Supporting Information for

Mechano-Responsive Room Temperature Luminescence Variations of Boron Conjugated Pyrene in Air

Vivek C. Wakchaure,[a,b] Kayaramkodath C. Ranjeesh,[a,b] Goudappagouda,[a,b] Tamal Das,[b,c] Kumar Vanka,[b,c] Rajesh Gonnade,[b,d] and Sukumaran S. Babu*[a,b]

[a]*Organic Chemistry Division, National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune-411008, India.*

[b]*Academy of Scientific and Innovative Research (AcSIR), New Delhi-110020, India.*

[c]*Physical and Materials Chemistry Division, National Chemical Laboratory (CSIR-NCL), Dr.Homi Bhabha Road, Pune-411008, India.*

[d]*Centre for Materials Characterization, National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune-411008, India.*

Supplementary Methods

All chemicals, pyrene, 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane), potassium acetate, bromine, $PdCl_2$(dppf) were purchased from commercial suppliers and used as such without further purification. Dry solvents such as 1,4-dioxane, DCM and THF were purified prior to use according to the standard protocol and stored in molecular sieves. All spectroscopic grade solvents were purchased from commercial suppliers and used as such without further purification.

All the reactions were carried out in oven dried round bottomed flasks and Teflon-sealed Schlenk tube under argon atmosphere unless otherwise mentioned. The ^{1}H, ^{13}C, ^{11}**B** NMR spectra were recorded at Bruker-400 MHz NMR spectrometer instrument. The chemical shift values for ^{1}H and ^{13}C NMR are recorded in $CDCl_3$ and TMS is used as internal standard for ^{1}H NMR. MALDI-TOF MS spectrum was recorded using DHB (2,5-dihydroxybenzoic acid) as the inert matrix on a AB SCIEX MALDI TOF/TOF™ 5800. FT-IR spectra were recorded using a Bruker Alpha FT-IR spectrometer and are reported in frequency of absorption (cm^{-1}). UV-Vis spectra were recorded with a Shimadzu 1800 spectrophotometer, while all emission spectra were performed using PTI Quanta Master™ steady state spectrofluorometer. Phosphorescence spectra and lifetime were recorded using a Fluorolog-3 HORIBA JOBIN VYON spectrophotometer. Fluorescence and phosphorescence lifetimes were measured by time correlated single photon counting (TCSPC), using a spectrofluorometer (Horiba scientific) with LED excitation source of 374, 355 nm, respectively. The quality of the fit was judged by the fitting parameters such as χ^2 (<1.2) as well as the visual inspection of the residuals. FEI Tecnai G2 F20 XTWIN TEM with accelerating voltage of 200 kV was used for the TEM imaging, TEM copper grid (200 mesh) was purchased from TED PELLA, INC.. The Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku, MicroMax-

007HF equipped with a high intensity Micro focus rotating anode X-ray generator. The data was collected with the help of Control Win software. A Rigaku, R-axis IV++ detector was used for the wide-angle experiments using Cu K (1.54 Å) radiation outfitted with a Ni filter and Aluminium holder was used as sample holder. Solid sample luminescence quantum yield was measured using a Quanta-Phi 6″ model F-3029.

Details of DFT Calculations

Ground (S_0) state calculations were performed using restricted density functional theory (DFT). Singlet and triplet excited states were investigated using time-dependent density functional theory (TDDFT)[S1]. The ground state singlet (S_0) state was calculated using B3LYP/6-31+G(d)[S2] level of theory. Also the TDDFT calculations were done with same level of theory. All the geometries of the complexes in the S_0 state were optimized. The optimized Cartesian coordinates and total energies are listed below. On the basis of the Frank-Condon principle, the absorption properties were evaluated using the optimized S_0 state structure. The Gaussian09 software[S3] was used in all the DFT and TDDFT calculations.

Preparation of Thin Film on Whatman Paper

For, compound **1**; 7.0 mg were dissolved in 10 ml DCM (C = 1 mM) and the resulting solution was used for coating on Whatman paper. The thin film coated paper was kept at RT for 10 min to get a dried blue emitting paper. Similar procedure was followed for compound **2** also (3.78 mg in 10 ml of ethyl acetate).

Phosphorescence Experiments

All phosphorescence experiments have done by keeping the same experimental parameters. The window of maximum delay after flash was kept 10 ms for 77K and 3 ms for RT phosphorescence measurements of **1**.

Anaerobic grinding/scratching experiments

The experiments under anaerobic condition (Ar) were conducted by thorough grinding of a fresh sample **1** and scratching the same sample with metal spatula in a glove box. The sample was completely flushed with Argon, kept under high vacuum for 4 h and again flushed with Argon (10 times) before transferring into glove box. All these preventive measures made sure that no oxygen contamination occurred while handling the sample prior to anaerobic exposure.

Figures and Tables

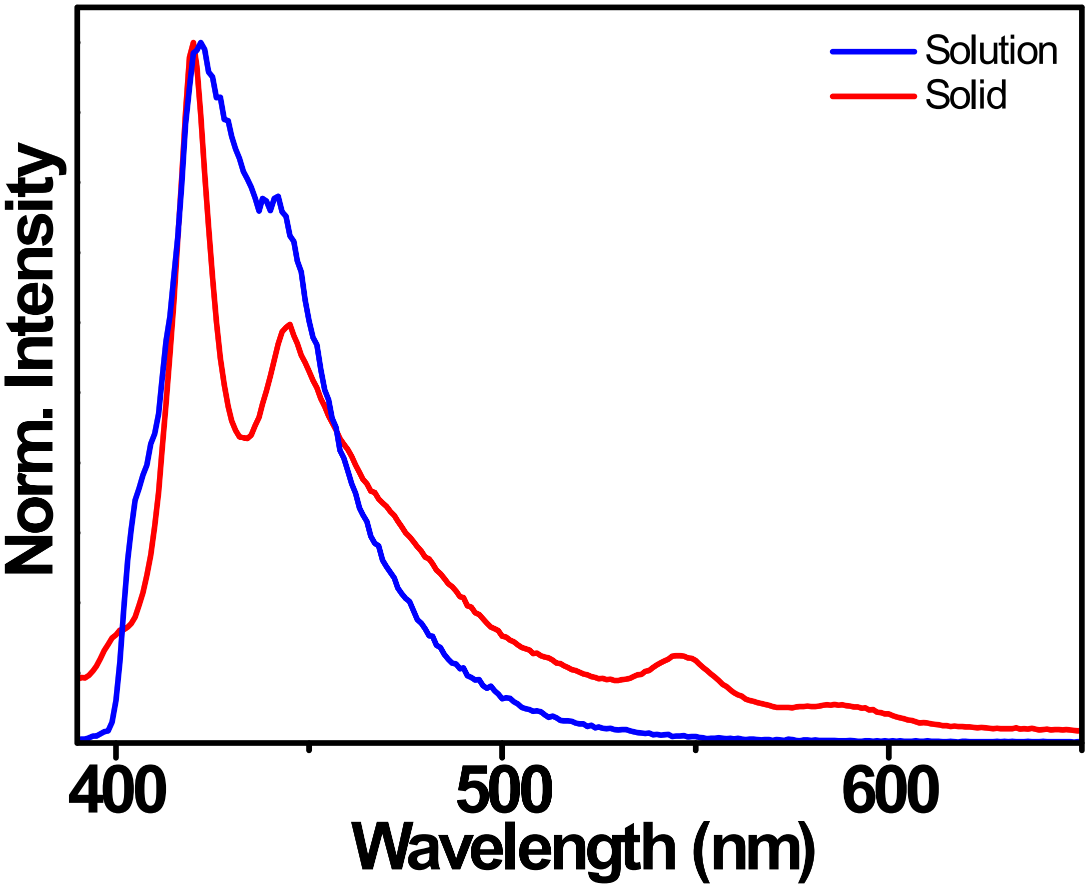


Figure S1. Normalized emission spectra of **1** in solution (—) and solid (—) at RT.

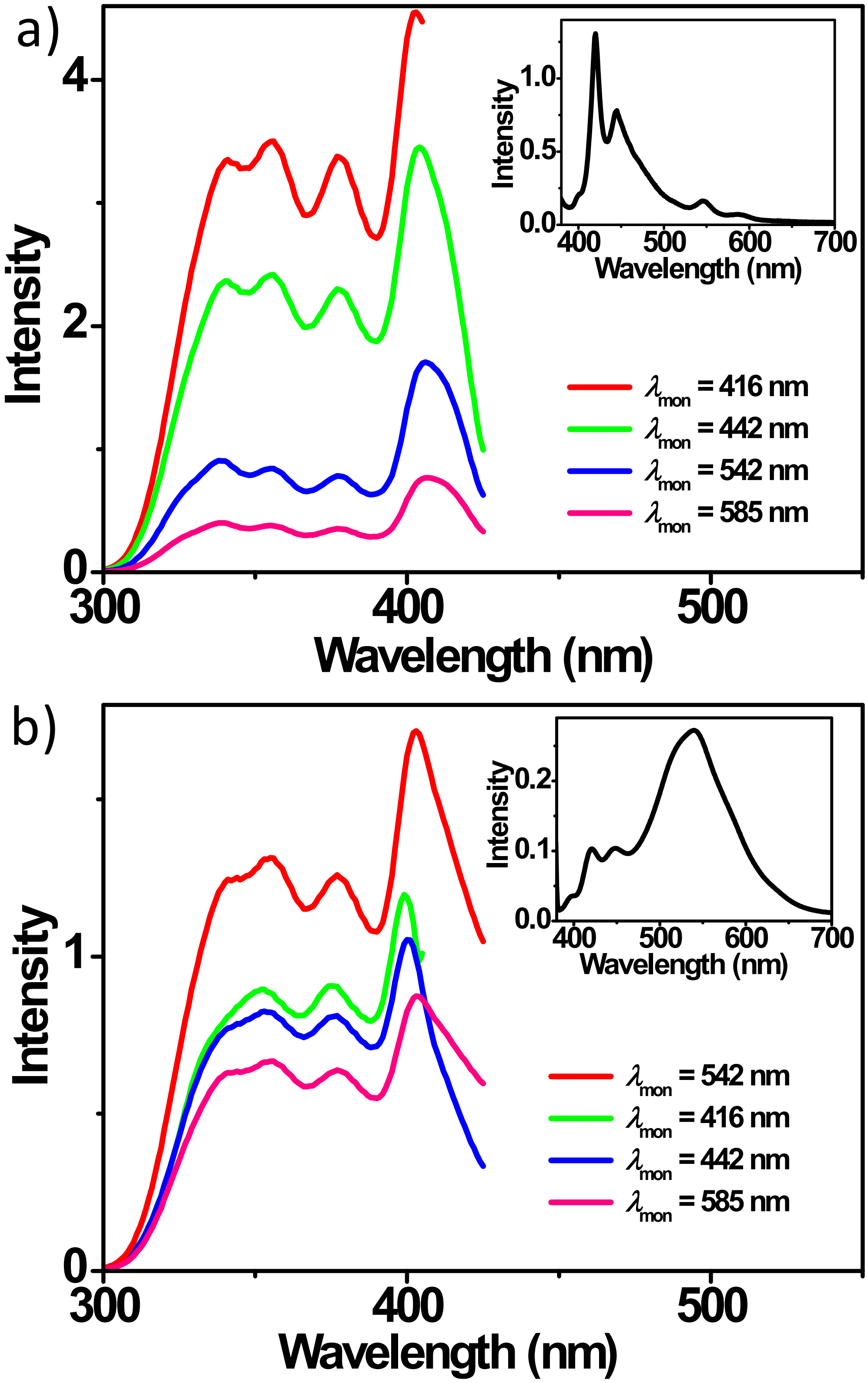


Figure S2. Excitation spectrum monitored at major emission peaks of **1** a) before and b) after grinding, insets show the corresponding emission spectra.

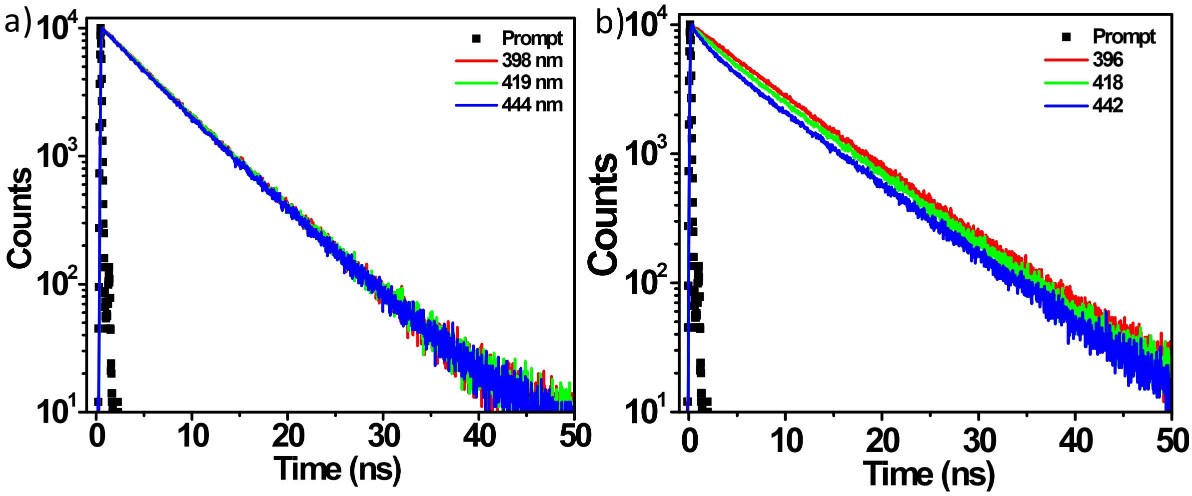


Figure S3. Fluorescence lifetime decay profile of a) **1** in DCM and b) **2** in EtOAc solution ($1x10^{-5}$ M, λ_{ex} = 374 nm).

Table S1. Comparison of the fluorescence lifetime (ns) decay profile of **1** in DCM and **2** in EtOAc solution.

1			**2**		
398 nm	419 nm	444 nm	396 nm	418 nm	442 nm
5.98 (100%)	3.24 (8.36%)	3.19 (9.65%)	4.07 (7.41%)	1.23 (3.52%)	1.41 (6.67%)
-	6.29 (91.64%)	6.29 (90.35%)	8.14 (92.59%)	7.81 (96.48%)	7.67 (93.33%)

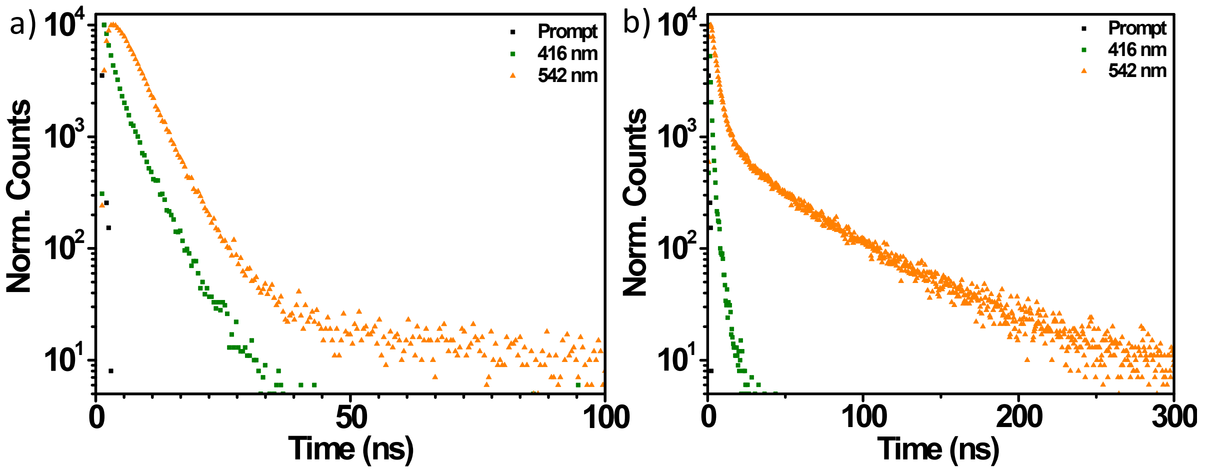


Figure S4. Fluorescence lifetime decay profile of **1** a) before and b) after grinding (λ_{ex} = 374 nm).

Table S2. Comparison of the fluorescence lifetime (ns) decay profile of solid **1** before and after grinding.

Before grinding		**After grinding**	
416 nm	542 nm	416 nm	542 nm
0.85 (30.36%)	4.74 (100%)	0.64 (70.70%)	28.1 (25.4%)
4.11 (69.64%)	-	3.30 (29.30%)	72.9 (24.9%)
-	-	-	3.75 (49.7%)

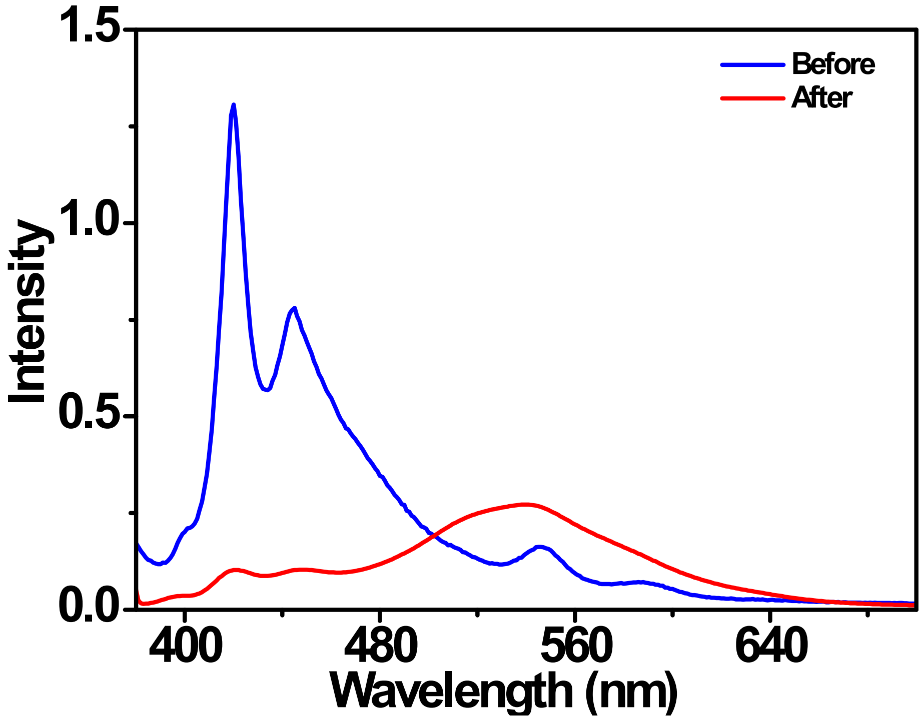


Figure S5. Emission spectral change of **1** before (—) and after (—) grinding.

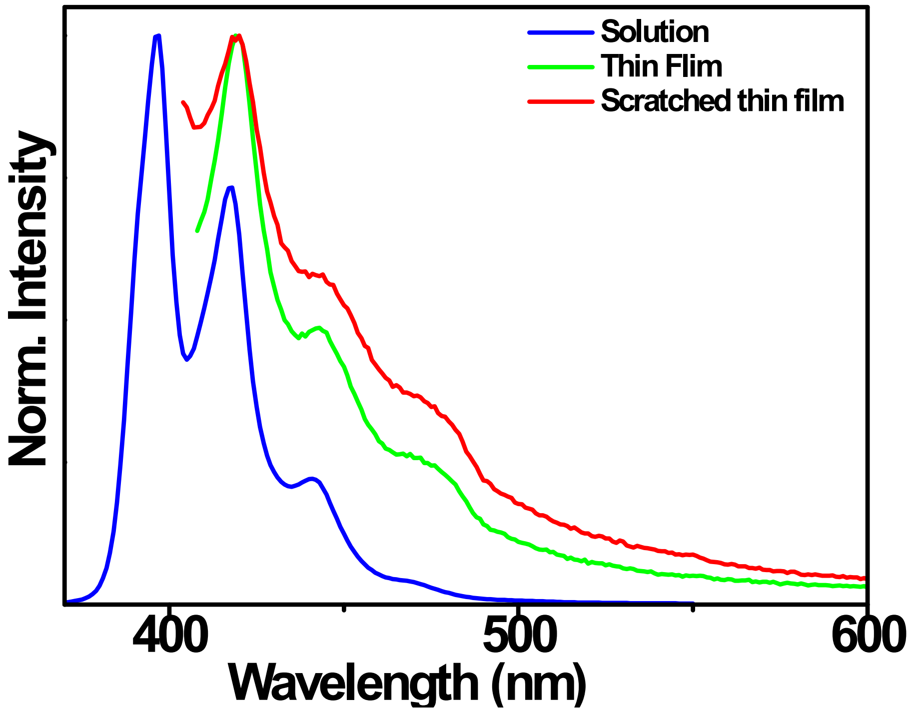


Figure S6. Normalized fluorescence spectrum of **2** in EtOAc solution (—, λ_{ex} = 364 nm), thin film (—, λ_{ex} = 368 nm) and thin film after scratching for 2 min (—, λ_{ex} = 368 nm).

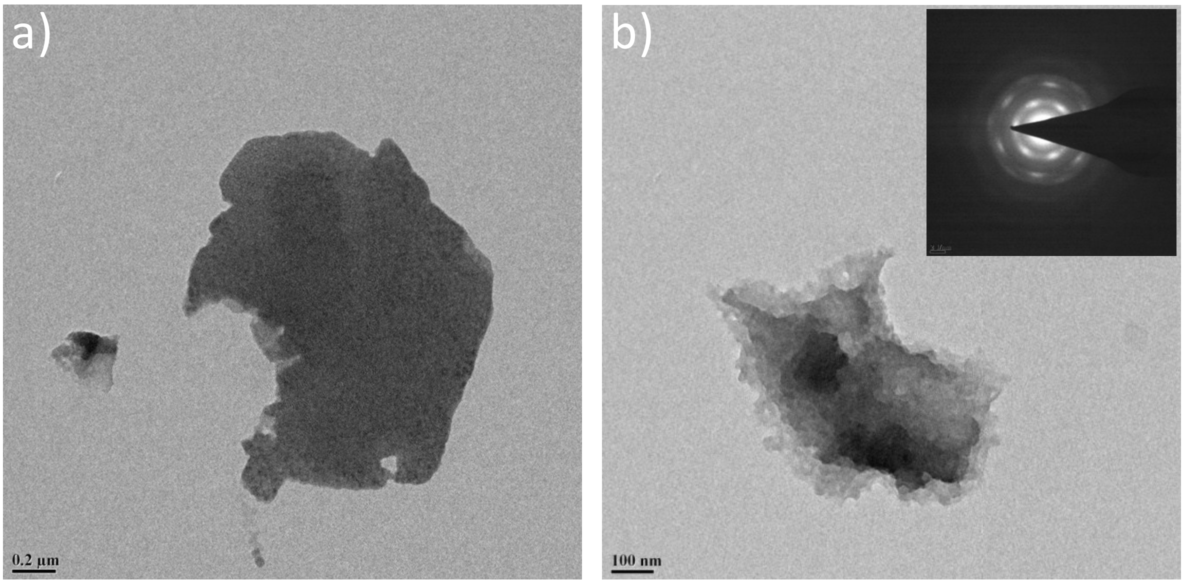


Figure S7. TEM image of the nanosheet assembly formed by **2**. Inset of b) shows the SAED pattern of the sheets.

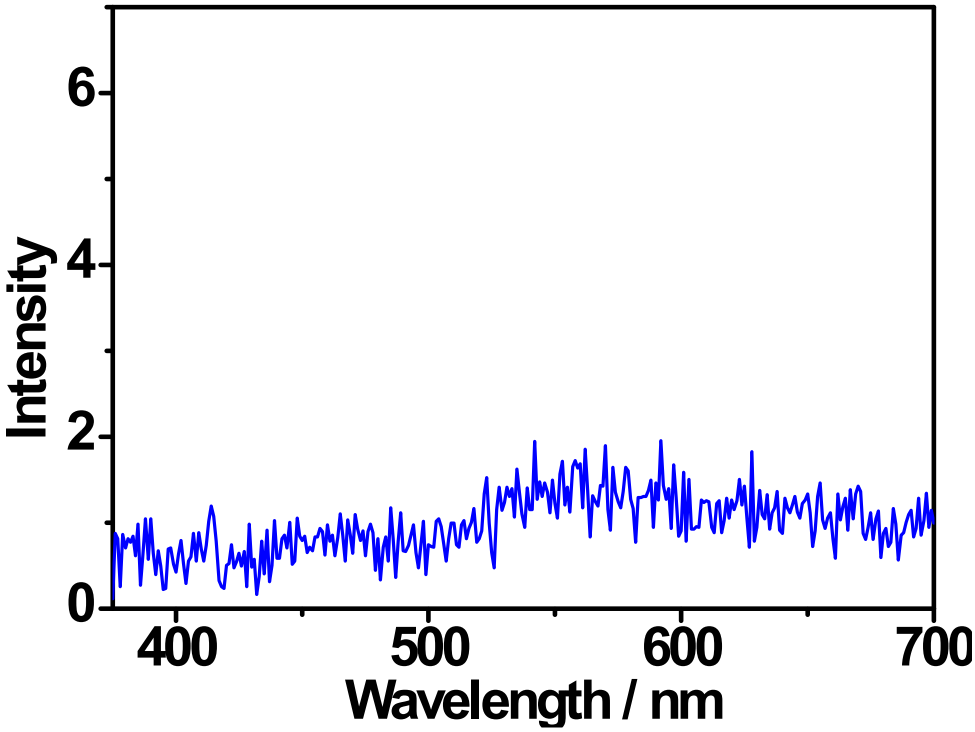


Figure S8. Phosphorescence spectrum of **2** (C = 1x10^{-3} M) in MTHF at 77K. Molecule **2** is not showing phosphorescence under similar conditions used for **1.**

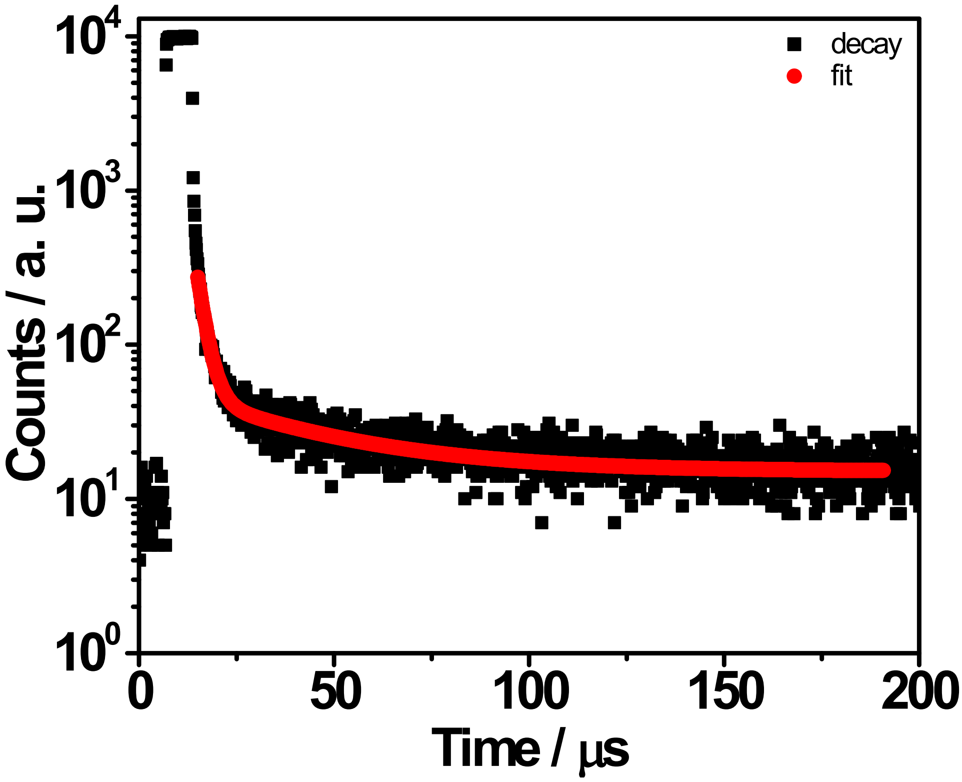


Figure S9. Phosphorescence lifetime decay profile of solid **1** at RT in air (λ_{ex} = 355 nm and λ_{mon} = 550 nm, data collected with 1% delay).

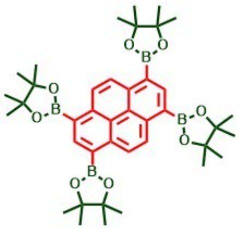
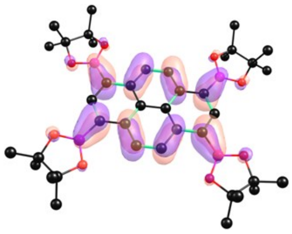
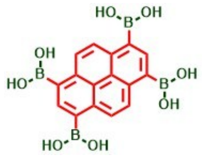
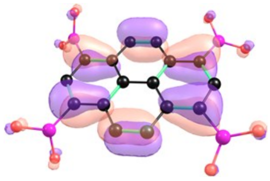
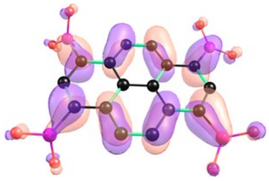
Chemical Structure	**HOMO**	**LUMO**	**Band Gap (eV)**
			**3.30**
			**3.40**

Figure S10. Chemical structure, corresponding HOMO-LUMO and energy band gap of **1** and **2**.

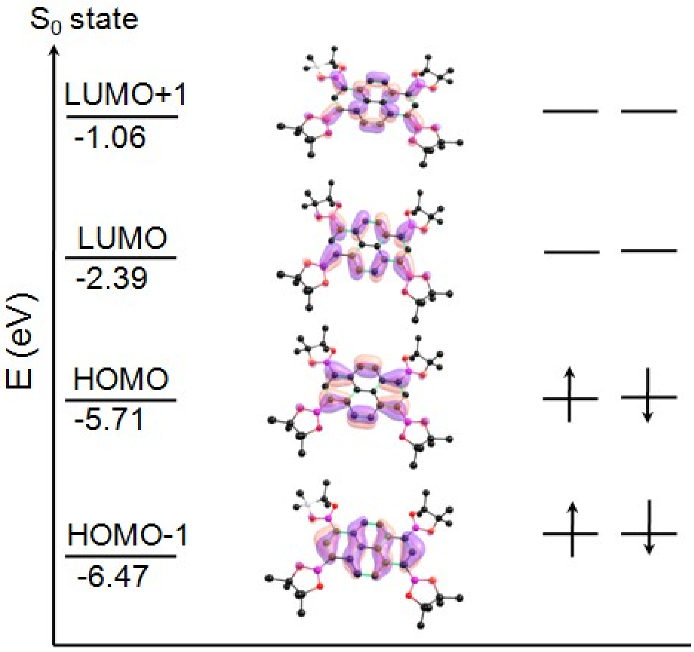


Figure S11. HOMO-LUMO profiles of **1** with corresponding energy and

*DFT calculation suggest that UV/Vis absorption of **1** originates from HOMO to LUMO electronic transition, where HOMO is located on the pyrene ring (π-type) and LUMO is a delocalized p-type orbital with significant B-C p-orbital overlap. π→π* excitation nature was observed in all of the selected excitations. On examining the relative computed energies for the singlet (S_n) and triplet (T_n) states of **1**, there is a triplet state (T_2) that is nearly degenerate with the singlet excited state (S_1). Thus it appears that **1** has energetically well-matched states to enable efficient singlet-triplet crossing to occur; once T_2 is populated, then relaxation through the triplet manifold to the T_1 state is possible, followed by emission.*

Table S3. π-π* Excitation properties of 1 calculated at the TD-B3LYP/6-31+G(d) level

	ΔE (eV)	λ (nm)	f	Configuration (orbital symmetry)	Coefficient
S_0 - S_1	3.0439	407.31	0.8564	HOMO (189) - LUMO (190)	0.69781
S_0 - S_2	3.4114	363.44	0.0495	HOMO–1 (188) - LUMO (190)	0.61975
S_0- S_3	3.8597	321.23	0.0000	HOMO–2 (187) - LUMO (190)	0.69895
S_0 - S_4	4.2279	293.25	0.5424	HOMO(189) - LUMO+1 (191)	0.61079
S_0 - T_1	1.8347	675.78	0.0000	HOMO (189) - LUMO (190)	0.69401
S_0 -T_2	2.9679	417.75	0.0000	HOMO–1 (188) - LUMO (190)	0.69853
S_0- T_3	3.2708	379.07	0.0000	HOMO–2 (187) - LUMO (190)	0.62120
S_0 -T_4	3.5061	353.62	0.0000	HOMO-3(186) - LUMO (191)	0.49103

*The excitation properties are calculated using the ground state singlet optimized geometries of **1**, where the vertical excitation approach is used on the basis of the Frank Condon principle.*

Optimized Cartesian coordinates of 1 (S_0 state) at the B3LYP/6-31+G(d) level of theory.

O	-3.378419	-3.818925	-0.143868
O	-5.149104	2.394406	-0.114937
O	-3.378579	3.818849	0.144048
O	-5.149039	-2.394581	0.114884
C	-4.429141	-5.122620	1.582964
H	-3.476770	-5.642929	1.729217
H	-5.238584	-5.809857	1.850829
H	-4.458181	-4.268081	2.266847
C	-4.536266	-4.679148	0.118369
C	-2.864368	-1.239631	-0.008706
C	-1.440992	-1.240356	-0.008576
C	-0.720014	-0.000012	0.000004
C	-4.429267	5.122568	-1.582849
H	-3.476903	5.642909	-1.729018
H	-5.238708	5.809799	-1.850749
H	-4.458258	4.268047	-2.266756
C	-4.536477	4.679021	-0.118269
C	-5.743081	3.701614	0.159876
C	-6.951581	3.886655	-0.755508
H	-6.689244	3.754333	-1.808110
H	-7.384669	4.885225	-0.626176
H	-7.720592	3.149494	-0.500938
C	-2.864395	1.239561	0.008758

C	-1.441024	1.240312	0.008593
C	0.681784	2.459285	0.012851
H	1.218216	3.400520	0.017398
C	-0.681850	2.459264	0.012846
H	-1.218306	3.400487	0.017359
C	-3.521530	-0.000046	0.000036
H	-4.606968	-0.000057	0.000050
C	-4.456666	-5.891590	-0.806050
H	-4.382021	-5.599042	-1.856203
H	-5.340350	-6.528151	-0.683020
H	-3.573379	-6.488446	-0.554537
C	-5.742923	-3.701786	-0.159967
C	-6.951547	-3.886845	0.755268
H	-6.689403	-3.754621	1.807928
H	-7.384681	-4.885369	0.625749
H	-7.720470	-3.149607	0.500637
C	-6.190817	-3.682928	-1.627652
H	-6.891442	-2.854487	-1.775241
H	-6.698720	-4.613647	-1.901828
H	-5.344163	-3.536295	-2.306385
C	-6.191118	3.682738	1.627530
H	-6.891647	2.854209	1.775068
H	-6.699166	4.613405	1.901624
H	-5.344512	3.536244	2.306355
C	-4.457048	5.891393	0.806227
H	-4.382567	5.598794	1.856376
H	-5.340715	6.527962	0.683091
H	-3.573728	6.488276	0.554887
B	-3.780680	-2.508143	-0.012936
B	-3.780751	2.508039	0.013013
O	3.378419	3.818925	0.143868
O	5.149105	-2.394405	0.114926
O	3.378579	-3.818849	-0.144037
O	5.149039	2.394582	-0.114890
C	4.429140	5.122623	-1.582963
H	3.476769	5.642932	-1.729213
H	5.238583	5.809860	-1.850827
H	4.458179	4.268085	-2.266847
C	4.536266	4.679148	-0.118368
C	2.864369	1.239631	0.008703
C	1.440992	1.240356	0.008573
C	0.720015	0.000012	-0.000007
C	4.429274	-5.122557	1.582864
H	3.476911	-5.642897	1.729041
H	5.238716	-5.809786	1.850764
H	4.458268	-4.268032	2.266764
C	4.536478	-4.679020	0.118279
C	5.743080	-3.701616	-0.159880
C	6.951585	-3.886648	0.755499
H	6.689254	-3.754319	1.808102

H	7.384674	-4.885219	0.626172
H	7.720594	-3.149489	0.500920
C	2.864395	-1.239561	-0.008761
C	1.441024	-1.240312	-0.008595
C	-0.681784	-2.459285	-0.012854
H	-1.218216	-3.400520	-0.017400
C	0.681851	-2.459264	-0.012848
H	1.218307	-3.400487	-0.017361
C	3.521530	0.000047	-0.000040
H	4.606968	0.000058	-0.000054
C	4.456667	5.891589	0.806054
H	4.382022	5.599039	1.856205
H	5.340351	6.528150	0.683024
H	3.573380	6.488445	0.554542
C	5.742923	3.701786	0.159965
C	6.951547	3.886847	-0.755269
H	6.689403	3.754625	-1.807930
H	7.384681	4.885371	-0.625749
H	7.720470	3.149609	-0.500640
C	6.190817	3.682924	1.627650
H	6.891442	2.854482	1.775237
H	6.698721	4.613642	1.901828
H	5.344163	3.536290	2.306383
C	6.191109	-3.682751	-1.627536
H	6.891640	-2.854224	-1.775084
H	6.699154	-4.613420	-1.901626
H	5.344501	-3.536259	-2.306357
C	4.457043	-5.891399	-0.806207
H	4.382556	-5.598807	-1.856358
H	5.340711	-6.527967	-0.683072
H	3.573724	-6.488280	-0.554858
B	3.780680	2.508143	0.012932
B	3.780751	-2.508039	-0.013013

Table S4. π-π^* Excitation properties of 2 calculated at the TD-B3LYP/6-31+G(d) level

	ΔE (eV)	λ (nm)	f	Configuration (orbital symmetry)	Coefficient
S_0 - S_1	3.196	387.91	0.6488	HOMO (97) - LUMO (98)	0.69501
S_0 - S_2	3.519	352.30	0.0191	HOMO–1 (96) - LUMO (98)	0.58420
S_0- S_3	4.055	305.73	0.0000	HOMO–2 (95) - LUMO (98)	0.68317
S_0 - S_4	4.279	289.72	0.1688	HOMO(97) - LUMO+2 (100)	0.52057
S_0 - T_1	1.9156	647.25	0.0000	HOMO (97) - LUMO (98)	0.69176
S_0 -T_2	3.1238	396.90	0.0000	HOMO–1 (96) - LUMO (98)	0.69169
S_0- T_3	3.3815	366.65	0.0000	HOMO–2 (95) - LUMO (98)	0.57228
S_0 -T_4	3.5285	351.38	0.0000	HOMO (97) - LUMO+1 (99)	0.68907

The excitation properties are calculated using the ground state singlet optimized geometries of ***2****, where the vertical excitation approach is used on the basis of the Frank Condon principle.*

Optimized Cartesian coordinates of 2 (S_0 state) at the B3LYP/6-31+G(d) level of theory.

O	-3.593810	-3.546779	-0.925422
O	-4.752267	2.771558	-0.907524
O	-3.593873	3.546695	0.925433
O	-4.752187	-2.771683	0.907561
C	-2.864746	-1.235243	0.028593
C	-1.445274	-1.234405	0.045365
C	-0.720362	-0.000008	-0.000001
C	-2.864783	1.235162	-0.028569
C	-1.445313	1.234366	-0.045358
C	0.671675	2.457530	-0.142376
H	1.202508	3.398067	-0.209731
C	-0.690925	2.452760	-0.133901
H	-1.222374	3.397498	-0.209915
C	-3.530501	-0.000051	0.000017
H	-4.620224	-0.000067	0.000024
B	-3.738039	-2.551207	0.009162
B	-3.738115	2.551099	-0.009125
O	3.304262	3.769392	0.166359
O	5.114384	-2.289532	0.426996
O	3.304411	-3.769277	-0.166426
O	5.114300	2.289718	-0.427049
C	2.860068	1.241515	-0.059605
C	1.436822	1.242342	-0.060819

C	0.718766	0.000014	-0.000009
C	2.860111	-1.241417	0.059565
C	1.436863	-1.242291	0.060794
C	-0.690848	-2.452775	0.133903
H	-1.222266	-3.397529	0.209929
C	0.671753	-2.457503	0.142364
H	1.202615	-3.398023	0.209717
C	3.511683	0.000060	-0.000022
H	4.595851	0.000078	-0.000028
B	3.791220	2.512001	-0.112402
B	3.791313	-2.511868	0.112356
H	-4.804514	2.096046	-1.599381
H	-2.928883	3.349127	1.600900
H	3.952378	4.489148	0.113582
H	5.685294	3.072772	-0.424445
H	5.685413	-3.072562	0.424380
H	3.952559	-4.489004	-0.113659
H	-2.928843	-3.349186	-1.600906
H	-4.804443	-2.096174	1.599420

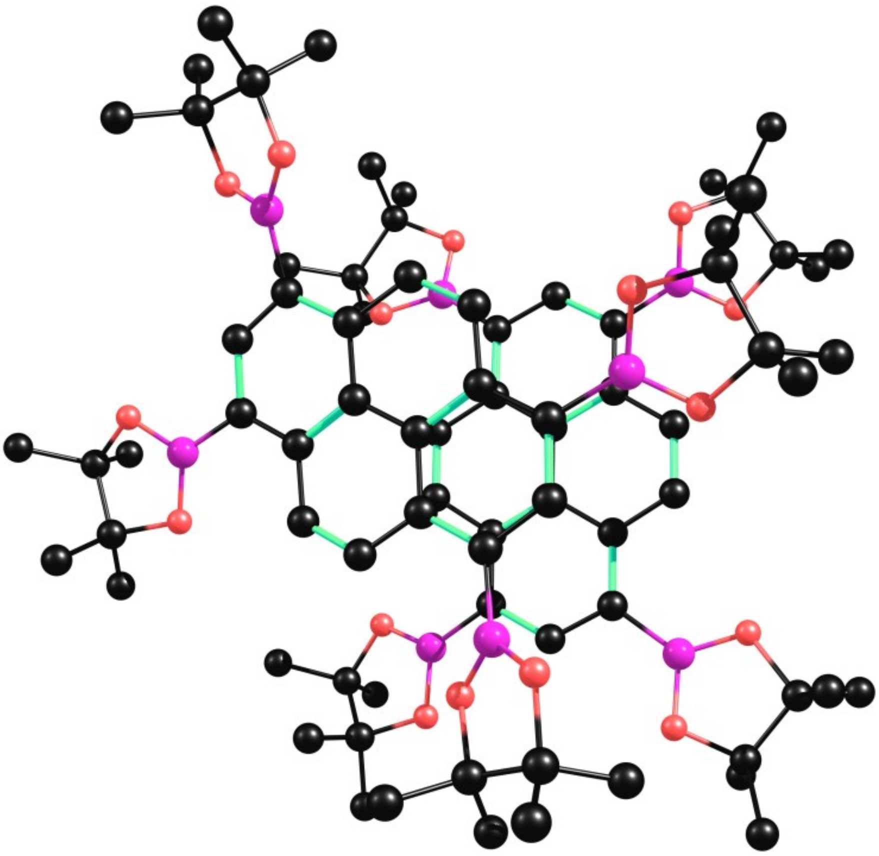


Figure S12. Energy minimized structure of the dimer formed by **1**.

DFT calculation suggests that a displaced dimer formed upon mechanical grinding is stabilized by 19.4 kcal, when compared to the monomer. The relative energies for the singlet (S_n) *and triplet* (T_n) *states for dimer* ***1*** *indicate that the triplet state* (T_3) *is nearly degenerate with the singlet excited state* (S_1)*. The presence of a partial π-overlap in dimer decreases the singlet excited states and thereby exists a smaller energy gap* (ΔE_{ST}) *of 0.02 eV between the singlet* (S_1) *and triplet* (T_3) *excited states. A reduced* ΔE_{ST} *and spin-orbit coupling between singlet* (S_n) *and triplet* (T_n) *states are the two supporting factors that control intersystem crossing.*

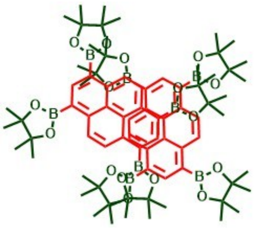
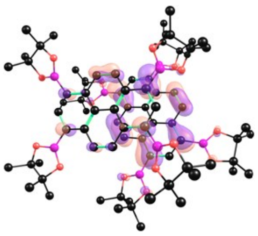
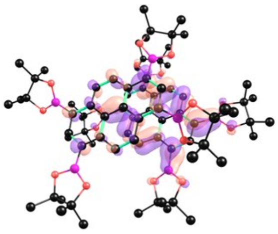
Chemical Structure	**HOMO**	**LUMO**	**Band Gap (ev)**
			**3.25**

Figure S13. Chemical structure, corresponding HOMO-LUMO and energy band gap of dimer formed by **1**.

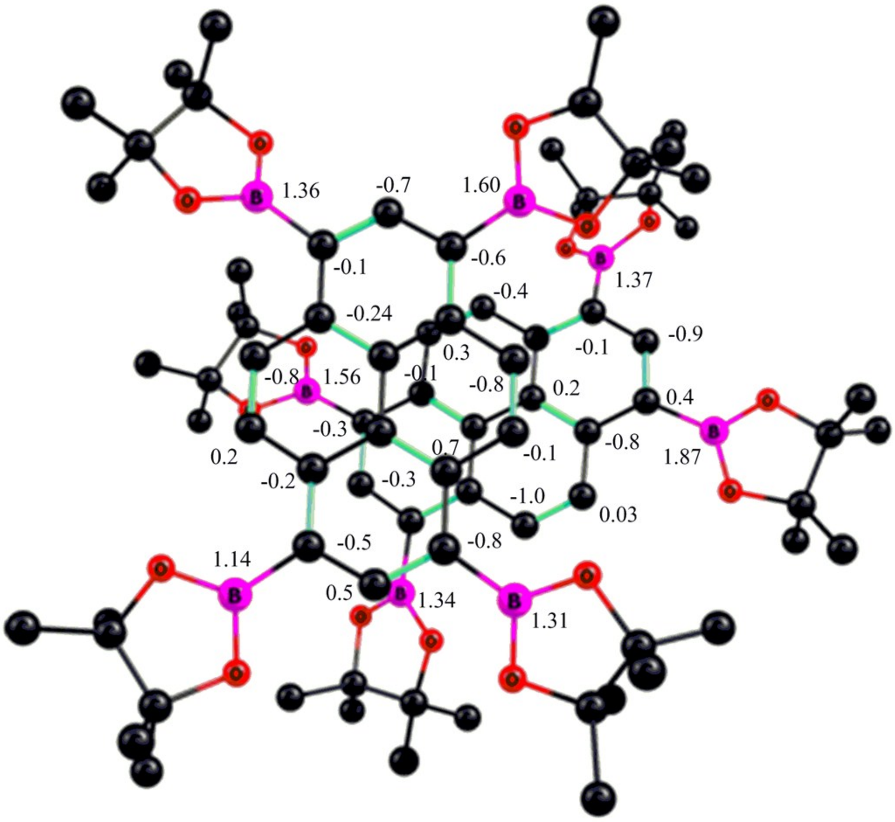


Figure S14. Natural Bond Orbital charge analysis for each atom in the stacked dimer of **1** with B3LYP/6-31+G(d) level of theory.

Natural Bond Orbital (NBO) charge analysis shows that there has been significant charge transfer between the two stacked rings in the dimer. The ring (upper ring in Figure S12) with higher net NBO charge (-3.57 a.u) is able to transfer the charge to the below ring with relatively less net charge (-2.63 a.u). The boron centres have dragged the electron density towards itself due to the high positive charge density (~1.54 a.u) on them.

Table S5. π-π* Excitation properties of **1** dimer calculated at the TD-B3LYP/6-31+G(d) level.

	ΔE (eV)	λ (nm)	f	Configuration (orbital symmetry)	Coefficient
S_0 - S_1	2.7709	447.45	0.0045	HOMO(378) - LUMO+1 (380)	0.54316
S_0 - S_2	2.7974	443.22	0.0057	HOMO-1 (377) - LUMO (379)	0.50624
S_0- S_3	3.0549	405.85	0.4032	HOMO (378) - LUMO (379)	0.49513
S_0 - S_4	3.1380	395.11	0.9314	HOMO-1 (377) - LUMO (379)	0.43644
S_0 - T_1	1.8436	672.51	0.0000	HOMO (378) - LUMO (379)	0.54523
S_0 -T_2	1.8677	663.85	0.0000	HOMO-1(377)- LUMO-1 (380)	0.47234
S_0- T_3	2.7503	450.81	0.0000	HOMO(378) - LUMO+1 (380)	0.48577
S_0 -T_4	2.7890	444.55	0.0000	HOMO-1(377) - LUMO(379)	0.54221

Optimized Cartesian coordinates of **1** dimer (S_0 state) at the B3LYP/6-31+G(d) level of theory.

O	2.85554200	-2.77866100	0.56616700
O	5.26550100	2.84995600	-0.88398500
O	3.65176300	4.37843800	-1.51185100
O	4.75917500	-2.10249600	-0.55339400
C	3.48971100	-5.00472700	-0.11021900
H	2.46259300	-5.32533800	0.11234800
H	4.16133300	-5.85935100	0.05237100
H	3.53741300	-4.71843600	-1.16856800
C	3.85352400	-3.83489300	0.80498400
C	2.69296100	-0.56925500	-0.79753300
C	1.28876900	-0.47381700	-0.99459400
C	0.67700200	0.81049900	-1.16915100
C	4.65934300	5.71364500	0.22041300
H	3.73217300	6.30281100	0.24115100
H	5.49216300	6.36791000	0.51411700
H	4.56909800	4.90417700	0.95883600
C	4.86062500	5.15869000	-1.19156500
C	5.98778700	4.06789300	-1.27368900
C	7.14937700	4.27626200	-0.31253700
H	6.81302700	4.27962900	0.73160300
H	7.65515000	5.23025600	-0.52245200
H	7.88293700	3.46735100	-0.43827100
C	2.90915600	1.87631100	-1.11323100
C	1.49181400	1.99304800	-1.19528500
C	-0.53248800	3.35944500	-1.33580000
H	-1.01040100	4.33678000	-1.41087000
C	0.83103100	3.26096500	-1.30206700
H	1.44466900	4.16115100	-1.34673800

C	3.45904000	0.59872100	-0.90555300
H	4.54256500	0.51715000	-0.79442600
C	3.76172800	-4.26013900	2.26482500
H	3.85991700	-3.40452500	2.94420900
H	4.55042200	-4.98954600	2.50075100
H	2.78907900	-4.73784800	2.44901000
C	5.20384800	-3.12012300	0.41229100
C	6.22814200	-4.01942800	-0.26395200
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H	6.66428700	-1.73869900	1.18354800
H	6.25464200	-3.04307400	2.32679100
H	5.11711300	-1.69155000	2.06335700
C	6.49941900	3.83825700	-2.69829600
H	7.12068800	2.93207400	-2.71059100
H	7.11122200	4.68303400	-3.04437300
H	5.66713400	3.69384600	-3.40208900
C	5.00214800	6.29310800	-2.19530600
H	4.96851500	5.92638500	-3.22812800
H	5.95436700	6.82062200	-2.03875000
H	4.18694900	7.01678800	-2.05872200
B	3.42263900	-1.85170000	-0.29351100
B	3.92360700	3.06045400	-1.17705500
O	-3.22010900	4.86785200	-1.69755200
O	-5.17217000	-1.28119700	-2.09697900
O	-3.74282000	-2.61018500	-0.86139100
O	-4.77467500	3.67262200	-0.47799900
C	-3.40617100	6.55850200	-0.00211800
H	-2.47674400	6.99977300	-0.38697900
H	-4.01134900	7.36148500	0.44158700
H	-3.14132200	5.83929800	0.78540400
C	-4.14371200	5.87177700	-1.15361100
C	-2.79335100	2.30035600	-1.33044100
C	-1.37518300	2.20064900	-1.32200400
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C	-4.22136300	-4.27927200	-2.51773300
H	-3.31198400	-4.80208900	-2.19111400
H	-4.93306900	-5.02854000	-2.89018700
H	-3.94347800	-3.60621500	-3.34097200
C	-4.80930800	-3.50380000	-1.33947200
C	-5.93801300	-2.48654900	-1.76032100
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C	-2.97142700	-0.16341800	-1.39081600
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C	-4.46393800	6.86893200	-2.26067100
H	-4.88121800	6.36842100	-3.14308600
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H	-3.54064400	7.37826100	-2.56783600
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C	-5.99855900	5.44703300	0.63989300
H	-5.27373100	5.42430500	1.46277900
H	-6.39475500	6.46899600	0.54827900
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H	-7.17551000	4.07822100	-1.40359000
H	-6.99468700	5.77692300	-1.90944600
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O	-6.04661100	4.35982200	-5.17094800
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C	-4.04745100	2.74503200	-5.13756300
C	-3.49407000	1.43202300	-5.14744400
C	-2.07738200	1.25345500	-5.00421700
C	0.73140800	6.93630700	-6.48406500
H	1.44847000	6.29761000	-7.01792300
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C	-0.44967500	7.19877300	-4.19424100
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H	0.81333700	3.02937300	-4.43340300
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C	-8.27121100	5.33436500	-4.98268300
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H	-9.28320600	5.35902800	-5.41280800
H	-7.86789200	6.35649100	-4.99633000
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H	2.18044700	6.29832400	-3.39907000
H	2.34936700	7.82514900	-4.31511500
H	2.87217600	6.28253600	-5.03304300
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B	-0.95713200	5.01984000	-4.70255300
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O	-2.18066100	-5.04012700	-5.52171800
O	-3.58172000	-3.74327900	-6.82177200
O	2.50711400	-3.05922500	-5.41812400
C	4.62422300	-0.92066300	-6.32805000
H	4.65325200	0.17092100	-6.20618200
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C	-4.06237000	-5.12592200	-6.98250600
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C	-3.24115000	-7.22158400	-5.65876000

H	-3.84502000	-6.97064900	-4.77798200
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H	-2.33645600	-7.74547500	-5.31921500
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C	-4.30514700	0.26374700	-5.31640300
H	-5.38521000	0.38516800	-5.37878200
C	-3.75660000	-0.98515300	-5.39577600
H	-4.40466400	-1.84976600	-5.54185200
C	-0.38281100	-2.62555800	-5.25631300
H	0.05768800	-3.62030500	-5.36035200
C	5.34969600	-1.21134800	-3.94185800
H	5.06799700	-1.54157900	-2.93535800
H	6.31017400	-1.67584200	-4.21158500
H	5.49192300	-0.12135000	-3.91623500
C	3.93978300	-3.08762900	-5.08597700
C	4.68100000	-3.83982500	-6.18191700
H	4.47644500	-3.41607800	-7.17270600
H	5.76550100	-3.80517800	-6.00204600
H	4.36903000	-4.89385400	-6.18405600
C	4.06223400	-3.81866600	-3.74967500
H	3.60795300	-4.81493100	-3.84143900
H	5.11398800	-3.93754200	-3.45565000
H	3.54227100	-3.26612400	-2.95521400
C	-1.82123900	-6.32337600	-7.52235800
H	-0.92983400	-6.74917800	-7.04165200
H	-2.21965200	-7.06391300	-8.23011500
H	-1.51479200	-5.42960500	-8.08384800
C	-4.39156500	-5.35124000	-8.45245200
H	-3.54051000	-5.11031800	-9.10098700
H	-4.67998300	-6.39865800	-8.62403000
H	-5.23862700	-4.71288200	-8.74123200
B	2.00913700	-1.84328300	-4.96536600
B	-2.54605000	-3.76071100	-5.90112300

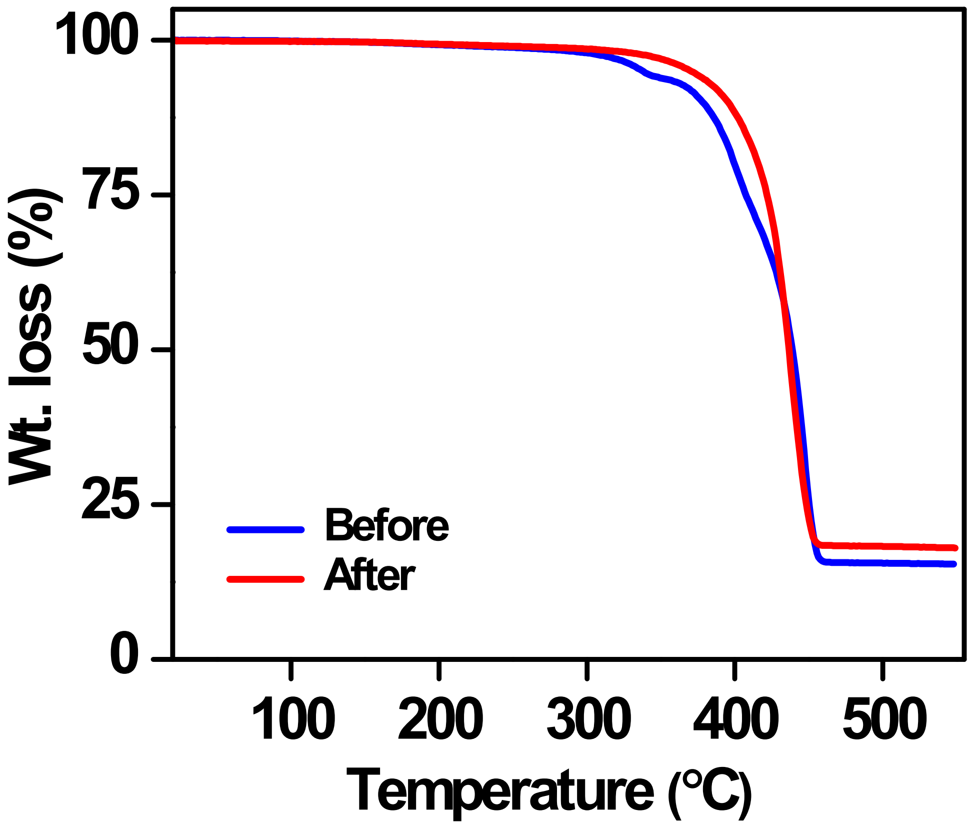


Figure S15. TGA of **1** before and after grinding under aerobic condition.

TGA of the pristine and sample ground under aerobic condition show same features. No decomposition is observed between 50-300 ^{o}C and even 5% decomposition is happened only at 370 ^{o}C.

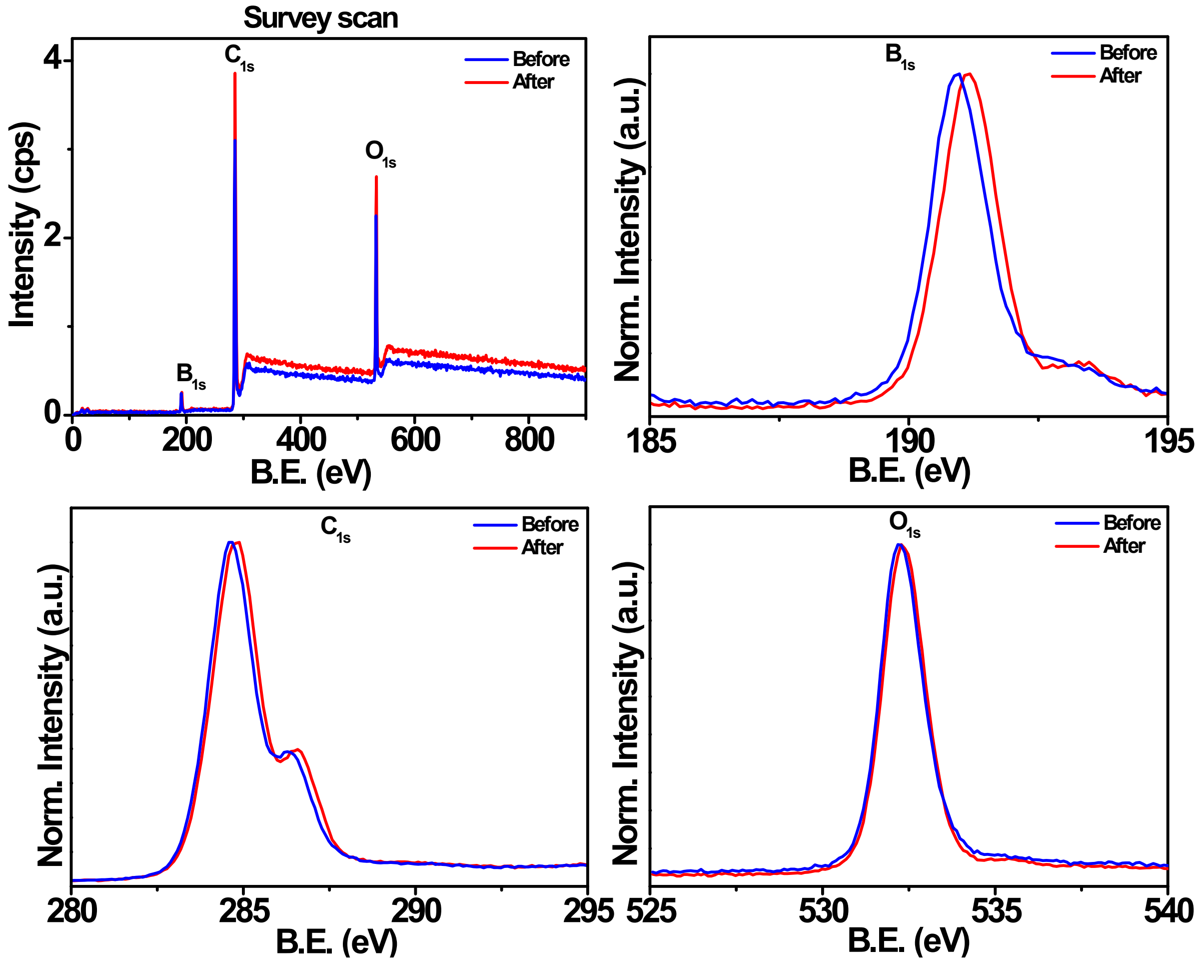
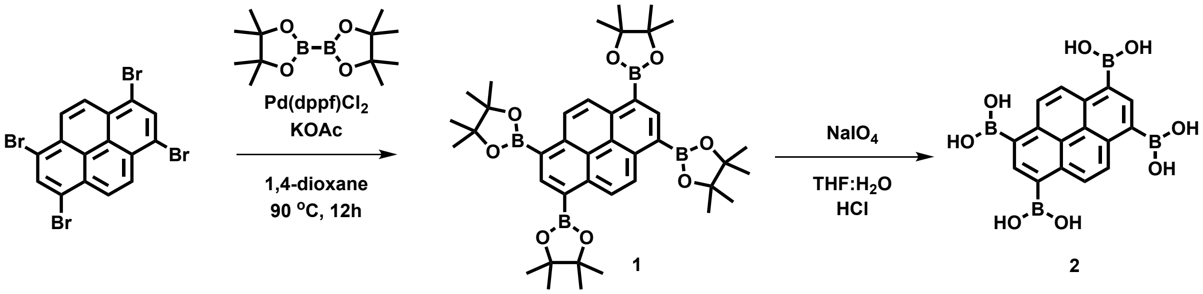


Figure S16. XPS of **1** before and after grinding under aerobic condition.

XPS experiments of both pristine and ground sample show same spectral features. There is no extra peak appearing in the XPS of the ground sample. Both samples are showing identical peak position for B1s (191 eV), C1s (284 eV) and O1s (532 eV) in the same region within the experimental error limit.

Synthesis and Characterization of 1 and 2



Scheme S1. Synthesis of **1** and **2**.

1,3,6,8-Tetrabromopyrene was prepared according to reported procedures.[S4]

1,3,6,8-tetrakis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (1).[S5]

1,3,6,8-tetrabromopyrene (500mg, 1 eq.) and B_2Pin_2 (1.47g, 6 eq.) were added to a 30 ml Teflon-sealed Schlenk tube. KOAc (948.0mg, 10 eq.) and 6 ml 1,4-dioxane were added to the flask. After adding, the flask was degassed with argon for 10 min. $PdCl_2$(dppf) (35.5mg, 0.05 eq.) were added and did the freeze-thaw cycle three times to removed trace amount of oxygen. After freeze-thaw cycles, Teflon-sealed Schlenk tube was capped tightly and run at 90 °C for 12 hr. Once the reaction was complete, the mixture was cooled to room temperature and 25 ml ethyl acetate was added to quench the reaction. Organic phase wash with DI water (25 ml) and brine solution 20 ml (2 times). Collected organic phase was dried over sodium sulphate and concentrate on rotary evaporator. Crude product was purified by silica column chromatography using dichloromethane as an eluent give a light yellow powder (559 mg, 82%).

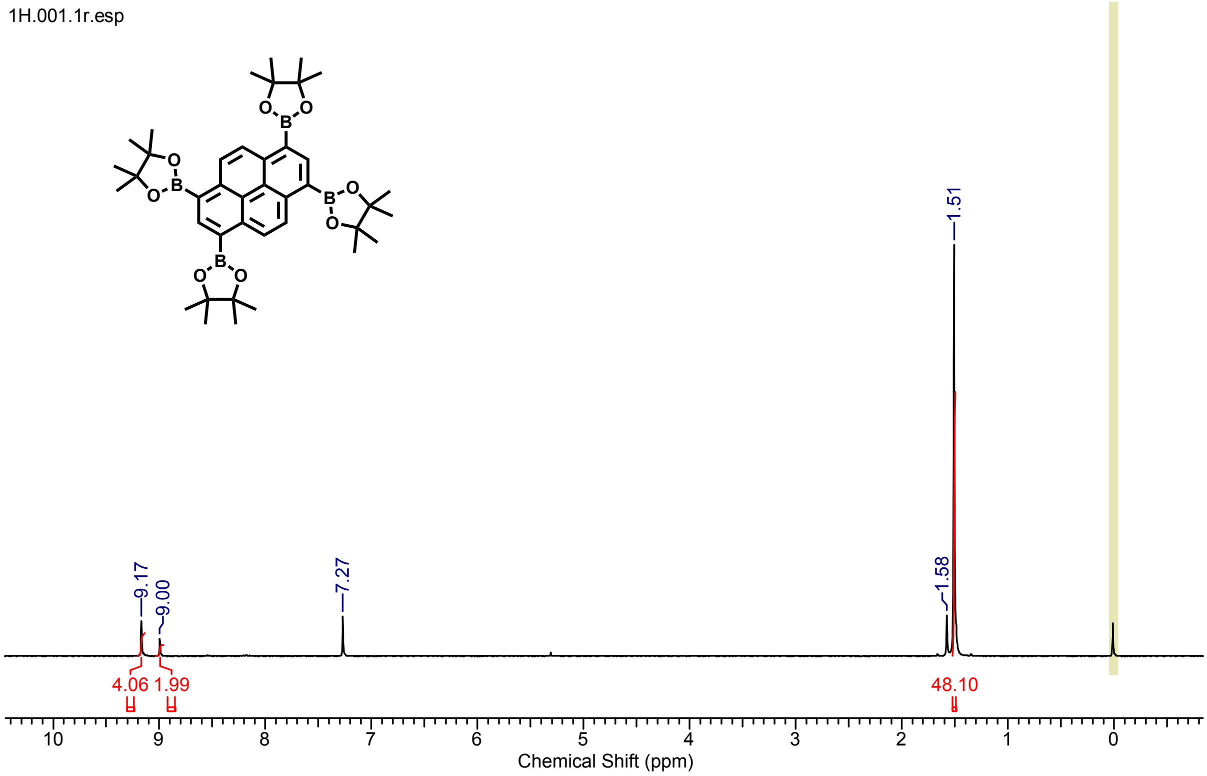
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.51 (s, 48H), 9.00 (s, 2H), 9.17 (s, 4H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ = 25.1, 83.8, 123.96, 129.4, 137.9, 141.3, 141.6 ppm; **^{11}B-NMR** (128 MHz,

$CDCl_3$): δ = 31.8; MALDI-TOF MS (in DHB matrix): calcd. for $C_{40}H_{54}B_4O_8$ = 706.1040, found 706.1282.

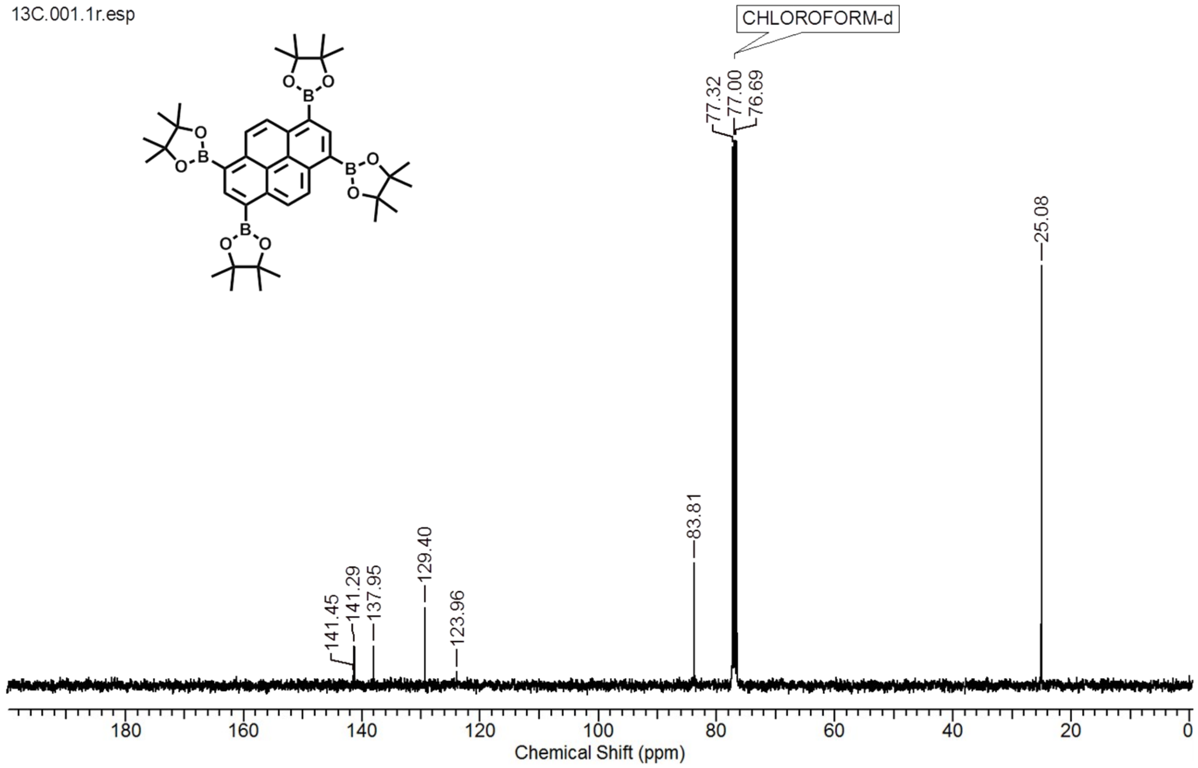
Pyrene-1,3,6,8-tetrayltetraboronic acid (2)[S6]

To the solution of **1** (200 mg, 1 eq.) in THF (10 ml) and water (2 ml) sodium periodate (727 mg, 12 eq.) was added. The cloudy suspension was stirred overnight at room temperature. Hydrochloric acid (2M, 0.5 ml) was added and the mixture stirred for another 24 hours. After the completion of the reaction, the mixture was poured into water, extracted with ethyl acetate. The organic solvent was removed after drying it with sodium sulphate. The product forms assembly giving a green colour solid (103 mg, 96%). 2D sheet like morphology of the product was confirmed by TEM. MALDI-TOF MS (in DHB matrix): calcd. for $C_{16}H_{14}B_4O_8$ = 378.1061, found 377.9276.

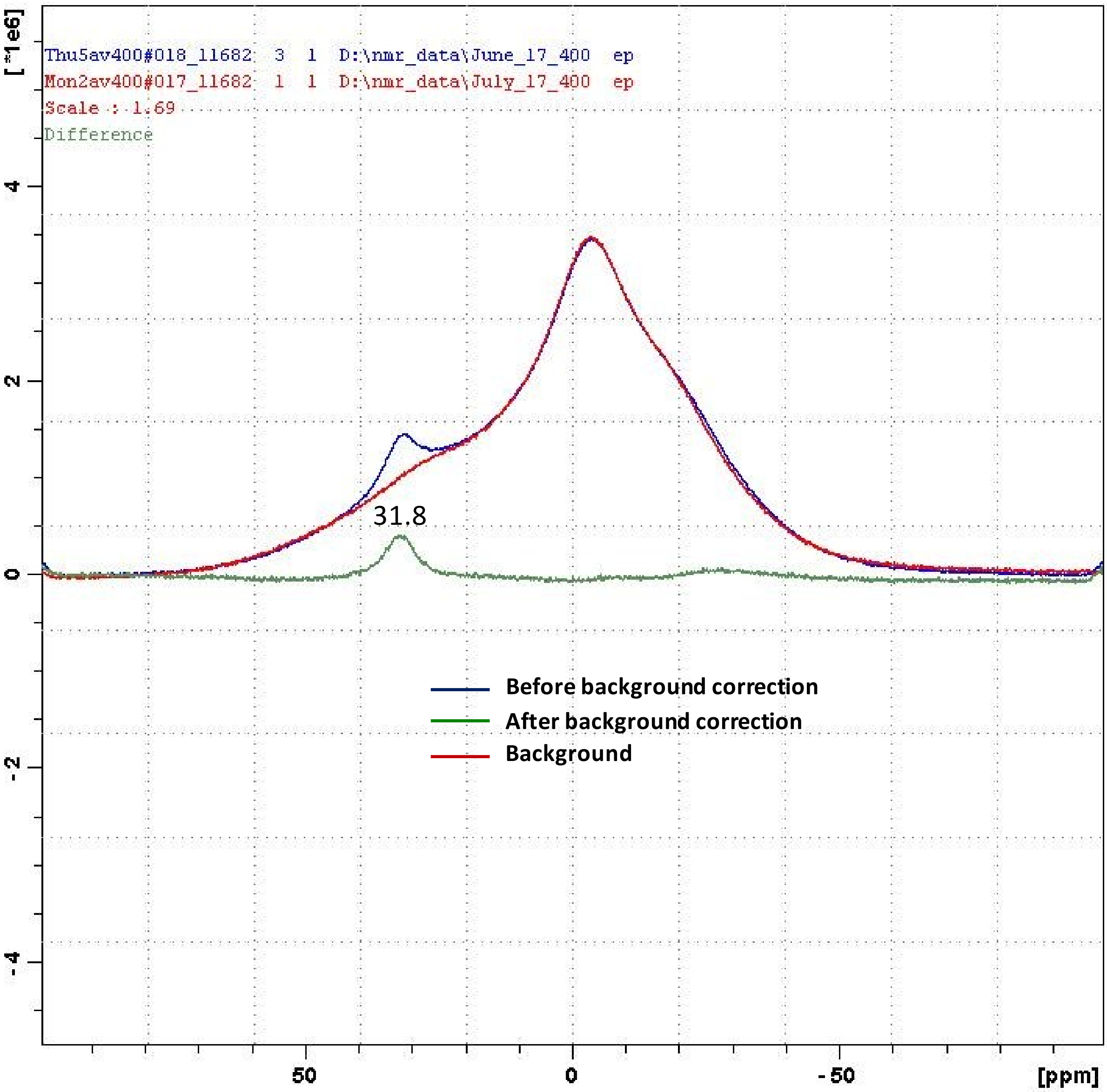
^{1}H spectrum of **1** in $CDCl_3$.



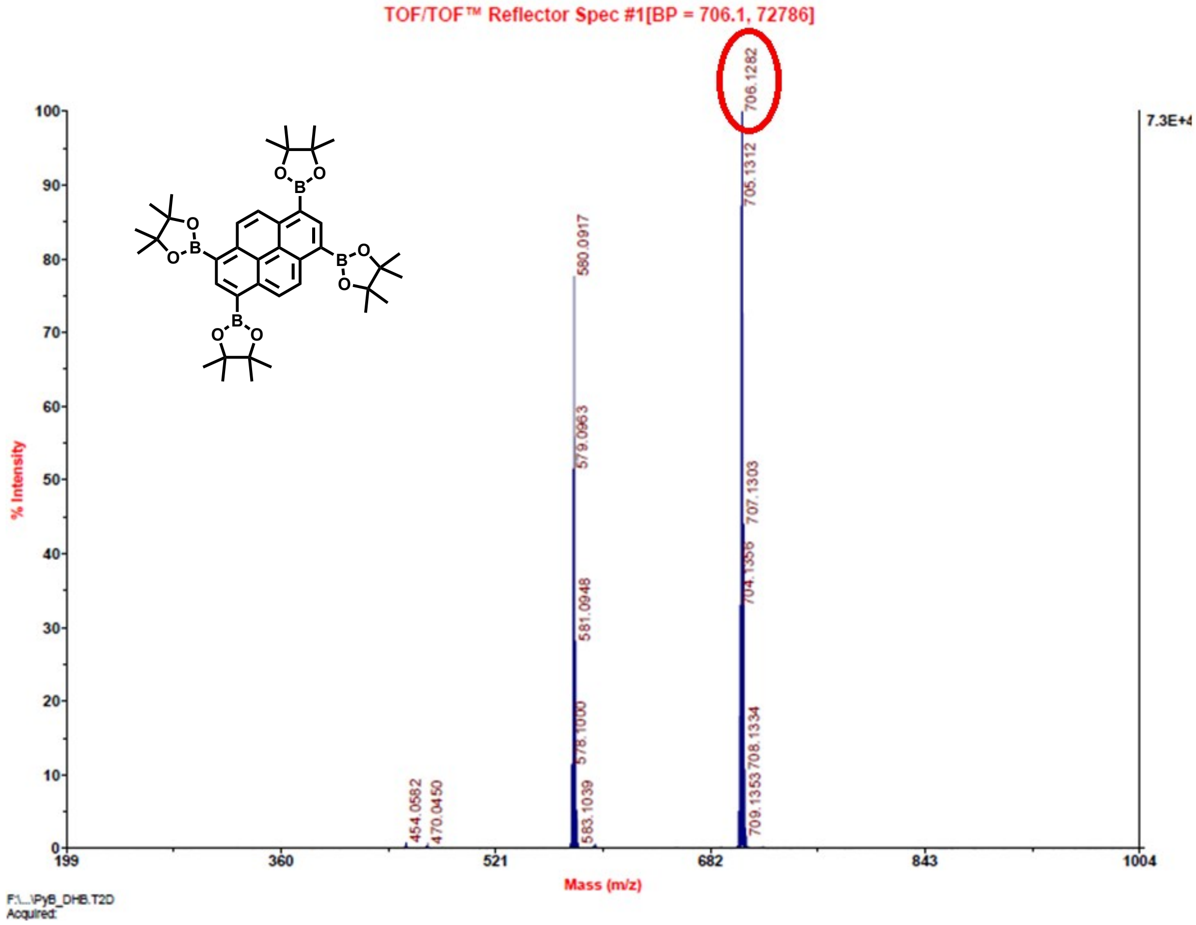
^{13}C spectrum of **1** in $CDCl_3$.



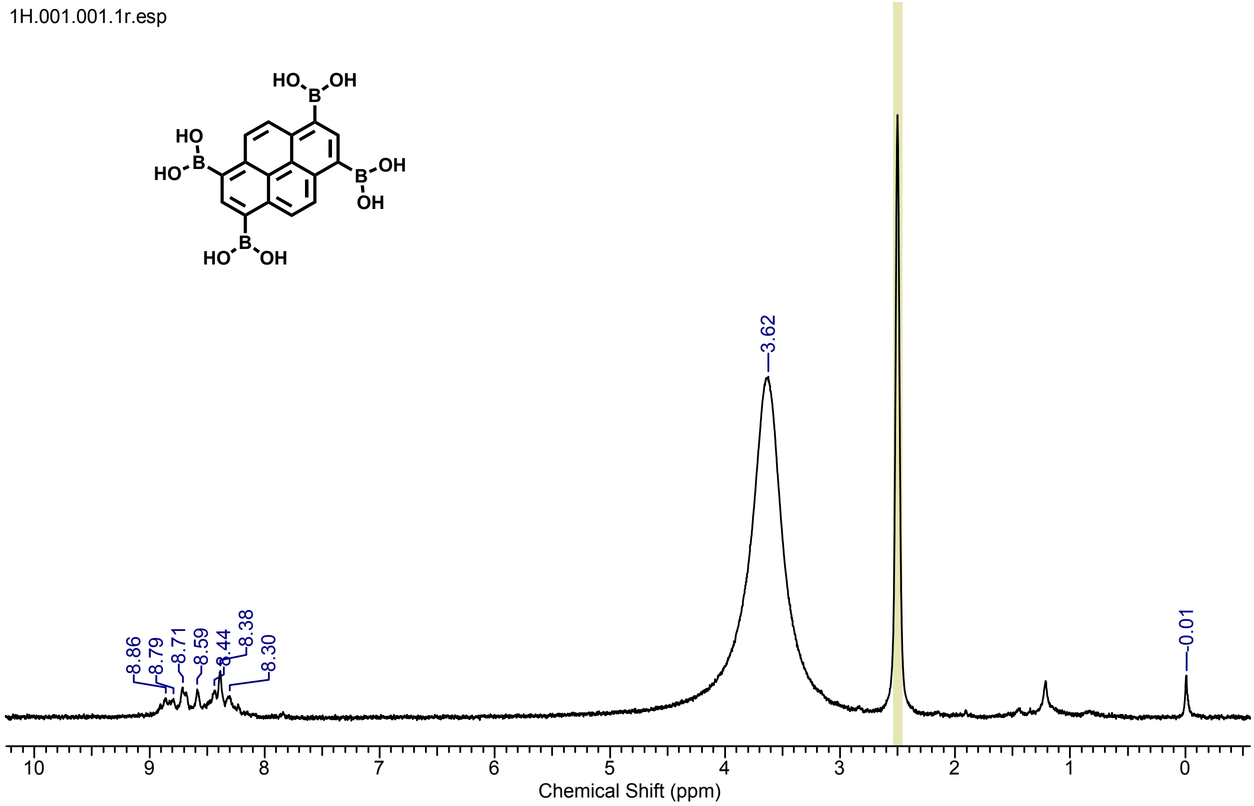
^{11}B spectrum of **1** in $CDCl_3$.



MALDI-TOF MS spectrum of **1** using DHB as matrix.

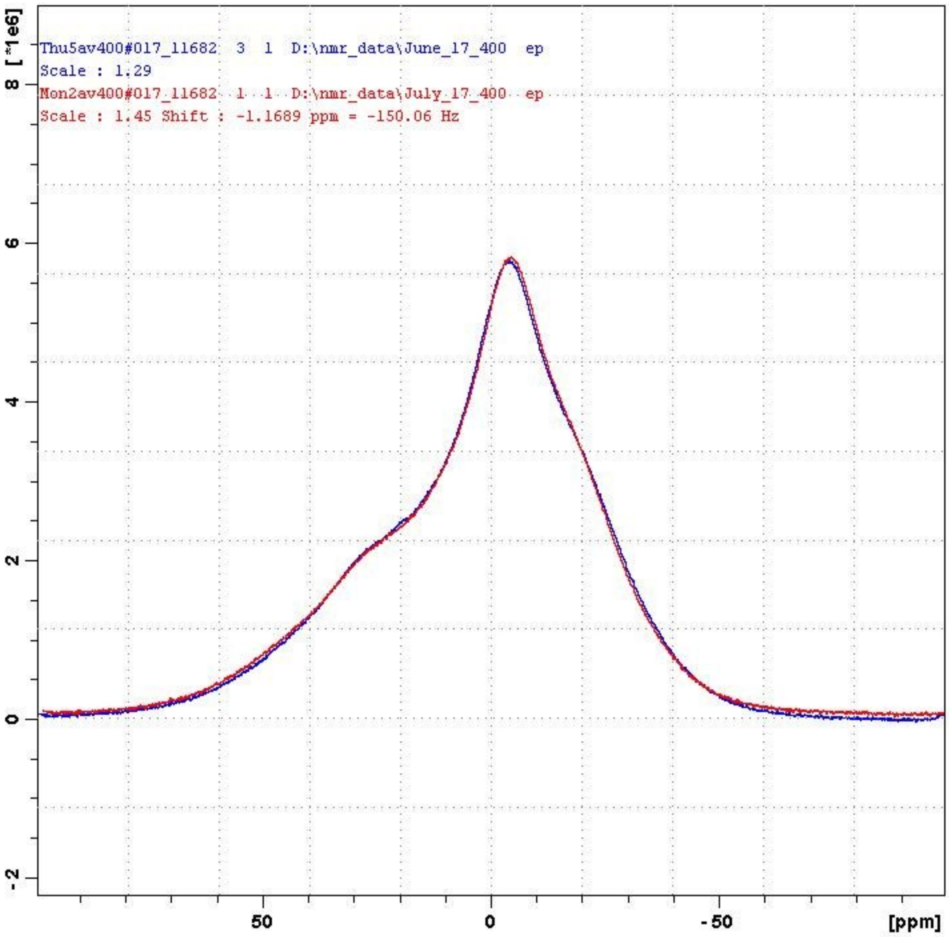


^{1}H NMR spectrum of **2** in DMSO-d$_6$.



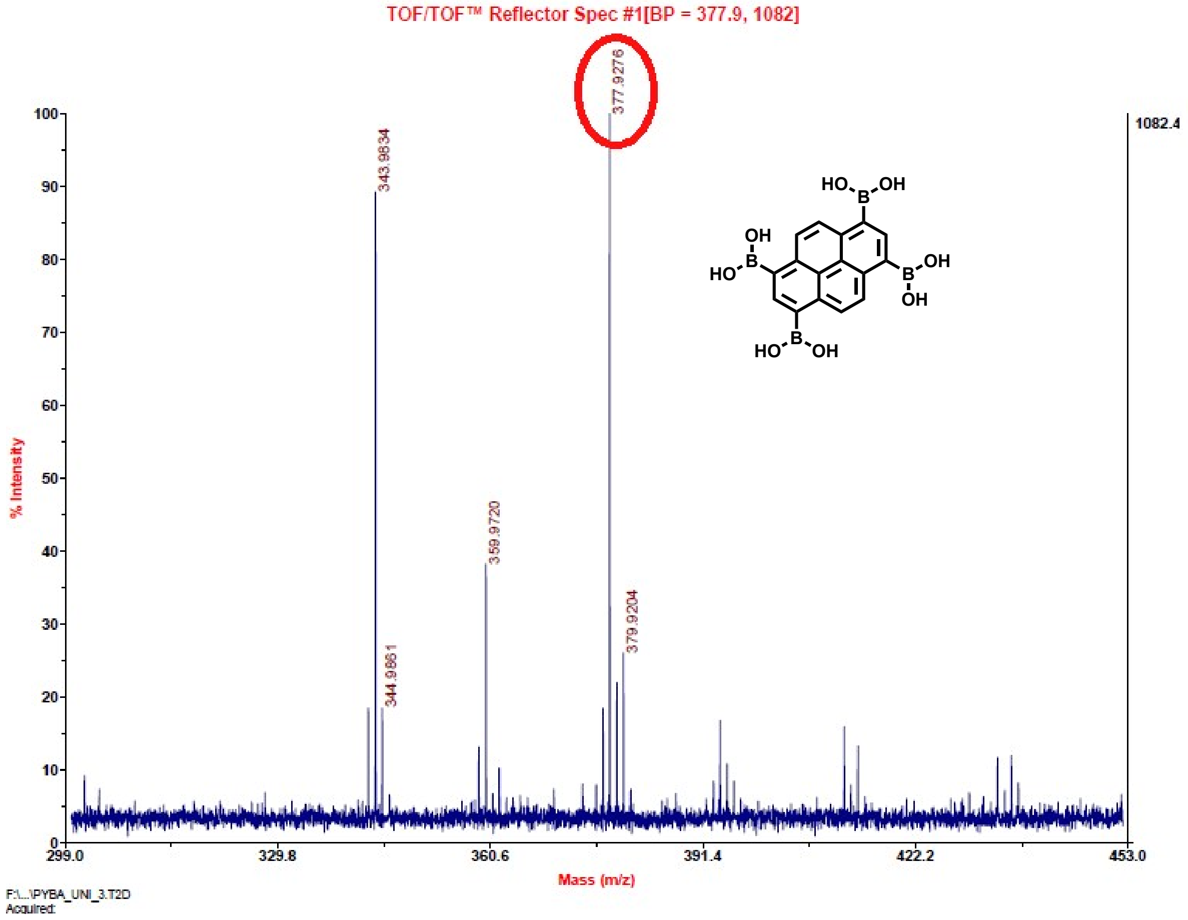
*Compound **2** gives very weak and broad signal ranging from 8.30 to 8.86 ppm at room temperature and hence even after repeated trials, a clean spectrum for both ^{13}C and ^{11}B NMR was not able to record.*

^{11}B NMR spectrum of **2** in DMSO-d_6.

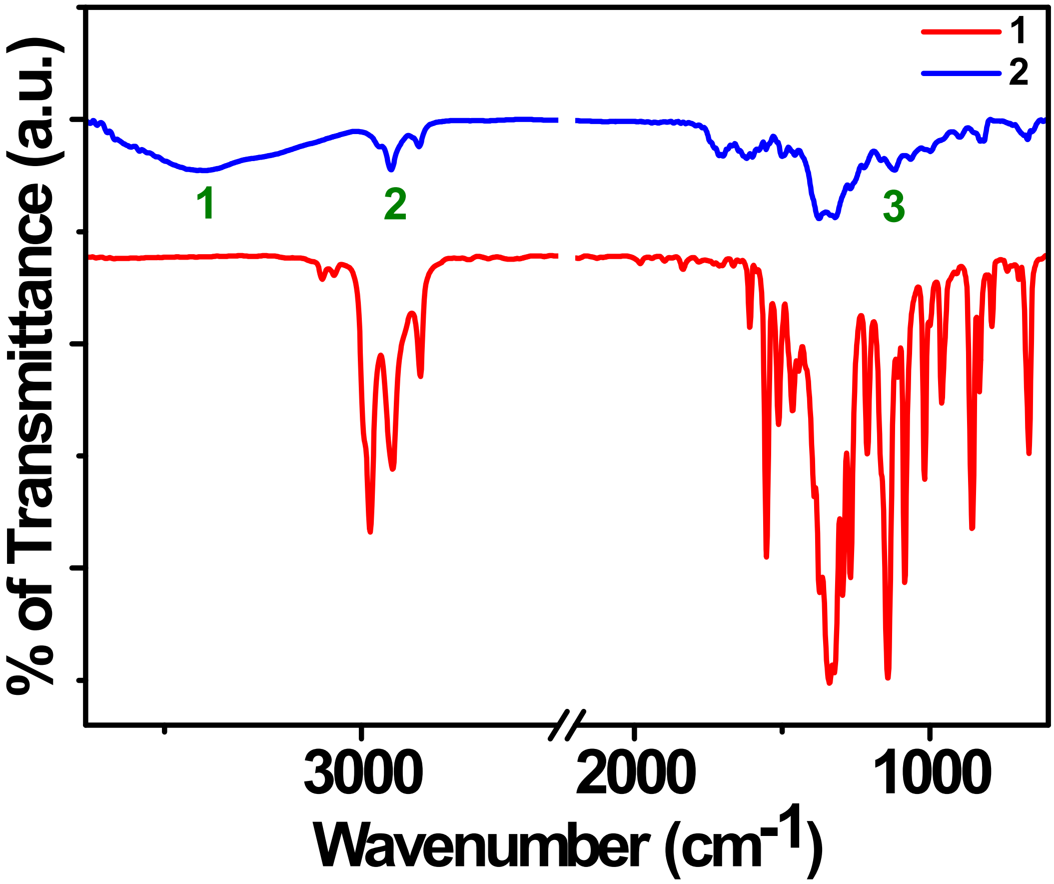


Unable to obtain a clear spectrum due to very low intensity of the compound peak compared to that of reference peak.

MALDI-TOF MS spectrum of **2** using DHB as matrix.



FT-IR spectra of **1**and **2**.



*Presence of OH stretching peaks, 2. Absence of SP^3 CH stretching peaks, 3. Absence of C-O stretching peaks, these 3 valid points clearly indicate the formation of **2** from **1**.*

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