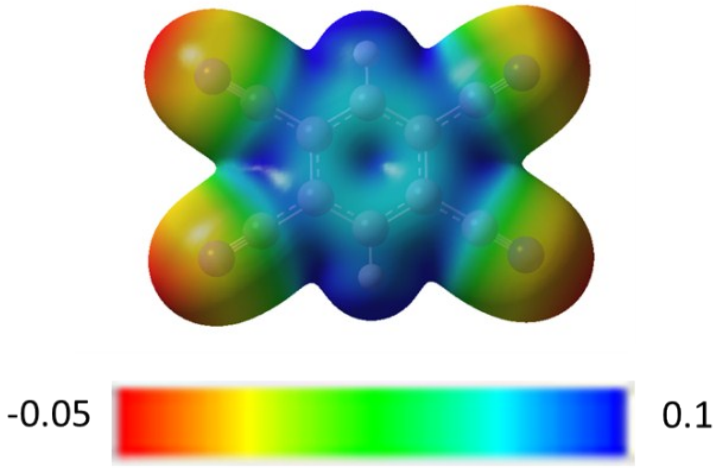

Fig. S5 MEP graph of TCNB monomer calculated at the ωB97X-D/6-311++G** level. The scale bar indicates the magnitude and the sign of the potential.

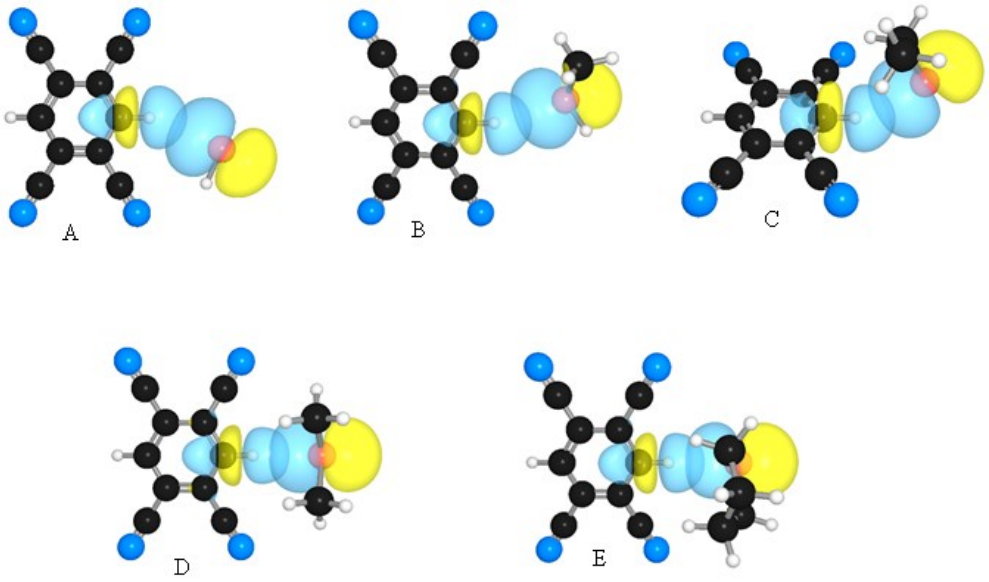

Fig. S6 Natural bond orbitals involved in the C-H···S H-bonding interactions. A) TCNB-H_2S, B) TCNB-MeSH, C) TCNB-EtSH, D) TCNB-DMS, E) TCNB-THT.

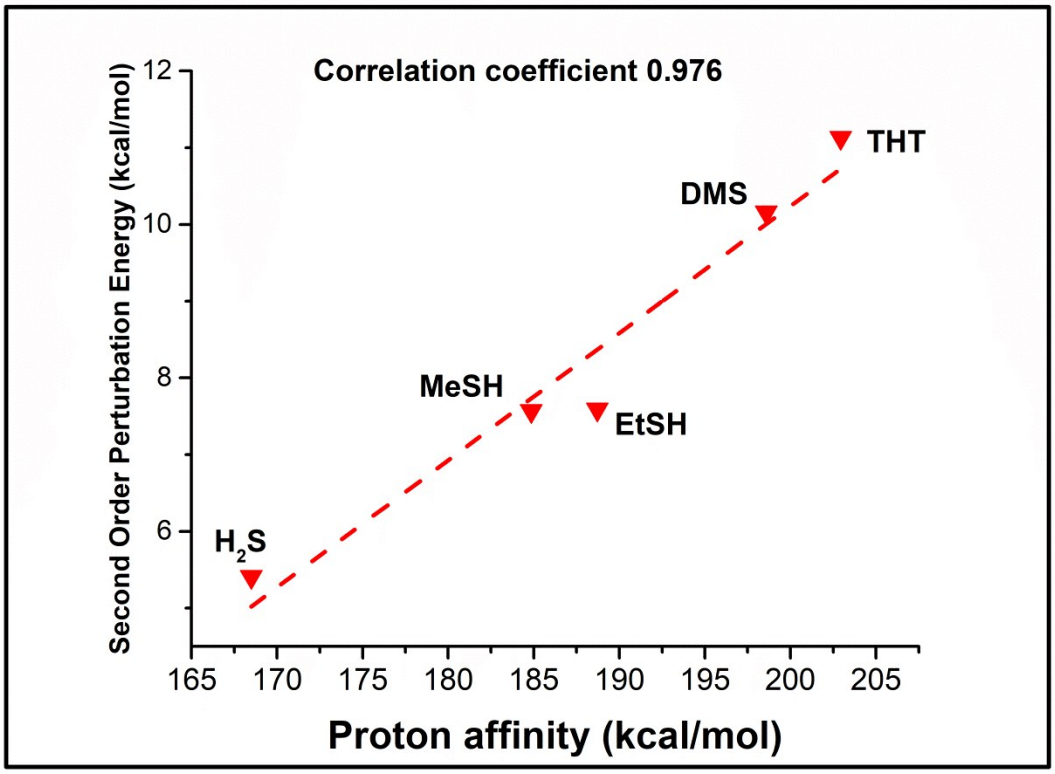

Fig. S7 Correlation plot of the second order perturbation energies for the C-H···S bound conformers and proton affinities of the solvents. Second order perturbation energies were calculated using NBO theory at the *cp*-ωB97X-D/aug-cc-pVDZ level.

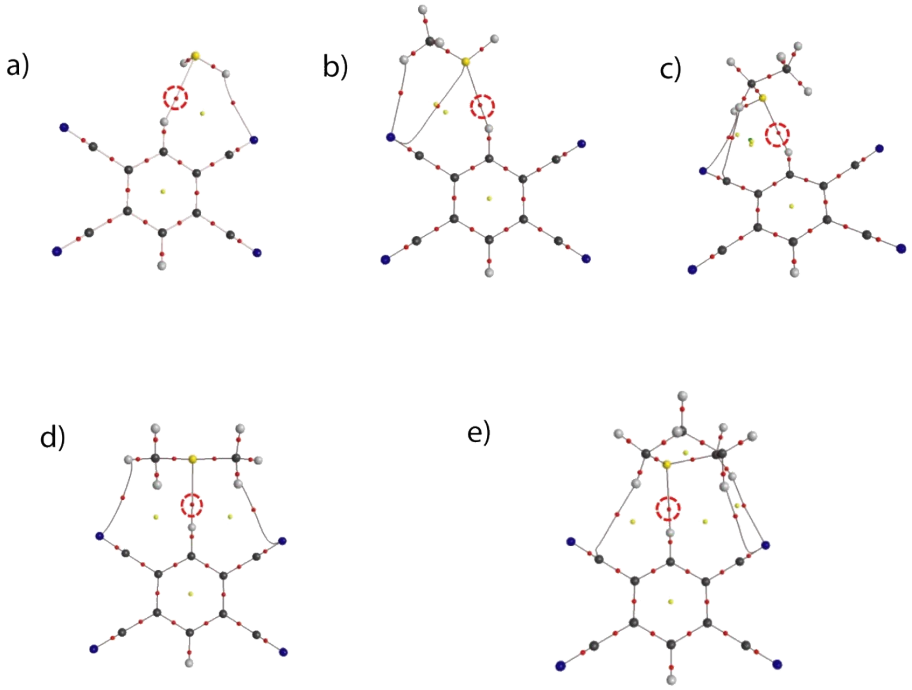

Fig. S8 Molecular graphs of the C-H···S H-bond bound conformers calculated using QTAIM calculation at the *cp*-ωB97X-D/aug-cc-pVDZ level. a) TCNB-H_2S, b) TCNB-MeSH, c) TCNB-EtSH, d) TCNB-DMS and e) TCNB-THT. Red dotted circles indicate BCPs at the C-H···S bond paths.

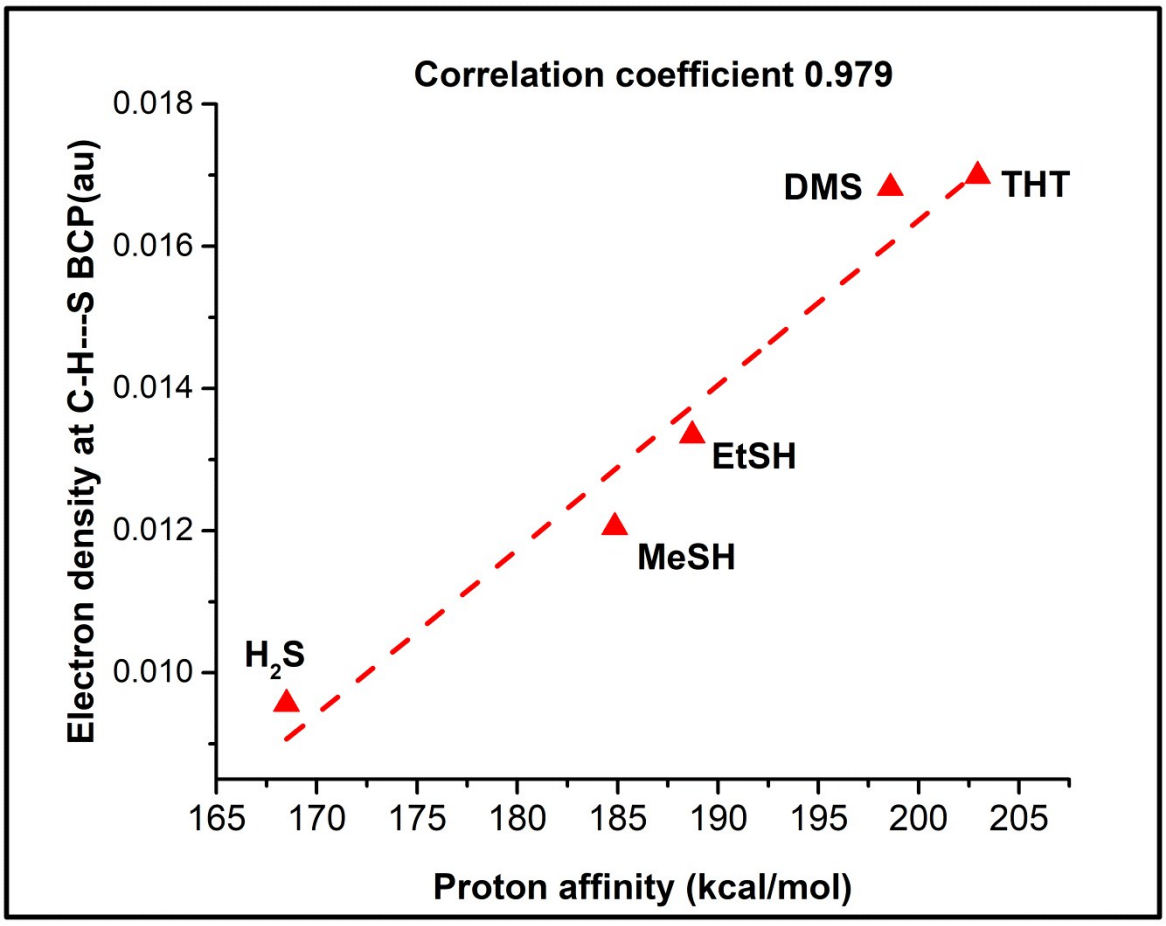

Fig. S9 Correlation plot of electron densities at the C-H···S BCPs versus the PA of the solvents. Electron densities are calculated using QTAIM analysis on the optimized geometries of the C-H···S bound conformers obtained at the *cp*-ωB97X-D/aug-cc-pVDZ level.

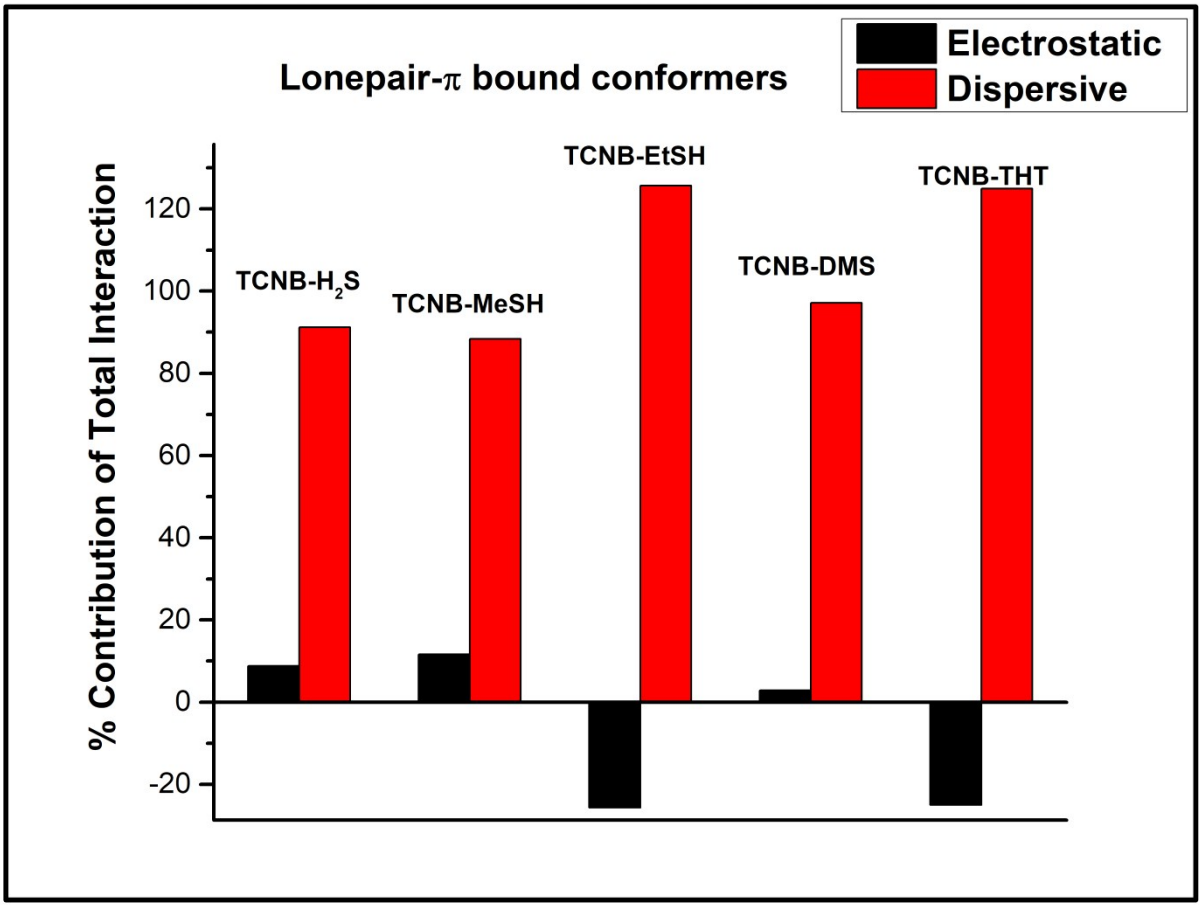

Fig. S10 % contribution of the electrostatic and dispersion interaction to the total stabilization energy of the lp-π bound conformers of TCNB with different S-containing solvents calculated at *cp*-ωB97X-D/cc-pVDZ level.

Table S1: H-bond related geometrical parameters of the C-H···S bound conformers of the TCNB complexes with different S-containing solvents computed at *cp*-MP2/aug-cc-pVDZ and *cp*-ωB97X-D/aug-cc-pVDZ levels.

Complex	C-H bond length (Å)	Increase in C-H bond length (Å)	C-H···S HB length (Å)	∠CHS (º)
cp-MP2/aug-cc-pVDZ				
TCNB	1.093	--	--	--
TCNB-H_2S	1.095	0.002	2.859	154
TCNB-MeSH	1.094	0.001	2.793	144
TCNB-EtSH	1.095	0.002	2.732	163
TCNB-DMS	1.099	0.006	2.547	162
TCNB-THT	1.099	0.006	2.565	160
cp-ωB97X-D/aug-cc-pVDZ				
TCNB	1.088	--	--	--
TCNB-H_2S	1.091	0.003	2.806	157
TCNB-MeSH	1.092	0.004	2.691	162
TCNB-EtSH	1.092	0.004	2.638	153
TCNB-DMS	1.095	0.007	2.518	164
TCNB-THT	1.095	0.007	2.512	166

Table S2: Free energies of formation ($\Delta_f G$) at 0.05, 5, 50, 100, 150, 200, 250 and 298.15 K for all the conformers of TCNB complexes with S-containing solvents computed at the *cp*-ωB97X-D/aug-cc-pVDZ level in kcal/mole.

Complex	Type of interaction	$\Delta_f G^{0.05}$	$\Delta_f G^{5}$	$\Delta_f G^{50}$	$\Delta_f G^{100}$	$\Delta_f G^{150}$	$\Delta_f G^{200}$	$\Delta_f G^{250}$	$\Delta_f G^{298.15}$
TCNB-H_2S	C-H···S	-3.19	-3.15	-2.13	-0.88	0.34	1.50	2.63	3.69
	lp-π	-3.63	-3.59	-2.52	-1.24	0.00	1.20	2.35	3.43
	S-H···N	-1.44	-1.41	-0.78	-0.06	0.61	1.23	1.81	2.33
TCNB-MeSH	C-H···S	-4.68	-4.61	-3.31	-1.87	-0.49	0.83	2.11	3.31
	lp-π	-5.96	-5.88	-4.41	-2.69	-1.04	0.56	2.11	3.57
	S-H···N	-2.31	-2.24	-0.85	0.77	2.36	3.92	5.47	6.94
TCNB-EtSH	C-H···S	-5.20	-5.10	-3.76	-2.29	-0.89	0.46	1.76	2.97
	lp-π	-6.22	-6.12	-4.58	-2.84	-1.17	0.45	2.01	3.49
TCNB-DMS	C-H···S	-5.71	-5.63	-4.25	-2.74	-1.32	0.05	1.37	2.60
	lp-πI	-7.26	-7.17	-5.63	-3.87	-2.17	-0.52	1.08	2.58
	lp-πII	-3.33	-3.24	-1.83	-0.31	1.13	2.50	3.83	5.07
TCNB-THT	C-H···S	-6.65	-6.55	-5.07	-3.46	-1.93	-0.46	0.97	2.31

Table S3: ΔZPE, BSSE, and BSSE and ZPE corrected binding energies (kcal/mol) of all the conformers of TCNB with different S-containing solvents computed at various levels using aug-cc-pVDZ basis set.

Complex	Type of interaction	ΔZPE	BSSE	Binding Energy
TCNB-H_2S				
cp-MP2	C-H···S	0.85	1.43	3.19
	S-H···N	0.63	0.86	1.44
	Lone pair-π	0.75	1.54	3.63
cp-B3LYP	C-H···S	0.74	0.21	1.37
	S-H···N	0.73	0.28	0.46
	Lone pair-π	0.81	0.23	0.34
cp-ωB97X-D	C-H···S	0.71	0.32	3.22
	S-H···N	0.80	0.24	0.98
	Lone pair- π	1.49	0.29	2.63
cp-M06-2X	C-H···S	1.77	0.34	2.06
	S-H···N	2.02	0.26	-0.40
	Lone pair- π	1.62	0.33	2.89
TCNB-MeSH				
cp-MP2	C-H···S	0.60	1.84	4.68
	S-H···N	0.42	1.46	2.31
	Lone pair- π	0.65	2.40	5.96
cp-B3LYP	C-H···S	0.51	0.36	2.29
	S-H···N	Converged to C-H···S		
	Lone pair- π	0.50	0.35	1.51
cp-ωB97X-D	C-H···S	0.67	0.53	4.43
	S-H···N	0.80	0.39	1.52
	Lone pair- π	0.71	0.57	5.23
cp-M06-2X	C-H···S	1.14	0.46	3.87
	S-H···N	1.10	0.55	1.26
	Lone pair- π	1.29	0.69	5.30
TCNB-EtSH				
cp-MP2	C-H···S	0.52	2.21	5.20
	Lone pair- π	0.39	4.31	6.22
cp-B3LYP	C-H···S	0.45	0.37	2.38
	Lone pair- π	0.44	0.36	1.42
cp-ωB97X-D	C-H···S	1.08	0.67	4.72
	Lone pair- π	0.92	0.93	4.97
cp-M06-2X	C-H···S	0.79	0.83	4.08
	Lone pair-pi	1.06	1.21	4.35
TCNB-DMS				
cp-MP2	C-H···S	0.40	2.99	5.71
	Lone pair-πI	0.60	3.26	7.26

	Lone pair-πII	0.22	4.13	3.33
cp-B3LYP	C-H···S	0.45	0.46	2.80
	Lone pair-πI	0.45	0.54	1.72
	Lone pair-πII			Not stable
cp-ωB97X-D	C-H···S	0.67	0.85	5.56
	Lone pair-πI	0.75	0.81	6.26
	Lone pair-πII	0.82	1.07	2.62
cp-M06-2X	C-H···S	0.67	0.97	4.79
	Lone pair-πI	0.70	0.95	6.76
	Lone pair-πII	0.39	1.27	2.16
TCNB-THT				
cp-MP2	C-H···S	0.37	3.61	6.65
	Lone pair-π			
cp-B3LYP	C-H···S	0.42	0.53	3.03
	Lone pair-π	Converged to C-H···S		
cp-ωB97X-D	C-H···S	0.58	0.83	6.47
	Lone pair-π	0.48	1.07	6.41
cp-M06-2X	C-H···S	0.58	0.92	5.25
	Lone pair-π	0.85	0.92	6.62

Table S4: Different components of the interaction energy for the C-H···S bound conformers of the complexes of TCNB with different S-containing solvents using NEDA. All the components are in kcal/mol.

Complex	Electrical (ES+POL +SE)	Charge transfer	Core (EX+DEF -SE)	E_{int}	E_{disp}	E_{total}	% Dispersion
TCNB-H_2S	-7.84	-7.30	13.68	-1.47	-2.62	-4.09	64.02
TCNB-MeSH	-9.61	-9.78	17.44	-1.95	-3.20	-5.15	62.15
TCNB-EtSH	-10.23	-11.80	22.15	0.11	-5.95	-5.84	101.88
TCNB-DMS	-11.51	-14.58	25.71	-0.37	-5.65	-6.02	93.85
TCNB-THT	-12.22	-16.07	28.39	0.10	-7.03	-6.93	101.44

E_{total} = BE of the complexes predicted by dispersion corrected function *cp*-ωB97X-D/cc-pVDZ level.
$E_{int} = E_{electrostatic}$ = Electrical (ES+POL+SE) + Charge Transfer + Core (EX+DEF–SE);
ES= Static energy, POL= Polarization energy, SE= Self-energy, EX= Exchange energy, DEF= Deformation energy.
$E_{disp} = (E_{total} - E_{int})$

Table S5: Different components of the interaction energy of the lp-π bound conformers calculated using NEDA. All the components are in kcal/mol.

Complex	Electrical (ES+POL +SE)	Charge transfer	Core (EX+DEF -SE)	E_{int}	E_{disp}	E_{total}	% Dispersion
TCNB-H_2S	-7.60	-3.71	10.98	-0.33	-3.42	-3.75	91.19
TCNB-MeSH	-10.99	-6.77	17.14	-0.63	-4.78	-5.41	88.36
TCNB-EtSH	-9.39	-6.07	16.96	1.50	-7.34	-5.84	125.70
TCNB-DMS	-13.06	-8.24	21.11	-0.18	-6.11	-6.29	97.14
TCNB-THT	-11.59	-8.42	21.61	1.60	-8.00	-6.40	124.99

Coordinates of all the atoms in the C-H···S bound optimized conformers in XYZ format computed at *cp*-MP2/aug-cc-pVDZ level

TCNB-H_2S

C	-0.62555100	1.74397700	-0.00307100
C	0.50035200	0.87593200	0.03779200
C	0.31946100	-0.52116100	0.05361600
C	-0.98291600	-1.05739200	0.02994400
C	-2.11084500	-0.19155100	-0.01091900
C	-1.92664800	1.20498600	-0.02759800
C	-1.16663300	-2.48597100	0.04881100
C	-3.44413000	-0.73557000	-0.03498600
C	1.83447300	1.41929000	0.06445000
C	-0.44121900	3.17219500	-0.01887400
N	-4.54993900	-1.17671300	-0.05467500
N	-1.31347000	-3.66742200	0.06656100
N	2.94497400	1.84833400	0.08843400
N	-0.29461300	4.35380200	-0.03157600
H	1.19231700	-1.18128900	0.08222200
H	-2.79328800	1.87010000	-0.05917100
S	3.98257900	-1.75417700	-0.15911900
H	4.31736100	-2.19853700	1.07101600
H	4.31561500	-0.47785000	0.13562300

TCNB-MeSH

C	-1.04856100	1.72851200	-0.01905800
C	0.11698200	0.92257500	0.10520900
C	0.00567700	-0.47996600	0.17229600
C	-1.26562200	-1.08345800	0.11593500
C	-2.43321800	-0.28043200	-0.00880300
C	-2.31854200	1.12194300	-0.07596300
C	-1.37672500	-2.51813100	0.18417800
C	-3.73464700	-0.89449800	-0.06676000
C	1.41779600	1.53880400	0.16707300
C	-0.93644700	3.16274000	-0.08621600
N	-4.81443400	-1.39398400	-0.11482100
N	-1.46135100	-3.70432800	0.24212000
N	2.49205000	2.04932400	0.22492500
N	-0.85094500	4.34909600	-0.14116100
H	0.91112300	-1.08926300	0.25516000
H	-3.21518800	1.73935300	-0.17193700
C	4.75441300	-0.60463600	0.55947200
S	3.55283900	-1.34305500	-0.61293100
H	4.59273000	0.48114400	0.51207600
H	4.57056300	-0.95325800	1.58406500
H	5.78275800	-0.83421400	0.25184600
H	3.86870200	-2.63636400	-0.38593600

TCNB-EtSH

C	2.67819800	-0.36222800	-0.09409400
C	1.47239200	-1.10023900	0.06605700
C	0.24491600	-0.42624600	0.21839600
C	0.21669800	0.98220700	0.21233200
C	1.42045400	1.72322700	0.05194900
C	2.64597200	1.04604400	-0.10068600
C	-1.03839000	1.67208000	0.36899300
C	1.39174500	3.16308300	0.04455200
C	1.50240000	-2.54049800	0.07454500
C	3.93504200	-1.04800800	-0.24997900
N	1.37402000	4.35364700	0.03716500
N	-2.07294500	2.24845100	0.49543800
N	1.52621400	-3.73089800	0.08362900
N	4.97893700	-1.60593900	-0.37941600
H	-0.68985600	-0.98450000	0.33943700
H	3.57205200	1.61312400	-0.22401400
C	-4.17115100	0.08743400	-1.51092400
C	-4.39557700	-0.21391000	-0.02918700
S	-3.33773900	-1.65095700	0.44148300
H	-4.42741900	-0.78187300	-2.13677000
H	-4.80231900	0.93523500	-1.81898100
H	-3.12107600	0.35948700	-1.70176400
H	-4.11802000	0.65226900	0.58704700
H	-5.44554900	-0.48009400	0.15991400
H	-3.62376900	-1.65283500	1.76196900

TCNB-DMS

C	2.04674900	1.22307600	0.03872500
C	0.65627900	1.21885900	-0.26107900
C	-0.03292800	0.00006000	-0.41504600
C	0.65911200	-1.21718000	-0.26149100
C	2.04963400	-1.21816800	0.03838400
C	2.73664200	0.00325100	0.18441500
C	-0.05958900	-2.45804300	-0.40169500
C	2.75817300	-2.46198400	0.19608400
C	-0.06604400	2.45763800	-0.40069300
C	2.75233200	2.46854100	0.19676300
N	3.34913200	-3.48708600	0.32922100
N	-0.67414200	-3.47251200	-0.50860500
N	-0.68512600	3.46943100	-0.50673700
N	3.34089900	3.49498400	0.33017300
H	-1.10686800	-0.00105700	-0.64791900
H	3.80518500	0.00453500	0.41392800
S	-3.64145800	-0.00752300	-0.39825900
C	-3.48759900	-1.37672600	0.79666400
C	-3.50523100	1.37442000	0.78402000
H	-3.49957300	-2.32043900	0.23209700
H	-2.53665000	-1.30469400	1.34974200
H	-4.32965500	-1.36358400	1.50500100
H	-2.55286300	1.32042100	1.33658500
H	-3.53027000	2.31267400	0.21086400
H	-4.34649500	1.35632600	1.49316900

TCNB-THT

C	2.12594400	1.50526000	0.04423500
C	0.81642900	1.21452000	-0.42884800
C	0.41671300	-0.11948200	-0.64237300
C	1.31789900	-1.16811700	-0.37304200
C	2.62860200	-0.88255500	0.10089500
C	3.02681400	0.45363600	0.30374000
C	0.89490500	-2.53154600	-0.56723900
C	3.55067700	-1.95338500	0.37852500
C	-0.12032700	2.27917200	-0.68207000
C	2.53379500	2.86898900	0.26273000
N	4.31817400	-2.83334400	0.61200200
N	0.52990700	-3.65526000	-0.71702500
N	-0.91209400	3.14633700	-0.88197700
N	2.87571800	3.99456600	0.44734600
H	-0.59848800	-0.33363900	-1.00413200
H	4.03385900	0.67415000	0.66666800
C	-2.79320200	-1.53301700	0.68106800
C	-3.64565500	0.87567300	-0.19688800
C	-3.15651400	0.82452100	1.25500400
C	-3.41347400	-0.60895300	1.73804600
S	-3.13177200	-0.73559800	-0.95691800
H	-3.23057200	-2.54170100	0.67864200
H	-1.70316700	-1.62242100	0.82529900
H	-3.19886800	1.70029000	-0.77088800
H	-4.74276800	0.95070700	-0.24375600
H	-2.07421600	1.04317200	1.29238500
H	-3.67600100	1.57515700	1.87291600
H	-2.97874300	-0.80135500	2.73266400
H	-4.50026600	-0.78919100	1.79575800