Supporting Information

Modulating Photophysical Properties in a Flexible Porous Host by Regulating Guest-Assisted Charge Transfer Interactions

*Rohan Jena[a], Faruk Ahamed Rahimi[a], Tarak Nath Das[b], Soumya Kanti Mondal[a], Jatin Chauhan[a] and Tapas Kumar Maji[a,b]**

[a]Molecular Materials Laboratory, Chemistry and Physics of Materials Unit, School of Advanced Materials (SAMat), Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Post, Bangalore- 560064.

[b]New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Post, Bangalore- 560064.

Email: tmaji@jncasr.ac.in

Materials

All the reagents employed were commercially available and used as provided without further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) 2,6-naphthalene dicarboxylic acid (H_2ndc), 1,10-phenanthroline (o-phen), N,N-dimethylformamide (DMF), fluorene, carbazole, dibenzofuran and dibenzothiophene were purchased from Sigma Aldrich chemicals.

Synthesis of PCP (1): Synthesis of **1** was carried out according to the previously reported methodology. H_2ndc (0.022 g, 0.1 mmol) and o-phen (0.020 g, 0.1 mmol) were dissolved in 5 mL of DMF and mixed well, followed by the addition of $Zn(NO_3)_2 \cdot 6H_2O$ (0.030 g, 0.1 mmol). The mixture was sonicated and kept in a glass vial at 120 ºC for 36 h. The resulting compound was washed with DMF and dried at room temperature overnight. A single crystalline pale-yellow colored product was obtained with a yield of approximately 80%.

Synthesis of 1-FLU: H_2ndc (0.022 g, 0.1 mmol) and o-phen (0.020 g, 0.1 mmol) were dissolved in 5 mL of DMF and mixed well, followed by the addition of $Zn(NO_3)_2 \cdot 6H_2O$ (0.030 g, 0.1 mmol). 0.5 g of aromatic guest (fluorene) was added to this clear solution and at 120 ºC for 36 h. The resulting compound was washed with DMF and dried at room temperature overnight. A single crystalline yellow colored product was obtained with a yield of approximately 75%. Good quality crystals were chosen under optical microscope for single-crystal X-ray diffraction measurement.

Synthesis of 1-CBZ, 1-DBF, and 1-DBT: Similar procedure as **1-FLU** was followed except for the type of aromatic guests, i.e., 0.5 g of carbazole or dibenzofuran or dibenzothiophene was used for the synthesis of **1-CBZ** or **1-DBF** or **1-DBT** respectively.

Physical Measurements

Single crystal X-ray diffraction (SCXRD): Suitable single crystals of **1-FLU**, **1-CBZ**, **1-DBF**, and **1-DBT** were mounted on a thin glass fibre. X-ray crystallographic data of such crystals were collected on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromated Mo-Kα radiation. The program SAINT was used for integration of diffraction profiles, and absorption correction was made with SADABS3 program. Structures were solved by SIR 92 and refined by the full-matrix least-squares method using SHELXL-97. All hydrogen atoms were fixed in ideal positions by HFIX command. In addition, nonhydrogen atoms were refined anisotropically. All crystallographic and structure refinement data are summarized in Table S1-S4. All calculations were carried out using SHELXL-97, PLATON, SHELXS-97 and X-Seed Ver 4. The crystal structures can be obtained from Cambridge crystallographic database centre via CCDC numbers 2366677, 2366678, 2366679 and 2366680. **Powder X-ray diffraction (PXRD):** PXRD measurements were performed on a Bruker D8 discover instrument using Cu-Kα radiation. **Nuclear magnetic resonance (NMR):** ^{1}H-NMR spectra were recorded on a Bruker UltraSheild Plus 400 (at 400 MHz) with chemical shifts recorded as ppm and all spectra were calibrated against tetramethyl silane (TMS).

Photophysical Measurements: UV-visible absorption spectra were recorded using Perkin Elmer Model Lambda 900 spectrophotometer . Photoluminescence (PL), temperature dependent PL and excited-state lifetime studies were performed using Edinburgh FLS 1000 instrument.

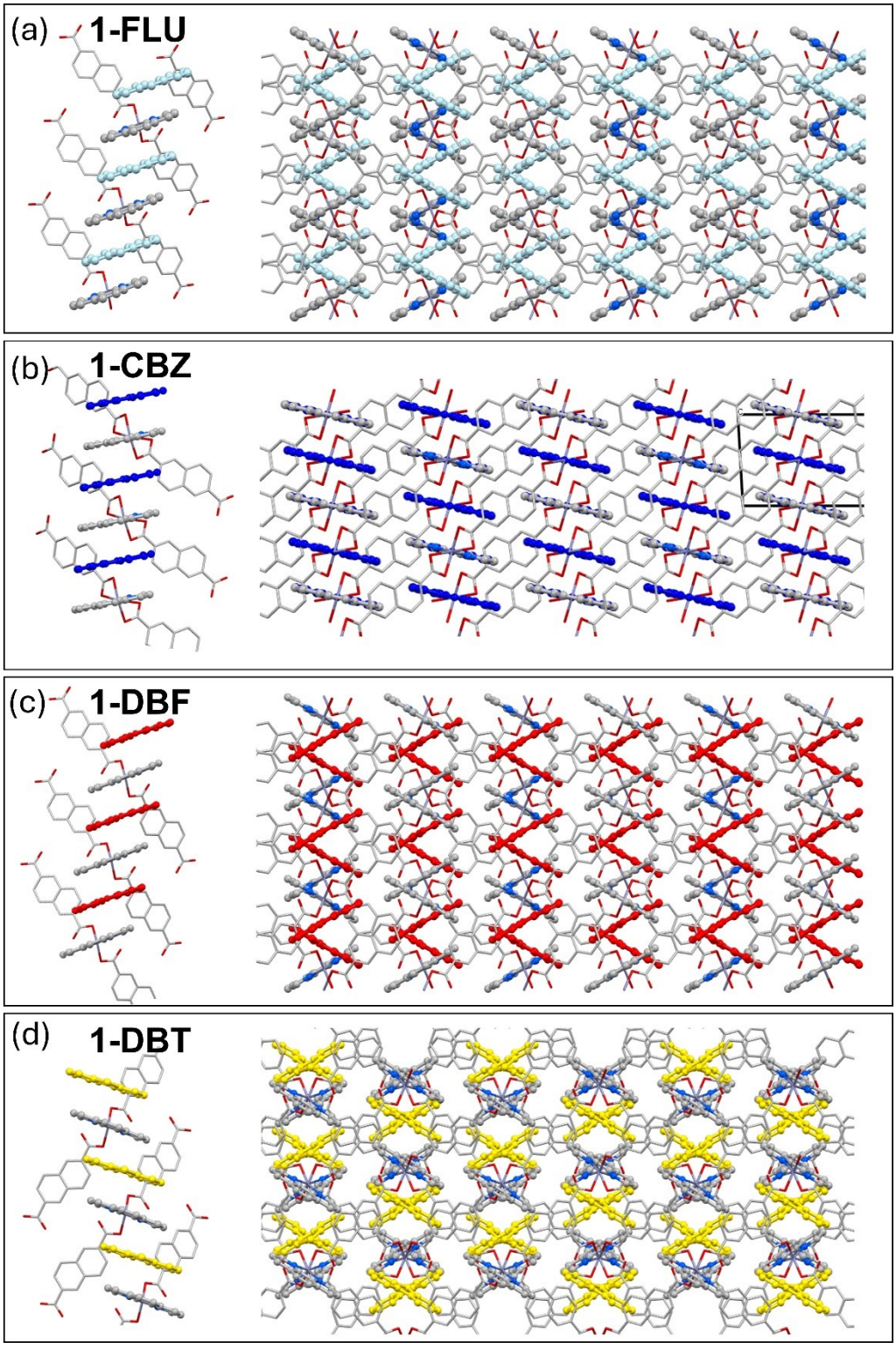

Figure S1: Extended structures of **(a) 1-FLU**, **(b) 1-CBZ**, **(c) 1-DBF** and **(d) 1-DBT** showing long range ordered donor-acceptor (D-A) arrangement. For visual representation the donor guest molecules are shown in different colours; fluorene (cyan), carbazole (blue), dibenzofuran (red) and dibenzothiophene (yellow.)

Table S1: Crystallographic parameters for **1-FLU**

Empirical formula	**C_{24} H_{14} N_2 O_4 Zn, C_{13} H_{10}**
Formula weight	625.97
Crystal system	orthorhombic
Space group	Pca21
***a* (Å)**	19.745(2)
***b* (Å)**	7.9099(9)
***c* (Å)**	17.683(2)
***α* (deg)**	90
***β* (deg)**	90
***γ* (deg)**	90
***V* (Å^3)**	2761.8(5)
Z	4
***T* (K)**	298
***D$_c$* (g cm^{-3})**	1.505
***μ* (mm^{-1})**	0.937
***F* (000)**	1288
***θ$_{max}$* (deg)**	26.0
***λ* (Mo Kα)**	0.71073
Total data	162932
Unique data, R_{int}	5418, 0.111
Data [*I* >2σ(I)]	4777
R[a]	0.0348
R_w[b]	0.0927
GOF	1.05

[a]$R = \sum||F_o| - |F_c||/\sum|F_o|$, [b]$R_w = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$.

Table S2: Crystallographic parameters for **1-CBZ**

Empirical formula	**C_{24} H_{14} N_2 O_4 Zn, C_{12} H_9 N**
Formula weight	626.96
Crystal system	monoclinic
Space group	C2/c
***a* (Å)**	7.2655(2)
***b* (Å)**	20.2802(6)
***c* (Å)**	18.6210(6)
***α* (deg)**	90
***β* (deg)**	93.122(1)
***γ* (deg)**	90
***V* (Å^3)**	2739.65(14)
Z	4
***T* (K)**	298
***D$_c$* (g cm^{-3})**	1.520
***μ* (mm^{-1})**	0.946
***F* (000)**	1288
***θ$_{max}$* (deg)**	26.0
***λ* (Mo Kα)**	0.71073
Total data	24638
Unique data, R_{int}	2691, 0.044
Data [*I* >2σ(I)]	2431
R^a	0.0583
R_w^{b}	0.1778
GOF	1.08

$^aR = \sum||F_o| - |F_c||/\sum|F_o|$, $^bR_w = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$.

Table S3: Crystallographic parameters for **1-DBF**

Empirical formula	**C_{24} H_{14} N_2 O_4 Zn, C_{12} H_8 O**
Formula weight	627.95
Crystal system	orthorhombic
Space group	Pca21
***a* (Å)**	19.7165(5)
***b* (Å)**	7.9538(2)
***c* (Å)**	17.5159(4)
***α* (deg)**	90
***β* (deg)**	90
***γ* (deg)**	90
***V* (Å^3)**	2746.86(12)
Z	4
***T* (K)**	298
***D$_c$* (g cm^{-3})**	1.518
***μ* (mm^{-1})**	0.945
***F* (000)**	1288
***θ$_{max}$* (deg)**	26.0
***λ* (Mo Kα)**	0.71073
Total data	110005
Unique data, R_{int}	5389, 0.096
Data [*I* >2σ(I)]	4709
R[a]	0.0302
R_w[b]	0.0770
GOF	1.03

[a]$R = \sum||F_o| - |F_c||/\sum|F_o|$, [b]$R_w = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$.

Table S4: Crystallographic parameters for **1-DBT**

Empirical formula	**C_{24} H_{14} N_2 O_4 Zn, C_{12} H_8 S**
Formula weight	644.01
Crystal system	monoclinic
Space group	P21/c
***a* (Å)**	7.9306(3)
***b* (Å)**	17.5614(8)
***c* (Å)**	20.1609(9)
***α* (deg)**	90
***β* (deg)**	100.522(2)
***γ* (deg)**	90
***V* (Å^3)**	2760.6(2)
Z	4
***T* (K)**	298
***D$_c$* (g cm^{-3})**	1.549
***μ* (mm^{-1})**	1.013
***F* (000)**	1320
***θ$_{max}$* (deg)**	26.0
***λ* (Mo Kα)**	0.71073
Total data	64519
Unique data, R_{int}	5426, 0.213
Data [*I* >2σ(I)]	2969
R[a]	0.0592
R_w[b]	0.1613
GOF	1.01

[a]$R = \sum||F_o| - |F_c||/\sum|F_o|$, [b]$R_w = [\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}]^{1/2}$.

PXRD Patterns

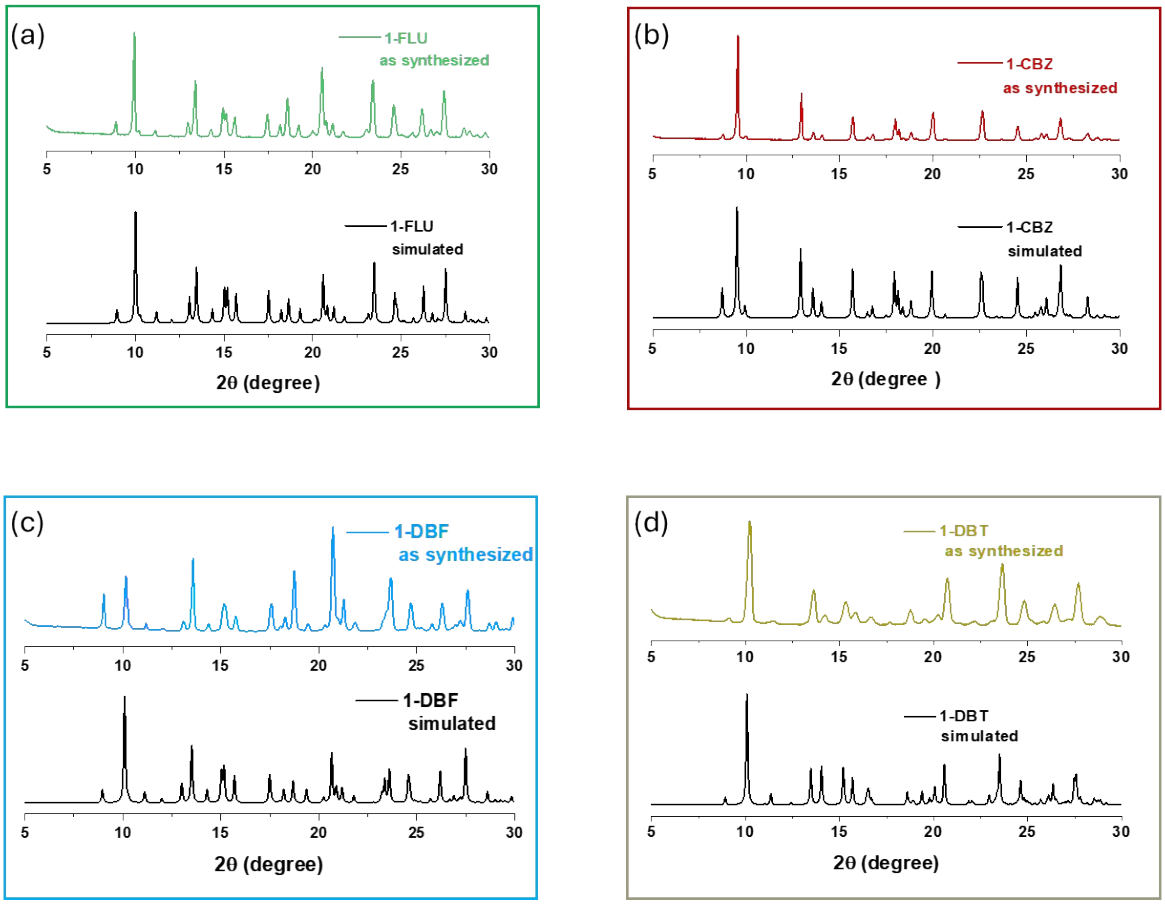

Figure S2: Comparison of as synthesized and simulated PXRD patterns for **(a) 1-FLU (b) 1-CBZ (c) 1-DBF** and **(d) 1-DBT**.

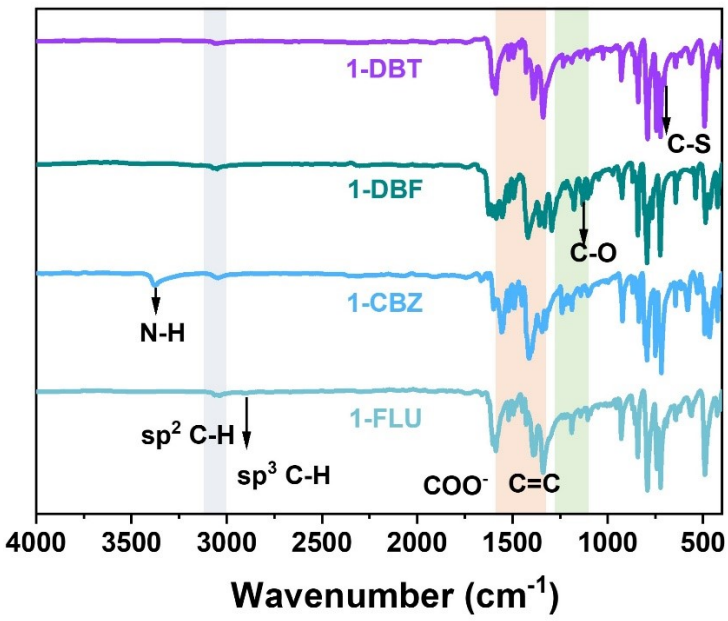

Figure S3: FTIR spectra for **1-FLU**, **1-CBZ**, **1-DBF** and **1-DBT**.

NMR Analyses

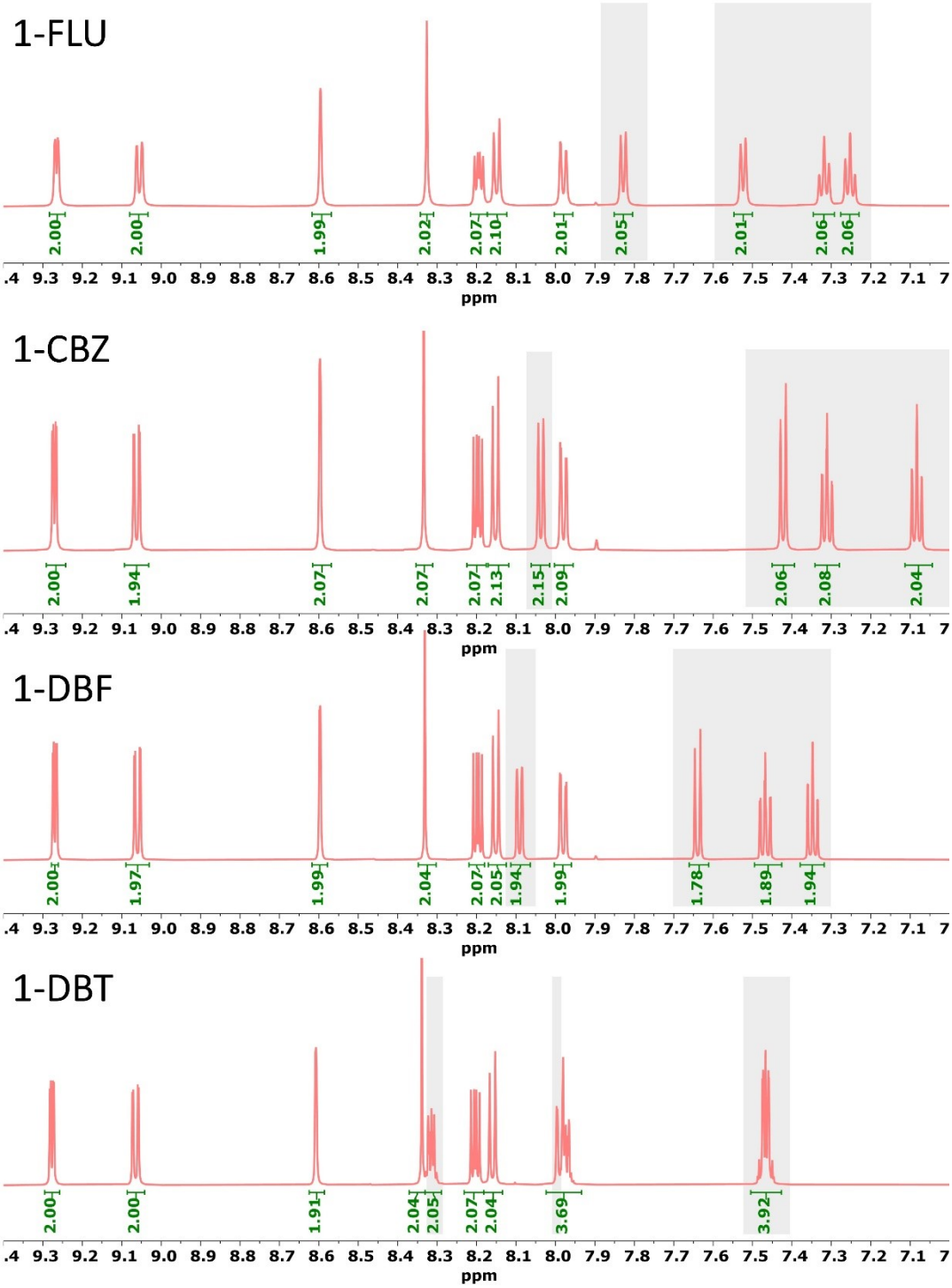

Figure S4: NMR spectra for digested crystals of **1-FLU**, **1-CBZ**, **1-DBF** and **1-DBT** in dil. HCl. and DMSO-d6. (Note: Grey shaded areas represent peaks for respective guest molecules within the PCPs.)

TDDFT Analyses

Table S5: TDDFT analysis for **1-FLU**, **1-CBZ**, **1-DBF**, **1-DBT** to assess the CT bands using 6-311++G** basis set.

Compound Name	Theoretical wavelength (nm)	Oscillator strength	Transition	Expt. Absorption maximum (nm)
1-FLU	421.64	0.0060	HOMO-2 to LUMO (92%)	425
1-CBZ	403.37	0.0138	HOMO-3 to LUMO (95%)	415
1-DBF	378.71	0.0051	HOMO-4 to LUMO (12%) HOMO-6 to LUMO (86%)	400
1-DBT	421.97	0.0005	HOMO-2 to LUMO (84%)	420

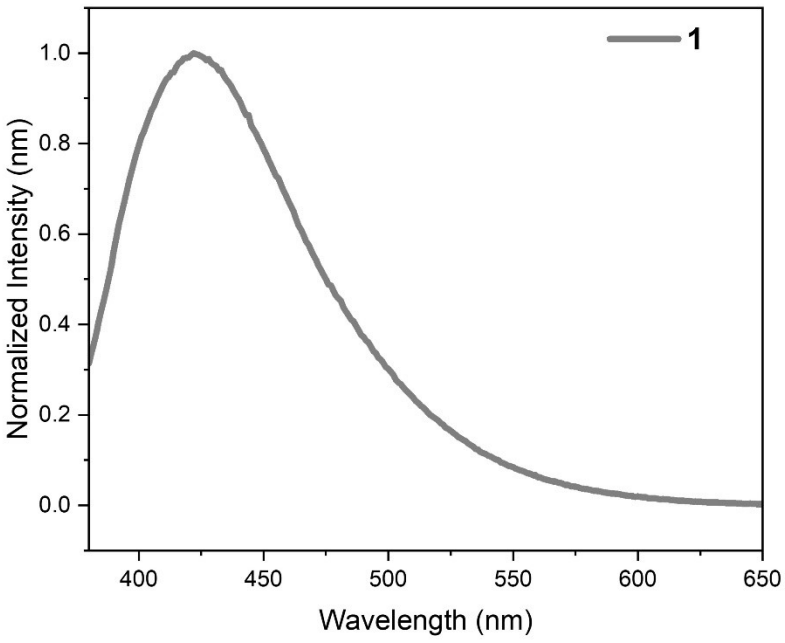

Figure S5: PL spectrum for **1**, excited at 370 nm.

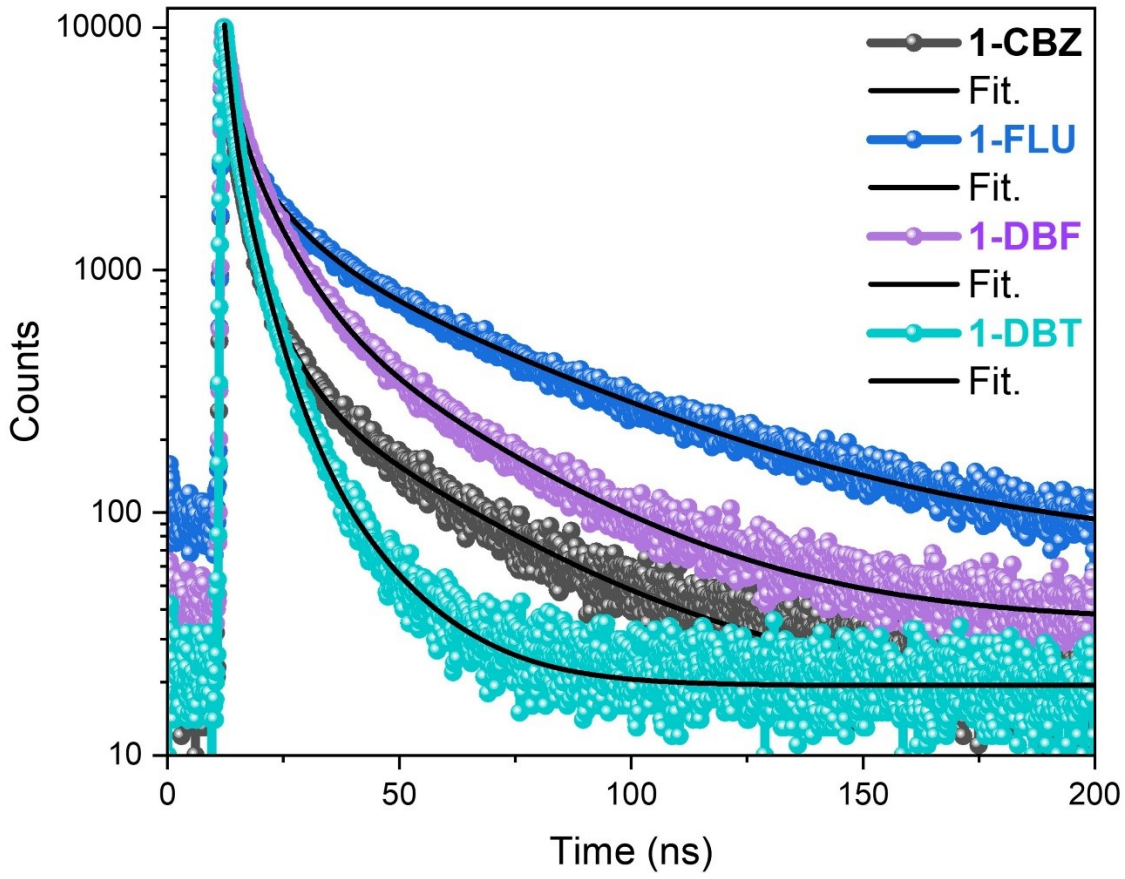

Figure S6: TCSPC (Lifetime measurements) for **1-FLU**, **1-CBZ**, **1-DBF** and **1-DBT** (λ_{Ex}= 405 nm).

Table S6: PL Lifetimes fitting parameters and average lifetimes for **1-FLU**, **1-CBZ**, **1-DBF** and **1-DBT**, corresponding to Figure S6.

Compound Name	t_1 (ns)	t_2 (ns)	t_3 (ns)	B_1 (%)	B_2 (%)	B_3 (%)	T_{avg} (ns)
1-FLU	1.476	9.054	46.14	8.67	23.49	46.14	**23.54**
1-CBZ	1.524	6.03	33	30.81	34.34	34.86	**14.04**
1-DBF	1.923	7.922	32.5	13.51	44.37	42.11	**17.46**
1-DBT	1.303	4.815	14.91	24.12	56.8	19.07	**5.89**

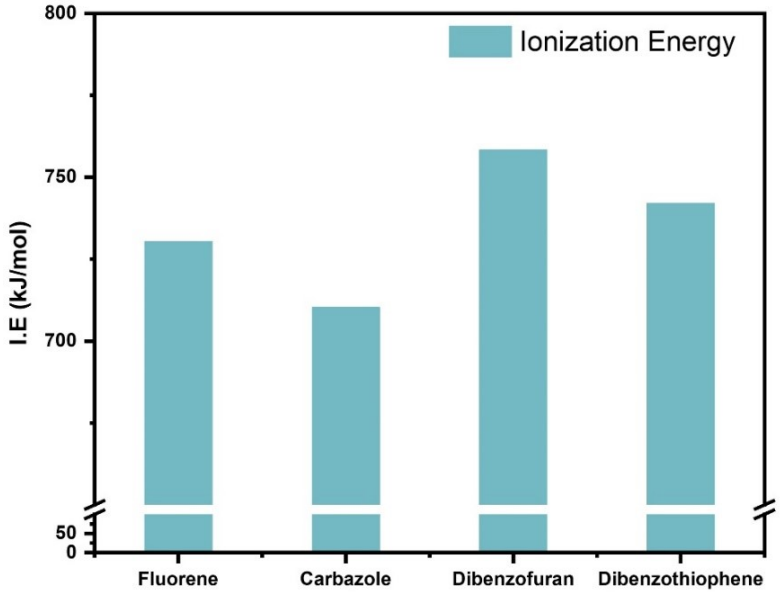

Figure S7: First ionization energy for individual guest molecules.

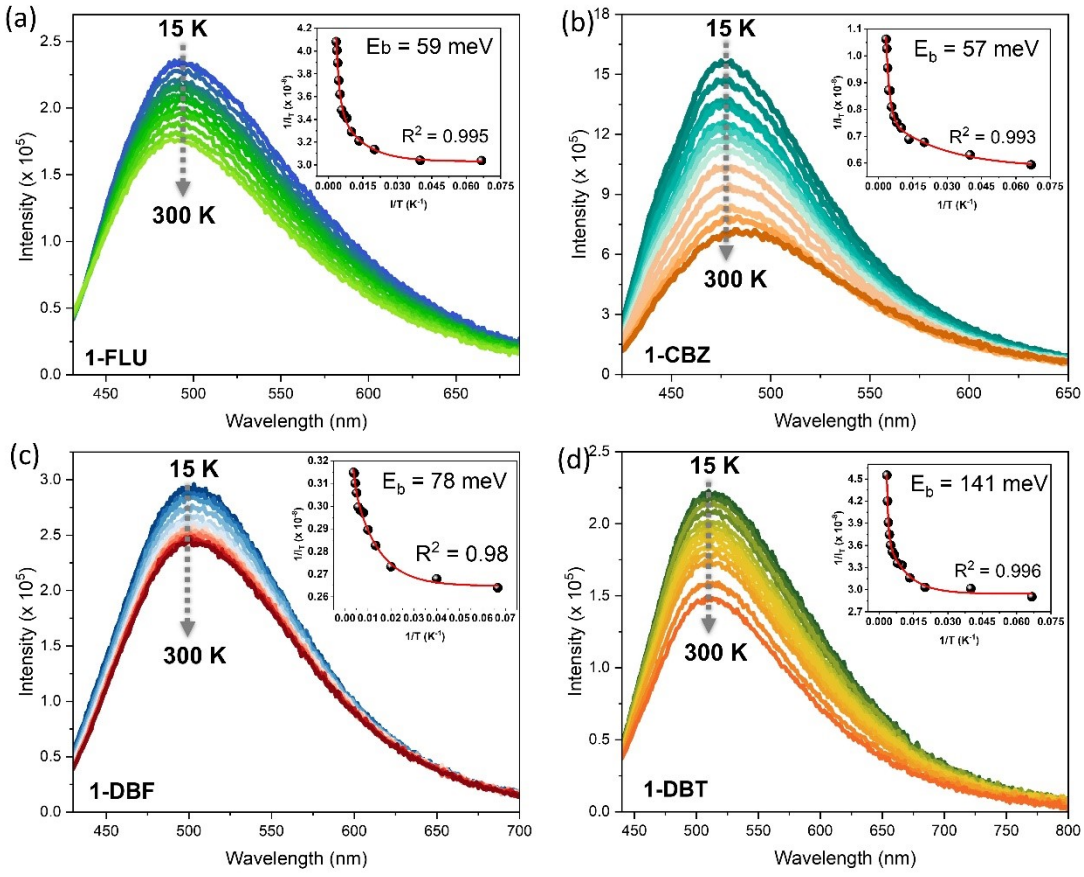

Figure S8: Temperature dependent PL spectra for (**a**) **1-FLU** (**b**) **1-CBZ (c) 1-DBF** and (**d**) **1-DBT** showing respective exciton binding energy values obtained from exponential fitting of $1/I_T$ vs I/T. Fitting curves are represented in the insets.

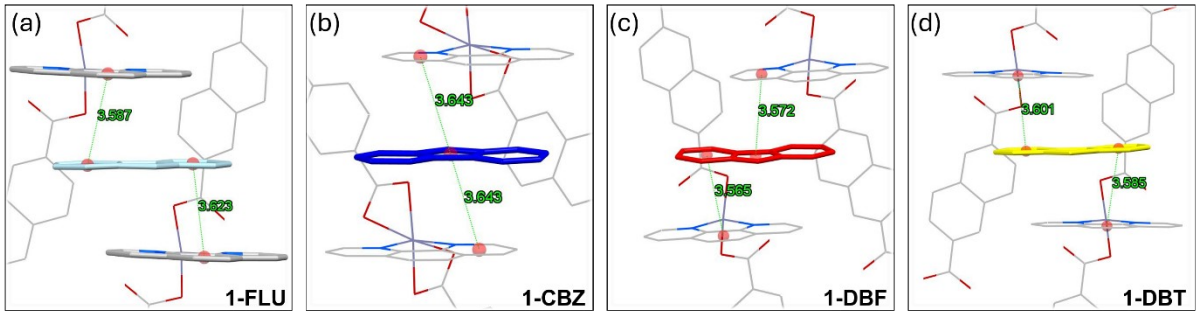

Figure S9: Guest stacking between o-phen units for **(a) 1-FLU**, **(b) 1-CBZ**, **(c) 1-DBF** and **(d) 1-DBT**. The corresponding centroid-to-centroid distances for each of the host-guest system were measured in Mercury (CCDC) and mentioned alongside each figure.

Computational Details

All the calculations were performed using density functional theory (DFT) in Gaussian16 program package.[1] The calculations were performed using B3LYP exchange-correlation functional along with 6-311++G** (single point energy and TDDFT calculations) or 6-31+G** basis set (optimization and frequency calculations) for all atoms except for Zn atom, for which LANL2DZ, which utilized a widely used effective core potential (ECP)-type basis set, was used.[2-10] The calculations were performed in the absence of any solvent. Grimme's d3 dispersion was also used to tackle weak interactions.[11-13] Single point energy calculations were performed to get molecular orbital diagrams. Time-dependent density functional theory (TDDFT) calculations were performed to assign the electronic absorption spectra. The pictures of the molecular orbitals were taken from Gauss View 6.0.16.[14]

Cartesian coordinates of the computed structures

Coordinates are given in standard XYZ format

Table S7: Geometry of **1-FLU (Fluorene)** (singlet) for single point calculation, directly obtained from single crystal X-ray Crystallographic structure, computed at the B3LYP-D3/ 6-311++G** (HCNO)/ LANL2DZ (Zn) level in the absence of any solvent.

Atom	x	y	z
Zn	0.52719900	0.01373100	-0.57027100
O	2.23647900	-0.79849500	-1.03915800
O	11.13124600	-3.12390000	-0.70866100
N	0.73109600	1.89522200	0.33123100
N	-0.00002400	1.24703200	-2.17070100

O	11.36665400	-2.85049100	1.47159200
O	2.38542200	-0.82438900	1.16258500
C	8.63513800	-2.35781100	1.84501600
H	9.16033300	-2.51281300	2.59737600
C	6.51150200	-1.79474200	0.87766900
C	7.07915300	-1.85617700	-0.42161900
C	9.22352700	-2.44991000	0.55830600
C	0.42027500	2.91365100	-0.50802800
C	7.32974600	-2.04868000	2.00275700
H	6.96661500	-2.00249800	2.85811600
C	4.35256500	-1.29201800	-0.10920700
C	8.45858400	-2.20314400	-0.53977700
H	8.84181000	-2.26189900	-1.38498600
C	0.02934000	2.57096400	-1.84991100
C	5.12401600	-1.49605500	0.99024700
H	4.73777800	-1.43916600	1.83415300
C	2.88986600	-0.96319800	0.03643900
C	-0.33888200	0.93672800	-3.40641800
H	-0.36891800	0.03760700	-3.64460700
C	0.47385400	4.26148500	-0.11222900
C	10.67506100	-2.83671000	0.38745300
C	4.93180200	-1.36025500	-1.40194100
H	4.40195800	-1.22701300	-2.15545400
C	-0.29890500	3.59120300	-2.75261000
C	-0.63665900	3.20017200	-4.04400200
H	-0.84989100	3.84154100	-4.68162100
C	6.27881400	-1.62398100	-1.54572000
H	6.65629600	-1.64863900	-2.39511600
C	-0.65456000	1.89216700	-4.37340900
H	-0.87674100	1.62835600	-5.23760200
C	1.18473300	3.50145200	2.02224900
H	1.44850000	3.67464800	2.89748700
C	-0.21960900	4.95935600	-2.29571700
H	-0.42318200	5.64583000	-2.88841000
C	0.13662700	5.26543900	-1.04716100
H	0.16420400	6.15701500	-0.78716000
C	0.88523900	4.51351200	1.20348700
H	0.95086100	5.39006700	1.50847200
C	1.10252200	2.18514600	1.56758700
H	1.31466900	1.49294000	2.15024700
O	-0.95417100	-0.84582600	0.36038200
O	-8.89947100	-6.36911600	-0.12964400
O	-1.09107400	-1.74901200	-1.65187600
O	-8.93226700	-5.23309400	1.76215500
C	-3.45146700	-1.85058600	1.13325100
H	-3.05128800	-1.20632900	1.67240800
C	-5.24581600	-3.39276100	0.72748300
C	-4.62209800	-3.81264900	-0.47618700
C	-2.81765100	-2.23311600	-0.07598500
C	-4.62231100	-2.40166700	1.52045600
H	-5.02118600	-2.12696100	2.31485500
C	-7.08963100	-4.90471300	0.27802600
C	-3.39434000	-3.18992000	-0.85301300
H	-2.98063000	-3.44356900	-1.64623400
C	-6.49462900	-3.98065300	1.07655800
H	-6.91165000	-3.72695900	1.86796500
C	-8.40421300	-5.52285100	0.67627400
C	-1.52837000	-1.58258000	-0.52355000
C	-6.45728500	-5.31248700	-0.92413600
H	-6.86803200	-5.94067100	-1.47453800

C	-5.23478000	-4.78020200	-1.28025300
H	-4.81650300	-5.06567500	-2.06007600
C	-2.42735300	3.28567300	1.85906600
C	-2.87230400	3.03039900	0.49670900
C	-2.42222400	4.66014600	2.08884100
C	-2.85994600	5.38266200	0.84721500
H	-2.15770100	5.96364500	0.51255800
H	-3.65711200	5.91120000	1.01033000
C	-3.13857400	4.25423200	-0.11307800
C	-2.06061800	2.39024600	2.85864200
H	-2.07042900	1.47311800	2.70746600
C	-1.66889300	4.26033500	4.31670900
H	-1.40159400	4.58321000	5.14709800
C	-2.05366200	5.15822100	3.31377700
H	-2.06017400	6.07512200	3.47445600
C	-3.59727700	4.31815700	-1.41733400
H	-3.75956400	5.13663400	-1.82622400
C	-3.07143000	1.84380900	-0.20870300
H	-2.88389500	1.01870900	0.17860600
C	-1.68227700	2.90399200	4.08243900
H	-1.42985800	2.32153400	4.76292600
C	-3.55528700	1.92922100	-1.50319800
H	-3.71243600	1.14670900	-1.97996700
C	-3.80867600	3.13007200	-2.09800400
H	-4.12758600	3.15148600	-2.97142100
H	-9.75837752	-5.71331542	1.85449966
H	12.06233267	-3.34066634	-0.62096686

Total electronic Energy = -2663.128687 (Hartree/Particle).

Table S8: Geometry of **1-CBZ (Carbazole)** (singlet) for single point calculation, directly obtained from single crystal X-ray Crystallographic structure, computed at the B3LYP-D3/ 6-311++G** (HCNO)/ LANL2DZ (Zn) level in the absence of any solvent.

Atom	x	y	z
Zn	0.42000200	0.00901200	0.61682000
O	-1.15561700	-0.44111400	-0.68437100
O	-0.89883500	-1.74967300	1.05196800
N	0.98603300	1.95419800	0.02044800
C	-4.51074700	-3.76386700	0.23633300
C	-3.28501800	-3.10598500	0.50066700
H	-2.77310000	-3.37387300	1.22981400
C	-2.83649500	-2.08405000	-0.29355300
C	-4.78355400	-2.28757700	-1.69996300
H	-5.27784200	-2.00680100	-2.43609400
C	-1.54272200	-1.39153100	0.04268100
C	0.47740300	2.91289500	0.81610200
C	-3.59850000	-1.67788700	-1.41467300
H	-3.28907500	-0.99104700	-1.96026000
C	1.80017100	2.31631600	-0.96827700
H	2.16195100	1.65966900	-1.51867600
C	0.74405200	4.28001000	0.62558100
C	2.12538100	3.64920000	-1.20210100
H	2.70159400	3.87187800	-1.89737500

C	1.60547700	4.61378300	-0.42169900
H	1.81957400	5.50421900	-0.58019800
C	0.15179000	5.23466600	1.49215500
H	0.33434800	6.13844000	1.37236600
O	-8.62889300	-6.66657900	0.02941600
O	-8.88561600	-5.35803400	-1.70684300
C	-5.27370500	-3.34384000	-0.89120700
C	-6.49949200	-4.00170800	-1.15562100
H	-7.01133000	-3.73379400	-1.88482300
C	-6.94801500	-5.02364300	-0.36140100
C	-5.00089800	-4.82013000	1.04508900
H	-4.50653000	-5.10088000	1.78116500
C	-8.24164900	-5.71615000	-0.69761000
C	-6.18593000	-5.42978000	0.75966500
H	-6.49535500	-6.11662100	1.30525100
N	-0.57051000	1.18159300	2.06733500
C	-0.37204500	2.50147300	1.89587500
C	-1.37978000	0.78371000	3.04626200
H	-1.52827100	-0.12634000	3.16733500
C	-0.95700900	3.47279700	2.72698900
C	-2.00984500	1.69038800	3.89359200
H	-2.57455000	1.38317700	4.56571000
C	-1.80083200	3.01033700	3.73895500
H	-2.21861900	3.61565800	4.30726400
C	-0.68157600	4.84567900	2.49802200
H	-1.07477200	5.48932600	3.04171100
O	2.14294300	-0.62375700	1.62142300
O	2.10221500	-0.90239800	-0.54971500
C	6.14878400	-2.08134900	-0.60881000
C	4.78272700	-1.70875100	-0.59093800
H	4.30518000	-1.69294700	-1.38905800
C	4.14921500	-1.37128000	0.57576200
C	6.17687400	-1.75987000	1.81996700
H	6.63471500	-1.77289300	2.62944600
C	2.70403300	-0.95087800	0.54434000
C	4.86082100	-1.40658000	1.79841500
H	4.42796200	-1.18766200	2.59210300
O	10.86405700	-3.56575500	-1.60378600
O	10.90478600	-3.28711300	0.56735100
C	6.85821700	-2.10816200	0.62644700
C	8.22427300	-2.48076000	0.60857400
H	8.70182000	-2.49656400	1.40669500
C	8.85778500	-2.81823100	-0.55812500
C	6.83012600	-2.42964200	-1.80233100
H	6.37228500	-2.41661900	-2.61181000
C	10.30296800	-3.23863400	-0.52670300
C	8.14618000	-2.78293200	-1.78077800
H	8.57903800	-3.00184900	-2.57446600
N	-1.96130900	2.33321200	-1.78131500
C	-1.37039900	3.45232200	-2.44494300
C	-0.51478800	5.87504500	-3.26141100
H	-0.20352200	6.70031200	-3.55746100
C	-1.80295300	4.55110200	-1.76286800
C	-0.12941100	4.71158100	-3.91709400
H	0.43497100	4.77273900	-4.65277800
C	-0.55741200	3.49199000	-3.50964400
H	-0.29741000	2.71504900	-3.95131100
C	-1.35674600	5.80357200	-2.17249600
H	-1.62054500	6.57392100	-1.72315900
C	-2.76556100	2.78118200	-0.68825500

C	-4.13963200	4.16724400	1.17159200
H	-4.62553000	4.62549600	1.81918900
C	-2.66772100	4.14133000	-0.69673100
C	-4.17750900	2.77847500	1.12805400
H	-4.68781900	2.32008600	1.75492100
C	-3.48824200	2.07829200	0.19461700
H	-3.51591400	1.14826800	0.16882300
C	-3.38267300	4.86315500	0.25373700
H	-3.35029500	5.79247700	0.26992500
H	-9.48519300	-6.06020600	-1.96964000
H	10.44103000	-2.74753800	1.21185800
H	-1.83115800	1.37696100	-2.04331700

Total electronic Energy = -2679.250524 (Hartree/Particle).

Table S9: Geometry of **1-DBF (Dibenzofuran)** (singlet) for single point calculation, directly obtained from single crystal X-ray Crystallographic structure, computed at the B3LYP-D3/ 6-311++G** (HCNO)/ LANL2DZ (Zn) level in the absence of any solvent.

Atom	x	y	z
O	-8.82899000	-6.44203000	-0.15531700
O	-1.08231300	-1.71809200	-1.69995200
O	-8.86376600	-5.31092700	1.74375700
O	-0.96703700	-0.81181400	0.31131500
C	-4.59344200	-3.81818300	-0.52289400
C	-6.46739500	-4.00174500	1.02970700
H	-6.88463500	-3.75208000	1.82288800
C	-3.36792100	-3.18059500	-0.89723000
H	-2.94747900	-3.43279400	-1.68812800
C	-7.05492800	-4.93124900	0.23708300
C	-5.22461900	-3.39702200	0.67919700
C	-2.80836200	-2.21924600	-0.12636800
C	-3.43976200	-1.83604700	1.08043900
H	-3.04215100	-1.19009800	1.61717000
C	-4.61791100	-2.39414000	1.46998400
H	-5.02420500	-2.11542900	2.25921700
C	-6.41311400	-5.32594900	-0.96506100
H	-6.81974500	-5.95573600	-1.51667000
C	-5.20225200	-4.79153100	-1.32547500
H	-4.78308800	-5.07682800	-2.10445700
C	-8.34811400	-5.57968400	0.65209300
C	-1.52211100	-1.54664200	-0.56851700
Zn	0.53674600	0.04510600	-0.58232400
O	2.22677500	-0.78894200	-1.02146500
N	0.71078000	1.90034100	0.36285200
O	11.13468900	-3.08475000	-0.71697900
O	2.38410400	-0.81874900	1.18347400
N	0.04721300	1.31615100	-2.17418900
O	11.35771200	-2.83030000	1.46591000
C	7.07166100	-1.84881800	-0.41872500
C	5.11249400	-1.51722400	0.99818000
H	4.72836000	-1.46770100	1.84408100
C	8.45811700	-2.18415400	-0.53678700
H	8.84440100	-2.22940200	-1.38212300

C	4.33687500	-1.30966100	-0.09395400
C	6.50350600	-1.80865300	0.88372300
C	9.21854700	-2.43671000	0.55389900
C	8.63835400	-2.36308200	1.84225000
H	9.16832700	-2.51732000	2.58975500
C	0.06204500	2.63131500	-1.80334200
C	0.40588500	2.93776100	-0.45272300
C	7.31962400	-2.07174500	2.00797600
H	6.95498100	-2.04483600	2.86353500
C	0.42411500	4.27311100	-0.00777000
C	4.92319200	-1.36840700	-1.38451800
H	4.39062100	-1.23728100	-2.13662900
C	6.26340800	-1.61644300	-1.53890100
H	6.63754700	-1.62909400	-2.38962600
C	2.87962700	-0.96626500	0.05980100
C	-0.25003000	1.02288900	-3.41854000
H	-0.26694900	0.12808400	-3.67202000
C	-0.54567400	2.00601000	-4.39199500
H	-0.73973200	1.76696600	-5.26908300
C	10.67856800	-2.81507200	0.38850800
C	-0.24252200	3.67706400	-2.69882600
C	1.05823700	2.16885100	1.61568500
H	1.26745100	1.46172900	2.18160500
C	0.80299100	4.48665700	1.32518900
H	0.83315200	5.35302700	1.66397700
C	-0.20595400	5.03389100	-2.19220200
H	-0.40312800	5.73452600	-2.77122300
C	-0.53716600	3.31824500	-4.00921000
H	-0.73169700	3.97845400	-4.63323400
C	1.12089500	3.45784300	2.11119500
H	1.38395700	3.60731100	2.99053900
C	0.09845400	5.31134600	-0.92568800
H	0.09909700	6.19609100	-0.63656300
O	-2.86953700	5.17353900	0.91672200
C	-2.88959600	2.91621300	0.46507400
C	-2.47213100	3.11264500	1.85792000
C	-2.13113900	2.29914600	2.89819000
H	-2.12446200	1.37543300	2.78771500
C	-2.48562500	4.47071900	2.05998800
C	-3.57459000	2.06628000	-1.63410300
H	-3.75262800	1.34438500	-2.19270400
C	-2.17835700	5.06626800	3.23461400
H	-2.20975700	5.99146500	3.33563400
C	-1.79579300	2.84954600	4.11079700
H	-1.55527800	2.30093900	4.82230300
C	-3.12730200	1.83328800	-0.35360200
H	-2.98839700	0.96516600	-0.04861500
C	-3.76232300	3.32618900	-2.10241500
H	-4.05361600	3.43940100	-2.97823200
C	-3.10793400	4.20007700	-0.02666200
C	-3.53829300	4.44494700	-1.32756500
H	-3.66520500	5.30682200	-1.65346600
C	-1.81827000	4.24410300	4.26895600
H	-1.58488000	4.61448600	5.08998500
H	12.06679456	-3.29932975	-0.63490967
H	-9.67752548	-5.81010448	1.84483323

Total electronic Energy = -2699.052613 (Hartree/Particle).

Table S10: Geometry of **1-DBT (Dibenzothiophene)** (singlet) for single point calculation, directly obtained from single crystal X-ray Crystallographic structure, computed at the B3LYP-D3/ 6-311++G** (HCNOS)/ LANL2DZ (Zn) level in the absence of any solvent.

Atom	x	y	z
Zn	0.68167900	0.06481800	0.58958600
O	-0.68903500	1.00821900	-0.43605800
O	2.48605400	0.66306300	1.00353400
O	-0.63018900	2.19328700	1.42329100
N	0.52558200	-1.93656600	0.01914000
N	-0.00841400	-0.78822600	2.37276800
O	2.62979600	0.33538900	-1.17627000
C	-4.87152800	3.73911400	-0.87066100
C	-2.96588600	3.55886600	0.65338500
H	-2.52042500	3.82979100	1.42360500
C	0.09777300	-2.74068400	1.03275900
C	-0.18788500	-2.12788600	2.29145700
C	7.33291900	1.57687400	0.31025600
C	-2.43135000	2.58176600	-0.10588500
C	-3.09183400	2.15048600	-1.26546100
H	-2.71974600	1.47205800	-1.78008800
C	-4.27812200	2.71548500	-1.64816700
H	-4.69837400	2.42478700	-2.42497700
C	-0.08575100	-4.12732800	0.87777400
C	-1.14975400	1.91497800	0.33709100
C	5.34769000	1.13029100	-1.08949300
H	4.94931700	1.03596600	-1.92497800
C	3.13501500	0.62018700	-0.10086000
C	4.59821400	0.97034600	0.02930100
C	-0.62940700	-2.88659600	3.36908300
C	5.20591100	1.10318300	1.28922100
H	4.68387300	0.99066300	2.05037800
C	0.76982000	-2.48878900	-1.16695100
H	1.05089900	-1.94356400	-1.86597300
C	6.53909300	1.39164100	1.44038300
H	6.90977400	1.46470800	2.29022000
C	-0.53010800	-4.89530000	2.00716200
H	-0.63753100	-5.81537500	1.92268700
C	-0.28525000	-0.19530900	3.53392700
H	-0.17407500	0.72638500	3.60078900
C	0.61547000	-3.86532000	-1.39852100
H	0.80436300	-4.22685400	-2.23388500
C	-0.79137700	-4.30021700	3.18643500
H	-1.08458600	-4.81866200	3.90115700
C	-0.91885400	-2.23817900	4.56773800
H	-1.23376000	-2.71552900	5.30035500
C	0.18896300	-4.65764500	-0.39024400
H	0.07581600	-5.56933500	-0.53914100
C	-0.73143900	-0.89383600	4.64651400
H	-0.90237400	-0.44364200	5.44255900
O	-8.37814600	6.91559800	-0.13218100
O	-8.43706300	5.73052100	-1.99160000
C	-4.19565400	4.18470300	0.30242200
C	-6.10136600	4.36494100	-1.22169400
H	-6.54675600	4.09402600	-1.99184400
C	-6.63590200	5.34204200	-0.46242400

C	-5.97534700	5.77333100	0.69722200
H	-6.34750600	6.45174900	1.21177900
C	-4.78913000	5.20832200	1.07985800
H	-4.36880700	5.49903000	1.85673800
C	-7.91749800	6.00882900	-0.90540000
O	11.59750400	2.36130000	-1.69779400
O	11.45385300	2.68907700	0.48204800
C	6.75071000	1.44749900	-1.00444600
C	8.73593900	1.89408200	0.39530300
H	9.13431200	1.98840700	1.23078800
C	10.94861400	2.40418500	-0.59332900
C	9.48541500	2.05402700	-0.72349100
C	8.87764700	1.92118000	-1.98348100
H	9.39975600	2.03371000	-2.74456800
C	7.54453600	1.63273200	-2.13457200
H	7.17378400	1.55965500	-2.98448000
S	-3.46947500	-5.40688500	-0.35024000
C	-2.99582800	-2.86977900	-0.81179500
C	-2.67451400	-3.55470300	-2.04099200
C	-2.88401000	-4.93464800	-1.92777300
C	-3.43096900	-3.75363900	0.16793700
C	-2.90498100	-1.51219400	-0.51313000
H	-2.60756600	-0.91279300	-1.15819700
C	-2.19358500	-3.06503500	-3.25349700
H	-2.05609000	-2.15228800	-3.36047200
C	-3.77666100	-3.29125600	1.43769300
H	-4.05525100	-3.88862000	2.09501200
C	-2.62657300	-5.79865500	-2.99065600
H	-2.78554300	-6.71057600	-2.91165600
C	-3.25124700	-1.06894900	0.72574100
H	-3.18584700	-0.16032200	0.91589000
C	-2.13628100	-5.26984500	-4.15226800
H	-1.94207400	-5.83500700	-4.86571600
C	-3.70181900	-1.93635800	1.71275200
H	-3.94930200	-1.61196400	2.54873500
C	-1.92433800	-3.91699400	-4.28048300
H	-1.59300300	-3.57865200	-5.08083200
H	-9.18849691	7.27170852	-0.50382292
H	12.51522058	2.59407347	-1.53900914

Total electronic Energy = -3022.092246 (Hartree/Particle).

Table S11: DFT-optimized geometry of **Fluorene** (singlet), computed at the B3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
H	-0.00003700	2.48870100	-0.88101300
C	3.01638800	-1.21395500	-0.00014300
C	3.46282200	0.11447800	-0.00014300
C	2.54533800	1.17427300	-0.00008900
C	1.18405400	0.88789400	-0.00003700
C	0.73420800	-0.44945500	-0.00003600
C	1.64882600	-1.50589900	-0.00008800
H	3.73971600	-2.02428200	-0.00018600

H	4.52838000	0.32477400	-0.00018300
H	2.89702900	2.20285500	-0.00009200
H	1.30662300	-2.53698900	-0.00008400
C	0.00000000	1.83364600	0.00002600
H	0.00003700	2.48867600	0.88108500
C	-1.18405400	0.88789400	0.00006000
C	-2.54533800	1.17427200	0.00011900
C	-3.46282200	0.11447800	0.00014800
C	-3.01638800	-1.21395500	0.00010400
C	-1.64882600	-1.50589800	0.00004800
C	-0.73420700	-0.44945500	0.00002700
H	-2.89702900	2.20285500	0.00014700
H	-4.52838000	0.32477500	0.00020100
H	-3.73971600	-2.02428200	0.00011800
H	-1.30662200	-2.53698900	0.00001900

Total electronic Energy = -501.471968 (Hartree/Particle).

Table S12: DFT-optimized geometry of mono cationic **Fluorene**$^{+}$ (doublet), computed at the UB3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
H	-0.00003700	2.52041800	-0.88099300
C	2.97694800	-1.24391200	-0.00014000
C	3.42758500	0.10239400	-0.00013800
C	2.53058100	1.18816100	-0.00008700
C	1.17654800	0.91954200	-0.00003800
C	0.71166000	-0.44186900	-0.00003800
C	1.62649600	-1.52842700	-0.00009000
H	3.70644800	-2.04671800	-0.00018000
H	4.49575700	0.29790000	-0.00017600
H	2.90593800	2.20642100	-0.00008800
H	1.27001500	-2.55304400	-0.00009100
C	0.00000000	1.86656500	0.00002400
H	0.00003700	2.52039800	0.88105400
C	-1.17654800	0.91954200	0.00006100
C	-2.53058100	1.18816100	0.00012300
C	-3.42758500	0.10239400	0.00014600
C	-2.97694800	-1.24391200	0.00010600
C	-1.62649600	-1.52842700	0.00004500
C	-0.71166000	-0.44186900	0.00002200
H	-2.90593800	2.20642100	0.00015400
H	-4.49575700	0.29790000	0.00019500
H	-3.70644800	-2.04671800	0.00012400
H	-1.27001500	-2.55304400	0.00001500

Total electronic Energy = -501.193797 (Hartree/Particle).

Table S13: DFT-optimized geometry of **Carbazole** (singlet), computed at the B3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
C	3.04405900	-1.15638100	-0.00013900
C	3.42990000	0.19802400	-0.00013900
C	2.48293700	1.22262400	-0.00008800
C	1.13388300	0.85761400	-0.00003700
C	0.72477100	-0.50347300	-0.00003600
C	1.69600100	-1.51249000	-0.00008800
H	3.80641700	-1.92934800	-0.00018000
H	4.48574200	0.45238200	-0.00017900
H	2.78578100	2.26573400	-0.00009100
H	1.40128000	-2.55799400	-0.00008700
C	-1.13388300	0.85761400	0.00006000
C	-2.48293700	1.22262300	0.00012200
C	-3.42990000	0.19802400	0.00014500
C	-3.04405900	-1.15638100	0.00011000
C	-1.69600100	-1.51249000	0.00004800
C	-0.72477000	-0.50347300	0.00002300
H	-2.78578100	2.26573400	0.00014800
H	-4.48574200	0.45238200	0.00019700
H	-3.80641700	-1.92934800	0.00012900
H	-1.40128000	-2.55799400	0.00001900
N	0.00000000	1.65754600	0.00002100
H	0.00000000	2.66462600	0.00002000

Total electronic Energy = -517.520771 (Hartree/Particle).

Table S14: DFT-optimized geometry of mono cationic **Carbazole**$^{+}$ (doublet), computed at the UB3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
C	3.06522500	-1.12412400	-0.00013200
C	3.44297200	0.22729500	-0.00012000
C	2.47954900	1.23709800	-0.00007600
C	1.13473900	0.83316900	-0.00004400
C	0.73262000	-0.53458100	-0.00005600
C	1.70415200	-1.51792900	-0.00010100
H	3.83386000	-1.89004100	-0.00016100
H	4.49476300	0.49070800	-0.00014900
H	2.75846700	2.28594300	-0.00007300
H	1.44251600	-2.57088500	-0.00010900
C	-1.13473900	0.83316900	0.00005800
C	-2.47954800	1.23709800	0.00013900
C	-3.44297200	0.22729500	0.00016500
C	-3.06522600	-1.12412300	0.00012300
C	-1.70415300	-1.51792900	0.00004000
C	-0.73262000	-0.53458100	0.00000800
H	-2.75846500	2.28594300	0.00017000
H	-4.49476300	0.49070900	0.00021900
H	-3.83386100	-1.89004000	0.00015000
H	-1.44251700	-2.57088400	0.00000600
N	0.00000100	1.61280000	-0.00000800
H	0.00000100	2.62780000	-0.00002500

Total electronic Energy = -517.250234 (Hartree/Particle).

Table S15: DFT-optimized geometry of **Dibenzofuran** (singlet), computed at the B3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
C	3.05907000	-1.11156600	-0.00013400
C	3.40260900	0.25269800	-0.00014200
C	2.42229500	1.24983000	-0.00009600
C	1.10116000	0.82320300	-0.00004200
C	0.72579500	-0.53472900	-0.00003400
C	1.72339300	-1.51694600	-0.00008300
H	3.84664300	-1.85885500	-0.00017300
H	4.44980000	0.53958900	-0.00018200
H	2.67234900	2.30497300	-0.00010200
H	1.46332200	-2.57118500	-0.00007700
C	-1.10116000	0.82320300	0.00006200
C	-2.42229500	1.24983000	0.00012200
C	-3.40260900	0.25269800	0.00014000
C	-3.05907000	-1.11156600	0.00011800
C	-1.72339300	-1.51694600	0.00005300
C	-0.72579400	-0.53472900	0.00002500
H	-2.67234900	2.30497300	0.00014300
H	-4.44980000	0.53958900	0.00019100
H	-3.84664300	-1.85885500	0.00013600
H	-1.46332100	-2.57118500	0.00002600
O	0.00000000	1.65263400	0.00001300

Total electronic Energy = -537.374115 (Hartree

Table S16: DFT-optimized geometry of mono cationic **Dibenzofuran**$^{+}$ (doublet), computed at the UB3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
C	3.02393200	-1.14176200	-0.00013300
C	3.37061400	0.24155300	-0.00012800
C	2.40714000	1.26704100	-0.00008100
C	1.09432100	0.85542200	-0.00003800
C	0.70427600	-0.52783300	-0.00004000
C	1.70537500	-1.54042300	-0.00008900
H	3.81810300	-1.88009800	-0.00017100
H	4.42136300	0.51497900	-0.00016300
H	2.68096600	2.31553400	-0.00008600
H	1.42980600	-2.58936300	-0.00008700
C	-1.09432100	0.85542200	0.00004800
C	-2.40713900	1.26704100	0.00011600
C	-3.37061400	0.24155300	0.00015600

C	-3.02393300	-1.14176200	0.00012100
C	-1.70537500	-1.54042300	0.00005700
C	-0.70427700	-0.52783300	0.00002000
H	-2.68096500	2.31553400	0.00013300
H	-4.42136300	0.51498000	0.00021000
H	-3.81810400	-1.88009700	0.00014700
H	-1.42980600	-2.58936200	0.00003600
O	0.00000000	1.67873900	-0.00000900

Total electronic Energy = -537.085272 (Hartree

Table S17: DFT-optimized geometry of **Dibenzothiophene** (singlet), computed at the B3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
C	-2.98361300	-1.44712600	0.00013100
C	-3.49590700	-0.13775100	0.00014300
C	-2.63940000	0.96188800	0.00010100
C	-1.25964700	0.73363200	0.00004600
C	-0.72707800	-0.57620900	0.00003400
C	-1.60955500	-1.66839000	0.00007700
H	-3.66643900	-2.29131300	0.00016400
H	-4.57020100	0.02087900	0.00018700
H	-3.03494900	1.97288300	0.00010800
H	-1.21805000	-2.68147400	0.00006900
C	1.25964700	0.73363200	-0.00005600
C	2.63940000	0.96188900	-0.00011400
C	3.49590700	-0.13775000	-0.00014200
C	2.98361400	-1.44712500	-0.00011300
C	1.60955500	-1.66839000	-0.00005500
C	0.72707800	-0.57620900	-0.00002500
H	3.03494900	1.97288300	-0.00013700
H	4.57020100	0.02088000	-0.00018500
H	3.66644000	-2.29131200	-0.00013900
H	1.21805200	-2.68147400	-0.00003400
S	-0.00000100	1.97284300	-0.00001300

Total electronic Energy = -860.352241 (Hartree

Table S18: DFT-optimized geometry of mono cationic **Dibenzothiophene**$^{+}$ (doublet), computed at the UB3LYP-D3/ 6-31+G** level in the absence of any solvent.

Atom	x	y	z
C	-3.01110300	-1.41067600	0.00013400
C	-3.51260700	-0.10251400	0.00014400
C	-2.63887800	0.98452300	0.00009900
C	-1.25712400	0.71787400	0.00004400

C	-0.73224500	-0.60265200	0.00003400
C	-1.62289800	-1.66735200	0.00007800
H	-3.70159400	-2.24788000	0.00017100
H	-4.58357800	0.06780200	0.00018700
H	-3.01266000	2.00329700	0.00010300
H	-1.26390100	-2.69146400	0.00007100
C	1.25712400	0.71787400	-0.00005400
C	2.63887600	0.98452400	-0.00011300
C	3.51260700	-0.10251200	-0.00014300
C	3.01110500	-1.41067400	-0.00011300
C	1.62290000	-1.66735100	-0.00005500
C	0.73224700	-0.60265100	-0.00002500
H	3.01265800	2.00329900	-0.00013500
H	4.58357900	0.06780600	-0.00018900
H	3.70159700	-2.24787700	-0.00013700
H	1.26390400	-2.69146300	-0.00003700
S	-0.00000200	1.91912400	-0.00001300

Total electronic Energy = -860.069632 (Hartree)

References

1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision A.03, *Gaussian, Inc., Wallingford CT,* **2016**.
2. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.
3. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.
4. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200-206.
5. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724.
6. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
7. Hariharan, P. C.; Pople, J. A. *Theor. Chem. Acc.* **1973**, *28*, 213-222.
8. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270.
9. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284.
10. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.
11. Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463-1476.
12. Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787-1799.
13. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104 (1-19).
14. Dennington, R.; Keith, T. A.; Millam, J. M. *GaussView, Version 6.0.16, Semichem Inc., Shawnee Mission, KS* **2016**.