Supporting Information

High Performance Non-Fullerene Acceptor Derived from Diathiafulvalene Wings for Solution-Processed Organic Photovoltaics

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S.1 UV-visible absorption

The UV-Vis absorption spectrum was recorded on a UV-1601 Shimadzu UV-Vis spectrometer. A UV-Vis spectrum of this new material was measured in chloroform ($CHCl_3$) solution. For UV-Vis absorption spectrum measurement in solution, concentrated solution (around 0.1 $mol \cdot L^{-1}$) was prepared independently, which was further diluted to get diluted solution (with concentration around 0.01 $mol \cdot L^{-1}$) of BAF-2HDT to measure UV-Vis absorption spectrum. The absorption spectrum of the dilute solution was recorded and the data point of the absorbance at a certain wavelength *vs.* concentration was then plotted. A good linear relationship was found for acceptor molecule.

S.2 Electrochemical behavior

Electrochemical data was obtained by cyclic voltammetry (CV) using a conventional three-electrode cell system consisting of a cylindrical platinum working electrode, platinum mesh counter electrode and *Ag*/*Ag*+ reference electrode was in saturated *KCl*, calibrated against ferrocene. All CV measurements were carried out at room temperature with a conventional three-electrode configuration under nitrogen atmosphere. The electrochemical CV was performed in a 0.1 $mol \cdot L^{-1}$ tetrabutylammonium perchlorate (TBAP)/dichloromethane (DCM) solution with a scan speed of 0.1 $V \cdot s^{-1}$. The surface was polished before use. A *Pt* sheet (~ 1 cm^2) and *Ag*/*AgCl* were used as the counter and reference electrodes, respectively. A ferrocene/ferrocenium (Fc/Fc^+) redox couple was

used as an external standard. CV measurement was carried out on the acceptor (3×10^{-4} M) in anhydrous and deoxygenated dichloromethane with 0.1 M of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte.

S.3 Photovoltaic results for variation in donor-to-acceptor weight ratio

To optimize the device performance, first the donor-to-acceptor (D/A) weight ratio was also varied. The D/A ratios were kept at 1:1, 1:1.3, 1:1.5, 1:1.7 and 1:2 while the additive concentration was kept fixed at 3% (v/v). The OPV devices made from the blend solution with D/A ratio of 1:1.5 showed the best device performance compared to all other D/A weight ratios (**Table S1**). A PCE of 7.13% was achieved when D/A ratio was 1:1.5. However, the value of V_{oc} increases with the increasing content of acceptor in the blend. The solar cell made from a D/A ratio of 1:2 showed the highest V_{oc} of 0.79 V with a PCE of 5.6%, whereas, 1:1.7 weight ratio of **PffBT4T-2OD:BAF-2HDT** gave rise to a V_{oc} of 0.78 V with PCE of 6.5%. In the second step of device optimization, different additive contents, e.g. 1, 2 and 3% (v/v), were used to prepare the active layer solution. However, the devices made from the 3% of DIO content showed the best performance (**Table S1**).

Table S1. Photovoltaic parameters of the devices fabricated with different D/A weight ratio and additive contents

D:A	Additive conc. (% v/v)	V_{oc} (V)	J_{sc} (mA·cm^{-2})	*FF* (%)	*PCE* (%)
1:1	3	0.73	11.67	0.59	5.02
1:1.3	3	0.75	13.17	0.60	5.93
1:1.5	3	0.77	14.64	0.64	7.13
1:1.5	2	0.75	12.51	0.57	5.34
1:1.5	1	0.74	10.89	0.53	4.27
1:1.7	3	0.78	13.63	0.61	6.48
1:2	3	0.79	12.82	0.55	5.57

Table S2. Average device performance efficiency and photovoltaic parameters of PffBT4T-2OD:**BAF-2HDT** based BHJ solar cells casted from 'thermally annealed' and 'vacuum dried' films.

Treatments	J_{sc} (mA·cm^{-2})	V_{oc} (V)	*FF*	*PCE* (%)
Thermally annealed	13.60 ± 0.09	0.75 ± 0.01	0.52 ± 0.01	5.31 ± 0.20
Vacuum dried	14.60 ± 0.04	0.76 ± 0.01	0.62 ± 0.02	6.88 ± 0.25

S.4 Device performance of reference solar cells

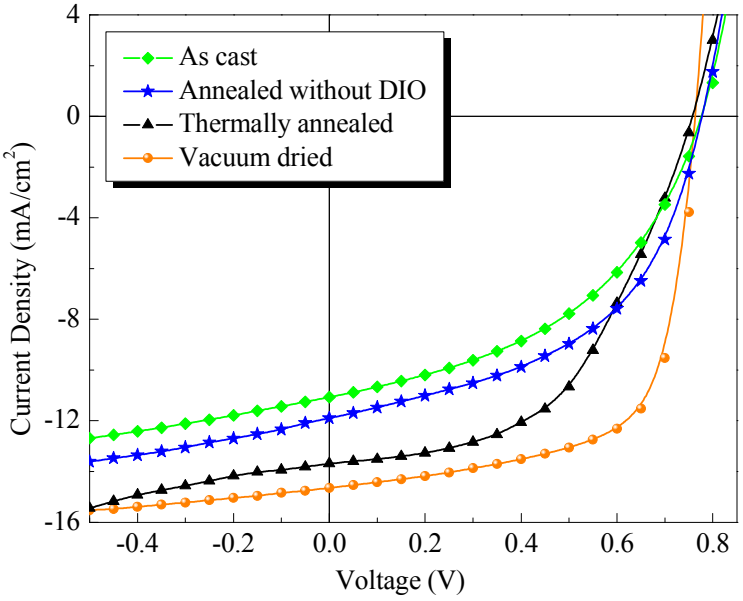


Figure S1. Light current density-voltage characteristics of the 'as cast' OSC (green) and the device casted from thermally annealed active layer without having DIO additive (blue). For the sake of comparison, characteristic *J-V* curves for 'thermally annealed' (black) and 'vacuum dried' (orange) devices are also added.

The light *J-V* characteristic of the solar cell fabricated from 'as cast' blend film without any further post-film formation treatment is shown in **Figure S1**. The device shows a PCE of 3.7% with

less J_{sc} and *FF* of 10.7 mA·cm^{-2} and 0.45, respectively. The device made from the thermally annealed blend film without using any additive shows comparatively better photovoltaic performance with *PCE* of 4.5%, V_{oc} of 0.776 V, J_{sc} of 11.89 mA·cm^{-2} and *FF* of 0.49.

Table S3. Photovoltaic parameters of the reference solar cells

Treatments	V_{oc} (V)	J_{sc} (mA·cm^{-2})	*FF*	*PCE* (%)	R_S (Ω·m^2)	R_{SH} (KΩ·m^2)
As cast	0.777	10.70	0.45	3.7	17.2	0.3
Annealed (without DIO)	0.776	11.89	0.49	4.5	12.4	0.3
Annealed (with DIO)	0.760	13.69	0.53	5.5	16.1	0.4
Vacuum dried (with DIO)	0.770	14.64	0.64	7.1	4.5	0.5

S.5 Grazing incidence X-ray diffraction spectroscopy

The Grazing incidence X-ray diffraction (GIXRD) pattern of pristine PffBT4T-2OD, **BAF-2HDT** and their blend films with vacuum drying and thermal annealing treatments are shown in **Figure S2**. The pure **BAF-2HDT** film appears to be amorphous in nature as no prominent peak was observed in the X-ray diffractogram. On the other hand, pure PffBT4T-2OD film shows two sharp peaks at q = 0.28 and 1.74 Å^{-1} in its GIXRD pattern originated from (1 0 0) plane in the direction of lamellar stacking and (0 1 0) plane in the direction of π-π stacking, respectively. The 'thermally annealed' blend film also shows lamellar stacking similar to that of in pristine PffBT4T-2OD film. The peak height significantly increases with the vacuum drying treatment of PffBT4T-2OD:**BAF-2HDT** bulk-composite film. So, it can be inferred that the vacuum drying certainly improves the crystallinity of the blend film. It can also be observed from **Figure S2** that the height of the GIXRD peak corresponding to *π-π* stacking got diminished in both the blend films. It is known that a strong

lamellar stacking and lower π-π stacking leads to an improved photovoltaic performance of the device.[1]

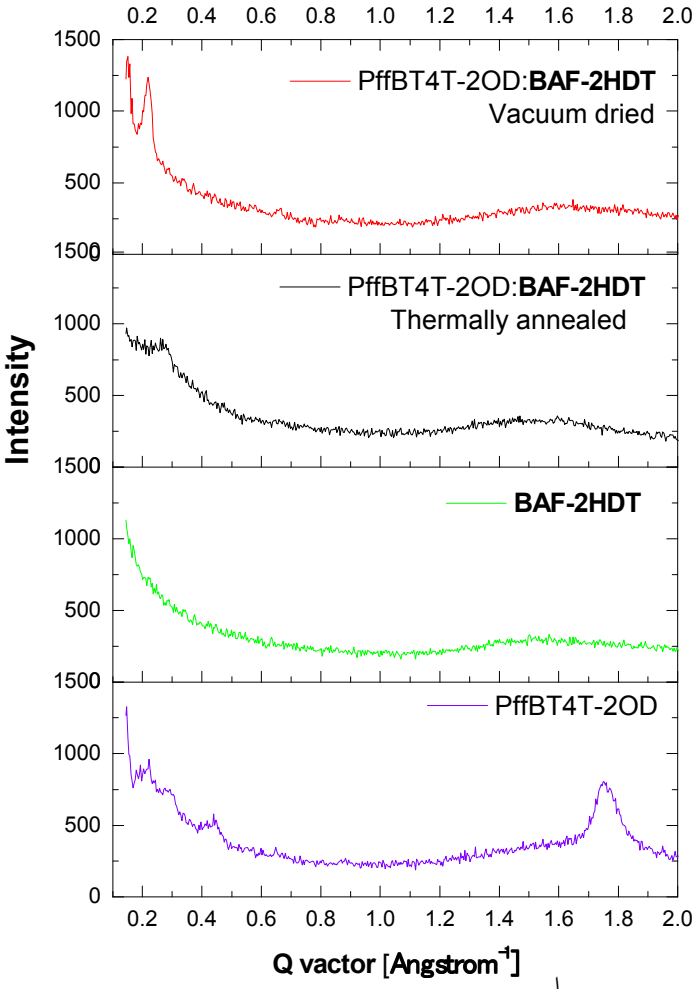


Figure S2. The GIXRD pattern of pristine PffBT4T-2OD, **BAF-2HDT** and their blend films with vacuum drying and thermal annealing treatments. The 'vacuum dried' PffBT4T-2OD:**BAF-2HDT** blend film clearly shows higher crystallinity compared to the 'thermally annealed' blend film.

S.6 Photoluminescence in Solid state

Photoluminescence (PL) quenching experiments were performed on thin films exciting both the donor and acceptor, individually. **Figure S3** represents the emission spectra of the pristine **BAF-2HDT** (blue curve), PffBT4T-2OD (black) and their blends (red, orange). The PL peak originated

at the wavelength of 526 nm in the emission spectrum of pure **BAF-2HDT** film because of the excitation at 480 nm gets completely quenched in the presence of donor molecule in the blend film. On the other hand, The PL peak observed at 750 nm in the emission spectrum of pristine PffBT4T-2OD film when excited at the wavelength of 650 nm also gets quenched significantly in the presence of acceptor in the blend. These results clearly confirm that our newly developed NFA molecule **BAF-2HDT** can accept electron efficiently from the donor molecule irrespective of solution or, solid form.

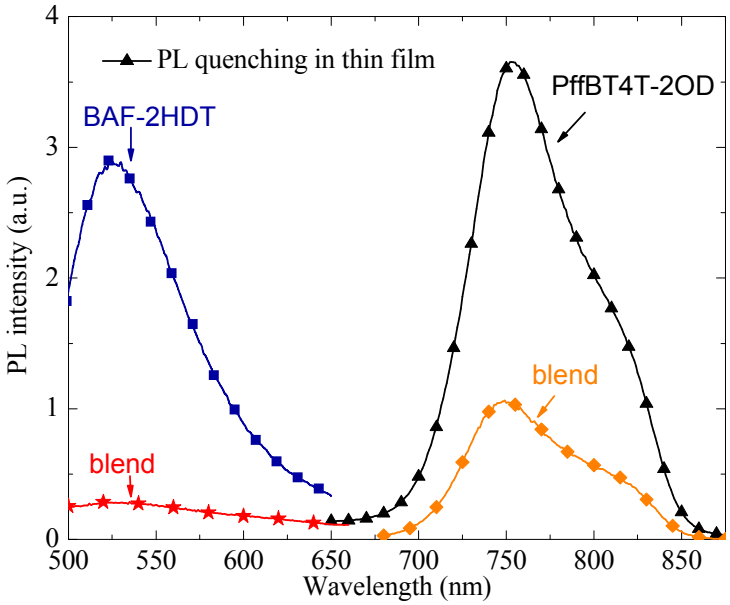


Figure S3. The PL quenching spectra of **BAF-2HDT** (blue curve), PffBT4T-2OD (black) and their blends (red, orange) in solid state form.

S.7 Synthesis and characterization of BAF-2HDT

The synthetic route of **BAF-2HDT** is described here. 9,9-didecyllfluorene-2,7-diboronic acid pinacol ester was reacted with an electron-withdrawing group bromo-2,1,3-benzothiadiazole-4-carboxaldehyde by Suzuki coupling reactions catalyzed by [$Pd(PPh_3)_4$] afforded the aryl dialdehyde intermediate (BAF-2CHO). The HDT group was introduced through Horner–Wittig reaction resulted **BAF-2HDT** in the dark pink color. The introduction of HDT in BAF-2CHO induced a

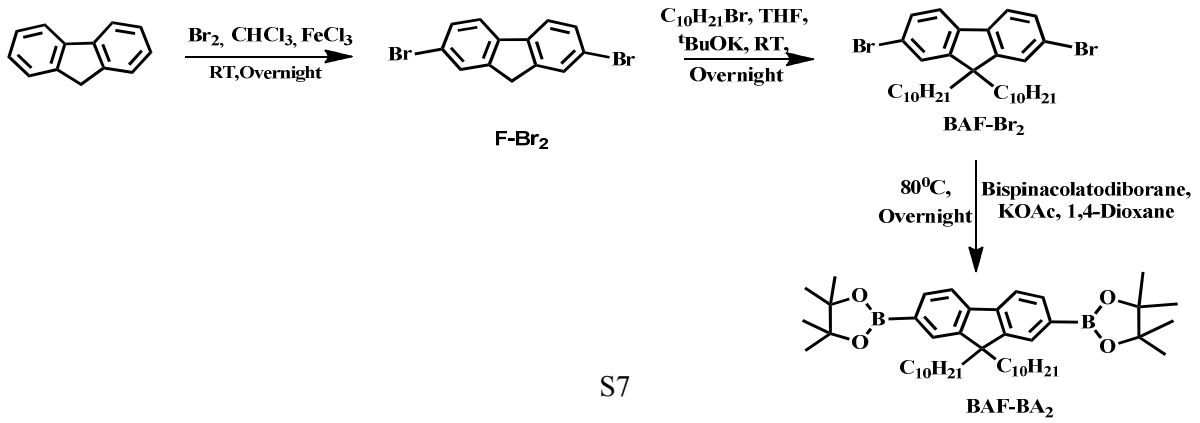
color change of the acceptors towards a more visible region (Red shift). This molecule shows good solubility in common organic solvents, such as dichloromethane, THF and chloroform at room temperature. The structure and purity of **BAF-2HDT** have been characterized and confirmed by ^{1}H NMR, ^{13}C NMR and MALDI-TOF MS measurement. The results are available in the supporting information.

Materials and Methods

The starting materials Fluorene and 2,3-diaminotoluene were purchased from Sigma-Aldrich. All the reagents were of analytical reagent grade and used without further purification except for THF, DCM and $CHCl_3$ were dried by distillation over calcium hydride and were distilled according to standard procedures and stored with $4^{0}A$ molecular sieves under a N_2 atmosphere. Hexadithiafulvene (HDT) was prepared according to published procedures.[2] PffBT4T-2OD (PCE11) was obtained from Flexink and $PC_{71}BM$ was purchased from Nano-C.

^{1}H and ^{13}C NMR spectra were collected on a Bruker AV-400 spectrometer and AV-300 spectrometer in $CDCl_3$ at 298 K and are reported in ppm relative to TMS as an internal standard in both cases. Matrix assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) was performed on Shimadzu Biotech Axima performance.

Synthesis of BAF-BA_2



2,7-Dibromo-9H-fluorene (F-Br_2)[3]:

In a 250 mL two neck round bottom flask Bromine (10.1 g, 63 mmol) was added drop wise into a suspension solution containing Fluorene(5.0 g, 30 mmol), $FeCl_3$ powder (26 mg, 4.6 mmol) in a catalytic amount and 60 ml of chloroform. The flask was cooled in ice water, and the temperature was controlled under 50 ^{0}C. The reaction was allowed to stand for 2 hours. The product was filtered and recrystallized with chloroform, to afford F-Br_2 as white crystals (8.95 g, 92% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: d7.67-7.65 (s, 2H), 7.61- 7.58 (d, J=8.31Hz, 2H), 7.50-7.48 (d, J 8.31Hz, 2H), 3.88-3.85 (s, 2H).

2,7-Dibromo-9,9-didecyl-9H-fluorene (BAF-Br_2)[3]:

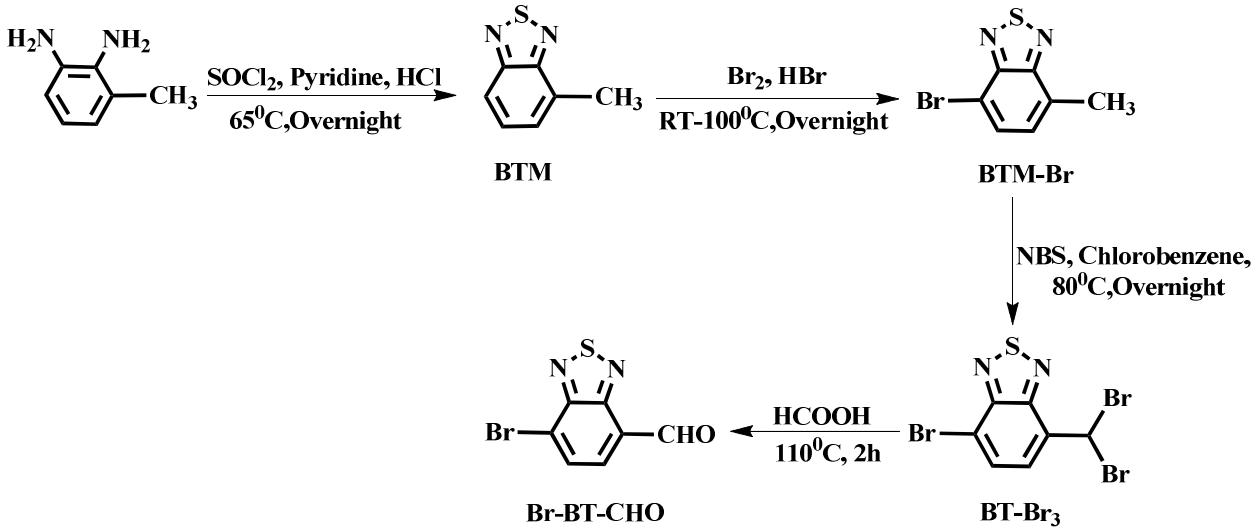
In a 100 ml of two neck round bottom flask a stirred solution of F-Br_2(2 g, 6.17 mmol) in 25 mL THF under nitrogen was added t-BuOK (1.4 g, 12.5 mmol) in 20 ml THF slowly at 0 ^{0}C. After 1 h, n-Decylbromide (2.6 ml, 18.51 mmol) was added to the reaction mixture and stirred at room temperature for 8 hours. The reaction mixture was filtered and the organic layer was concentrated under reduced pressure. The oily residue was purified by flash column chromatography (hexane) to afford a colorless liquid (3.5 g, 94% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: d 7.52-7.50 (d, J=7.83Hz, 2H), 7.439-7.432 (d, J=7.83Hz, 2H), 7.45-7.44 (d, J=7.83Hz, 2H), 1.94-1.88 (m, 4H), 1.22-1.04 (m, 32H), 0.86-0.84 (t, J=7.55Hz, 6H).

2,7-Bis(4,4,5,5-tetramethyl-1,2,3-dioxaborolane-2-yl)-9,9-di-n-decylfluorene (BAF-BA_2)[4]:

In a 100 ml of single neck round bottom flask a mixture of BAF-Br_2(2.5 g 4.1 mmol) , Bispinacolatodiborane(2.72 g 10.7 mmol), KOAc (0.075 g 0.76mmol), in 1,4-Dioxane (30 ml) was degassed before addition of [$PdCl_2(dppf)_2$] (20 mg) and subsequent degassing for 30 min. the reaction was heated under argon at 80^0 C overnight. After cooling to room temperature, the mixture

was extracted with DCM and the organic phase was dried over anhydrous sodium sulfate. After removal of the solvent, the residue was purified by silica gel column chromatography eluted with hexane to afford a white semi solid (1.9 g, 66% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ: d 7.81-7.79 (d, J=8.31Hz, 2H), 7.71-7.69 (d, J=8.31Hz, 2H), 7.34-7.32 (d, J=8.31Hz, 2H), 1.99-1.92 (m, 4H), 1.27-1.02 (m, 56H), 0.82-0.84 (t, J=7.17Hz 6H).

Synthesis of Br-BT-CHO



4-methyl-2, 1, 3-benzothiadiazole (BTM)[5]:

In a 250 ml of single neck round bottom flask $SOCl_2$ (0.67 ml, 40.9 mmol) was added drop-wise to a solution of 2,3-diaminotoluene (2 g, 16.3 mmol) in pyridine (12 ml) with the temperature maintained below 30 ^{0}C. HCl (8 ml) was then added drop-wise at 65 ^{0}C and the reaction was stirred at room temperature overnight. The reaction mixture was quenched with water and extracted with diethyl ether. After removal of the solvent, the crude product was then purified by was purified by silica gel column chromatography eluted with hexane to afford a colorless oil. (1.4 g, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ: d 7.81-7.79 (d, J=8.31Hz, 2H), 7.71-7.69 (d, J=8.31Hz, 2H), 7.34-7.32 (d, J=8.31Hz, 2H), 1.99-1.92 (m, 4H), 1.27-1.02 (m, 56H), 0.82-0.84 (t, J=7.17Hz 6H).

4-bromo-7-methyl-2,1,3-benzothiadiazole(BTM-Br)[5]:

In a 50 ml of two necks round bottom flask Bromine (0.34 ml, 6.5 mmol) was added slowly to a solution of BTM (1 g, 6.7 mmol) in 20 ml HBr under nitrogen atmosphere. The reaction mixture was heated to 80 ^{0}C for 30 min after which time a yellow solid had precipitated, the mixture was stirred overnight at 130 ^{0}C temperature. The reaction was neutralized with $NaHCO_3$ (aq.) solution, extracted with CH_2Cl_2 and dried over Sodium sulphate. After removal of the solvent, the crude product was then purified by column chromatography (Hexane/DCM) to give BTM-Br as a pale yellow solid (0.80 g, 53% yield). 1H NMR (400 MHz, $CDCl_3$) δ: 7.76-7.72 (d, J=7.2Hz, 1H), 7.3-7.27(d, J=6.8Hz, 1H), 3.01-2.98(s, 3H).

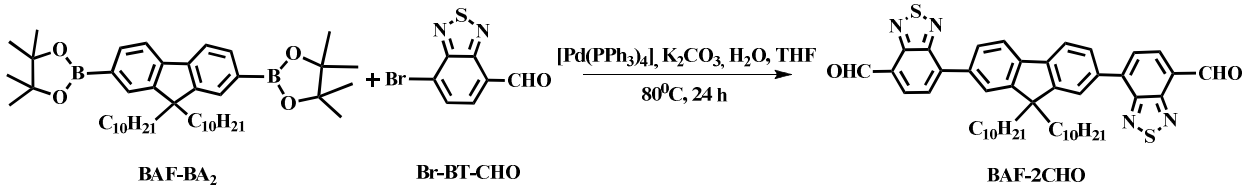
4-bromo-7-dibromomethyl-2,1,3-benzothiadiazole (BT-Br_3)[5]:

In a 50 ml of single neck round bottom flask a mixture of BTM-Br (1.5 g, 6.5 mmol), N-bromosuccinimide (3.49 g, 19.6 mmol) and benzoyl peroxide (0.317 g, 1.3 mmol) were dissolved in chlorobenzene (15 ml) and stirred overnight at 80 ^{o}C. After cooling to room temperature, the reaction was extracted with CH_2Cl_2 and dried over Sodium sulphate. After removal of the solvent, the crude product was then purified by column chromatography with hexane/CH2Cl2 (9:1) to afford BT-Br_3 as a white crystalline solid (1.4 g, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98-7.95 (d, J=7.7Hz, 1H), 7.93-7.90 (d, J=7.7Hz, 1H), 7.42-7.41 (s, 1H).

4-bromo-2,1,3-benzothiadiazole-4-carboxaldehyde (Br-BT-CHO)[5]:

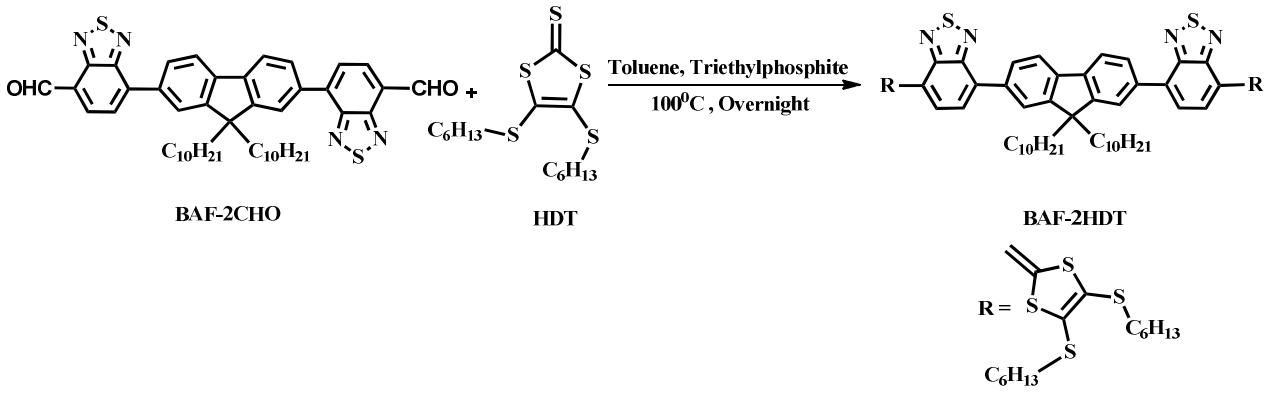
In a 50 ml of single neck round bottom flask a mixture of BT-Br_3 (1.2 g, 3.1 mmol) were dissolved in Formic acid (15 ml) and stirred 2 hours at 110 ^{0}C. After cooling to room temperature reaction mixture was poured into water. The resulting precipitate was filtered and washed with water until the filtrate was of neutral pH, then dried in vacuum to give an off-white crystalline solid (0.65 g, 86% yield). 1H NMR (400 MHz, $CDCl_3$) δ: 10.78-10.74 (s, 1H), 8.10-8.09 (d, J=7.6Hz, 1H) 8.07-8.06 (d, J=7.6 Hz, 1H).

Synthesis of BAF-2CHO[5]:

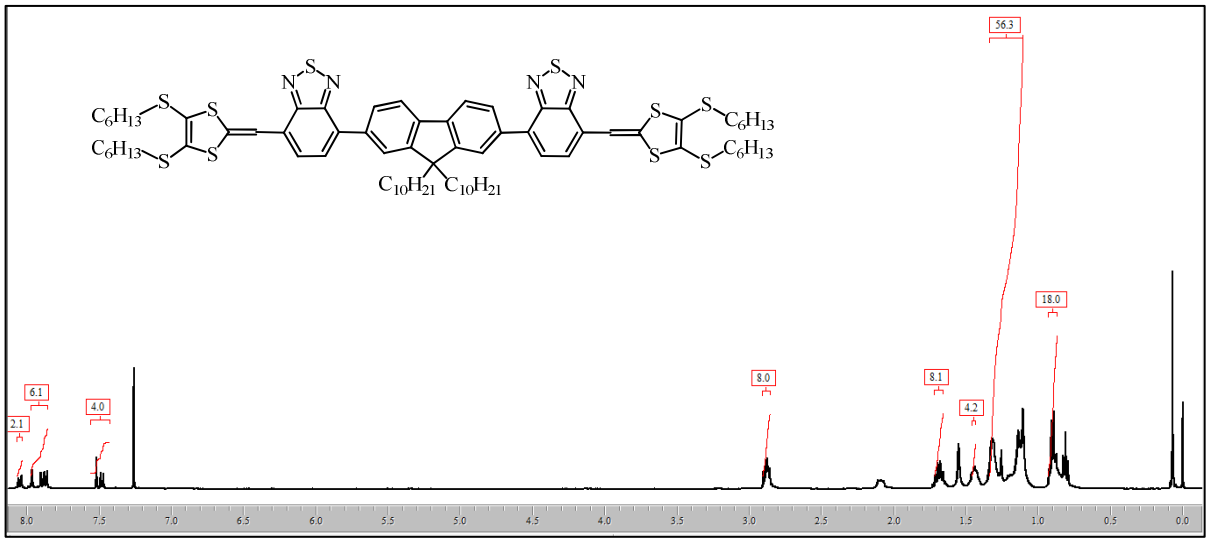


In a 50 ml of two neck round bottom flask a mixture of BAF-BA_2 (1.12 g, 1.7 mmol), Br-BT-CHO(1 g, 4.2 mmol), K_2CO_3 (2M Solution 5 mL), in THF (10 ml) was degassed for 1 hour before addition of [$Pd(PPh_3)_4$] (10 mg) and subsequent degassing for 10 minutes. The reaction mixture was heated under argon at 80 ^{0}C for 24 hrs. After cooling to room temperature, the reaction was quenched with water, extracted with CH_2Cl_2 and dried over Sodium sulphate. After removal of the solvent, the crude product was then purified by column chromatography with Hexane/DCM (1:4) to give BAF-2CHO as a pale brown semi solid (0.56 g, 44.44% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.83-10.82 (s, 2H), 8.36-8.34 (d, J=7.3Hz, 2H), 8.09-8.05 (m, 4H), 8.00-7.96 (m, 4H), 2.15-2.11 (m, 4H), 1.16-1.09 (m, 32H), 0.84-0.79 (t, J=6.8Hz, 6H).

Synthesis of BAF-2HDT



In a 50 ml of two necks round bottom flask a mixture of HDT (0.078 g 0.26 mmol) and BAF-2CHO (0.100 g, 0.129 mmol) were dissolved in Toluene (10 ml). Triethylphosphite (3 ml) was then added and the mixture heated at 100 ^{0}C for 24 hrs. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 and the crude product was purified by flash column chromatography on silica gel (CH_2Cl_2) yielding BAF-2HDT as a dark pink semi solid (0.068 g, 38% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08-8.06 (d, J=9.04Hz, 2H), 7.98-7.96 (s,2H), 7.91-7.85 (dd, J=7.9, 1.9Hz, 4H), 7.53-7.51 (d, J=7.4Hz, 2H), 7.49-7.46 (d, J=7.4Hz, 2H), 2.91-2.85(q, J=4.3Hz, 8H), 1.47-1.41 (m, 4H), 1.35-1.41 (m, 56H), 0.93-0.87 (t, J=6.72Hz, 18H). ^{13}C NMR (300 MHz, CDCl3) δ: 188.95, 163.98, 162.46, 154.10, 153.87, 153.46, 151.67, 145.37, 131.16, 128.29, 128.19, 128.09, 127.18, 124.87, 123.67, 123.61, 119.93, 108.6, 63.18, 63.64, 55.36, 40.25, 37.95, 36.66, 36.32, 31.82, 31.32, 29.66, 29.58, 29.52, 29.24, 22.60, 22.53, 14.06, 14.01. MS (MALDI-TOF-MS): m/z calcd for $C_{77}H_{106}N_4S_{10,}$ 1408.34; $[M]^+$, found 1408.



H^1 NMR of BAF-2HDT in *$CDCl_3$*

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