Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Direct Observation of Rise of Delayed Fluorescence in Dithienylbenzothiadiazole and its Role in the Excited State Dynamics of a Donor-Acceptor-Donor Molecule

Maneesha Esther Mohanty,[a]* Chakali Madhu, Vanammoole Lakshmi Reddy,[a] Mahalingavelar Paramasivam,[a] Prakriti Ranjan Bangal,[b]* Vaidya Jayathirtha Rao[a]*

Synthetic Procedure

Synthesis of 2,1,3-Benzothiadiazole (BT)[38]

Commercial o-phenylenediamine(1, 10.0 g, 92.5 mmol), dichloromethane (300 mL), and triethylamine (37.4 g, 370 mmol) were added in a 1000 mL round bottomed flask. The solution was stirred until total dissolution of diamine. Thionyl chloride (185 mmol, 2 equiv.) was added drop wise slowly, and the mixture was heated at reflux for 5 h. The solvent was removed under reduced pressure. Water (700 mL) was added to achieve a final pH of 1, concentrated HCl was added. The desired compound was purified by direct steam distillation. The steam distilled mixture was extracted with dichloromethane (5×200 mL), dried with Na_2SO_4, and filtered. The solvent was removed to afford pure compound 2 with 93% yield (11.7 g, 86 mmol). 1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, J = 3.2 Hz and J = 5.7 Hz, 2 H), 7.57 (dd, J = 3.2 Hz and J = 5.7 Hz, 2 H) ppm. 13C NMR (100 MHz, $CDCl_3$): δ = 154.6, 129.1, 122.4 ppm. M.p. 43.6–44.4 °C.

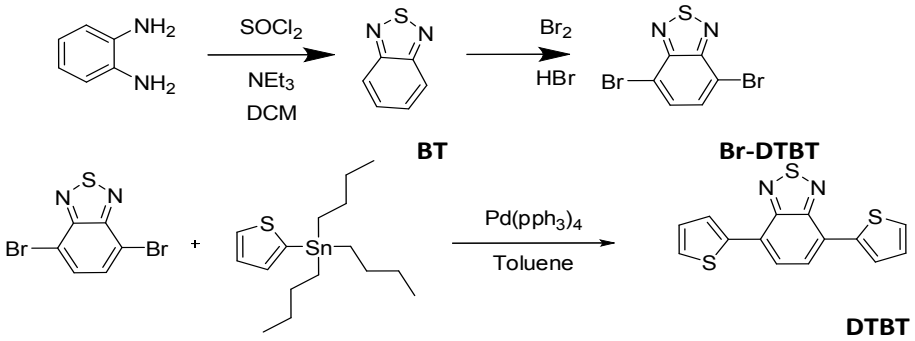
Synthesis of 4,7-Dibromobenzothiadiazole(Br-DTBT) [38]

In to a 500 mL two-necked round bottomed flask benzothiadiazole 2 (10.0 g, 73.4 mmol) and HBr (150 mL, 48%) were added. A solution containing Br_2 (35.2 g, 220.3 mmol) in HBr (100 mL) was added drop wise slowly. If necessary, an additional 100 mL of HBr can be added to the solution. After the total addition of Br_2, the reaction mixture was refluxed at 45^{o}C for 6 h. Precipitation of a dark orange solid was observed. The mixture was cooled to room temperature, and saturated solution of $NaHSO_3$ was added to neutralize excess Br2. The mixture was filtered under vacuum and washed exhaustively with water. The solid was then washed once with cold Et2O and dried under vacuum for 20 h to afford dibrominated product 3 having 95 % yield (20.5 g, 69.8 mmol). 1H NMR

(200 MHz, $CDCl_3$/[D6] DMSO, 8:2): δ = 7.73 (s, 2 H) ppm. 13C NMR (50 MHz, $CDCl_3$/ [D6] DMSO, 8:2): δ = 152.6, 132.1, 113.6 ppm. M.p. 189–190 °C.

Synthesis of 4,7-Di-2'-thienyl-2,1,3-benzothiadiazole (DTBT)[39]

In to a 100 mL two-necked round bottomed flask tributyl-(thiophen-2-yl)stannane (3.18 g, 0.0085 mol) was added (1 g, .0034 mol), and tetrakis-(triphenylphosphine) palladium(0) (100 mg, 5 % mol) were dissolved in toluene(50ml) . The mixture was refluxed overnight. The resulting mixture was extracted with chloroform and brine. The organic layer was separated, dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and purified by column chromatography over silica gel with n-hexane : ethyl acetate (95 : 5) as the eluent to give the desired product. A red solid was obtained (product yield 85%). 1H NMR ($CDCl_3$, ppm): δ 7.84 (s, 2H), 7.43 (d, 2H), 7.21 (t, 2H), 6.61 (d, 2H) 13C NMR (CDCl3, ppm): δ 155.1, 142.8, 135.2, 129.1, 128.0, 127.9, 127.1.

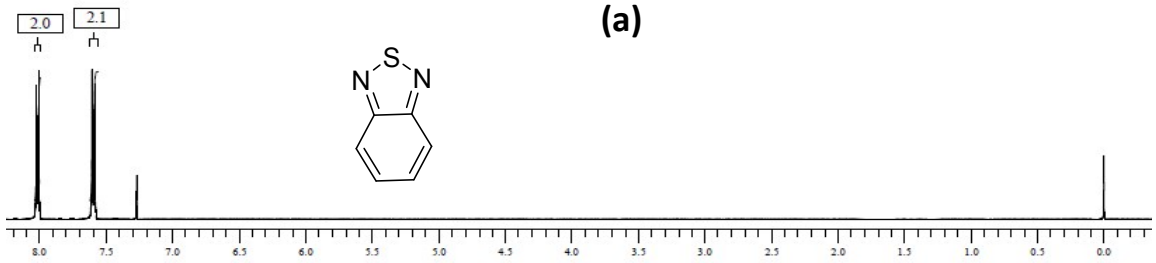


Scheme S1. Synthetic scheme for BT and DTBT

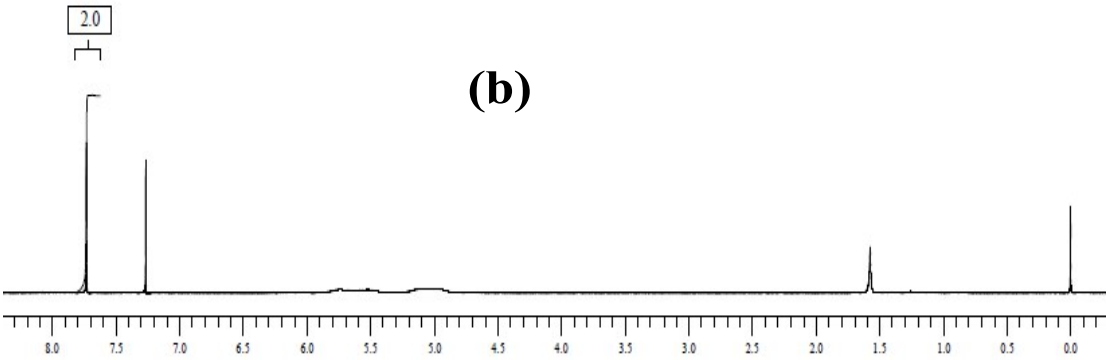
Synthesis of 4,7-Bis (5-(9-(2-ethylhexyl)-9H-carbazol-3-yl) thiophen-2-yl) benzo[c] [1,2,5] thiadiazole (CDTBT)[37]

The molecule CDTBT was synthesized using a procedure described elsewhere[37].

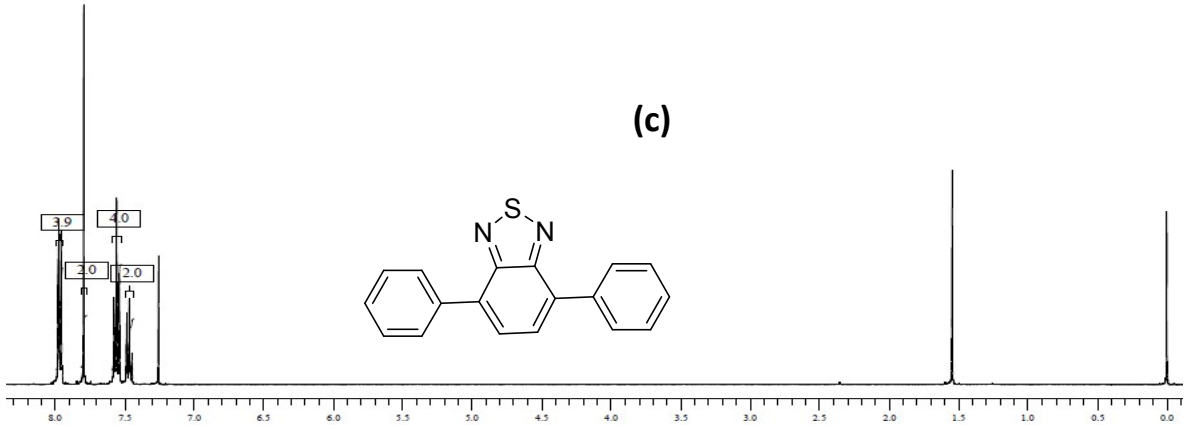
(a)


2.0
2.1
S
N
N
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

(b)


2.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

(c)


3.9
4.0
2.0
2.0
S
N
N
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

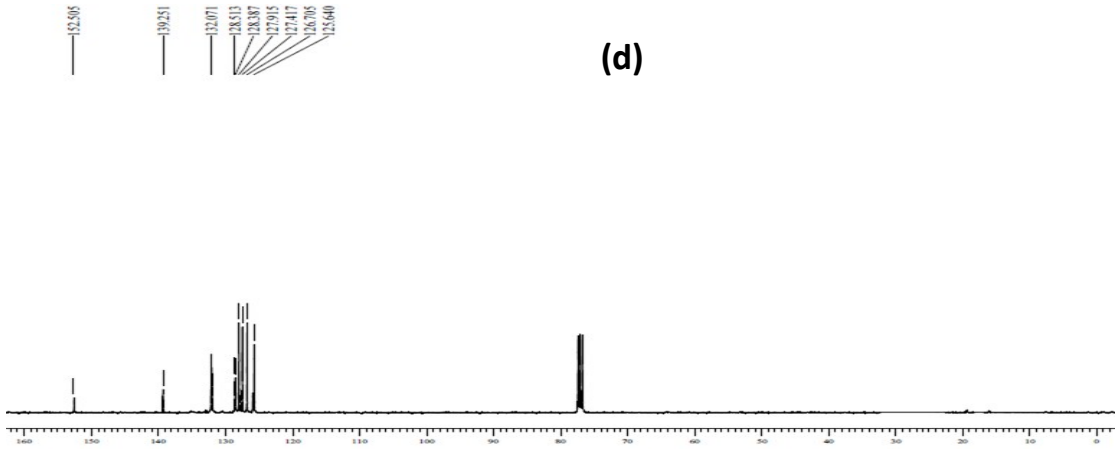


Fig. S1. NMR spectra of **BT** and **DTBT**. (a) ^{1}H NMR BT, (b) ^{13}C NMR of BT, (c) ^{1}H NMR of DTBT and (d) ^{13}C NMR of DTBT

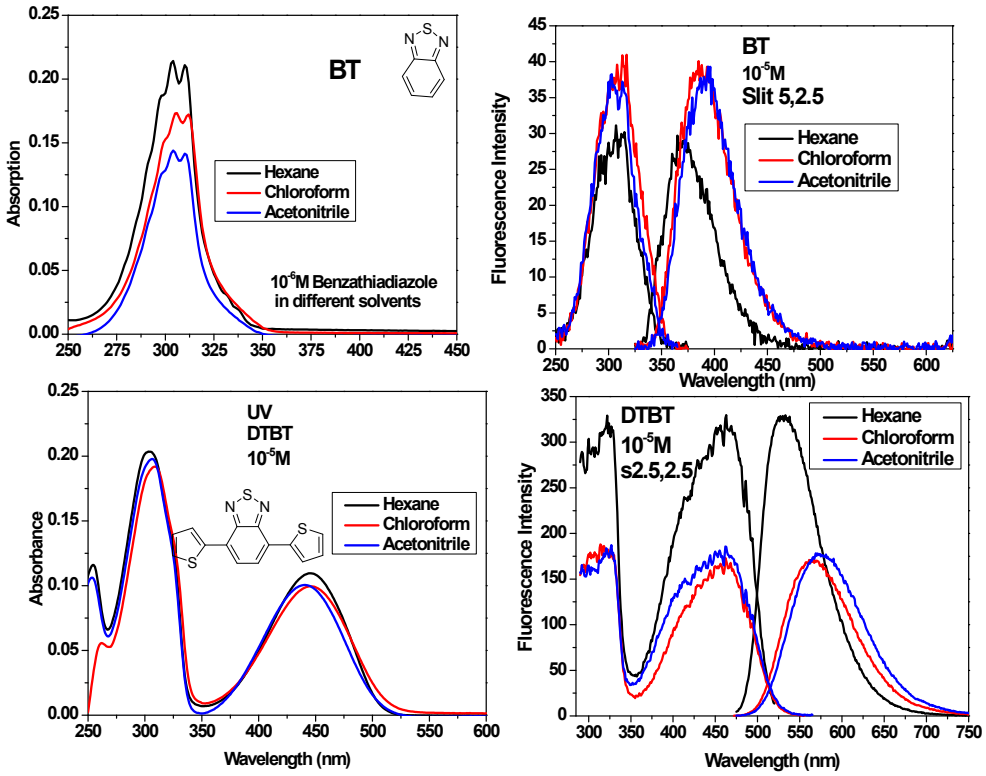


Fig. S2. Absortion and Emission spectra of BT and DTBT in hexane, chloroform and acetonitrile

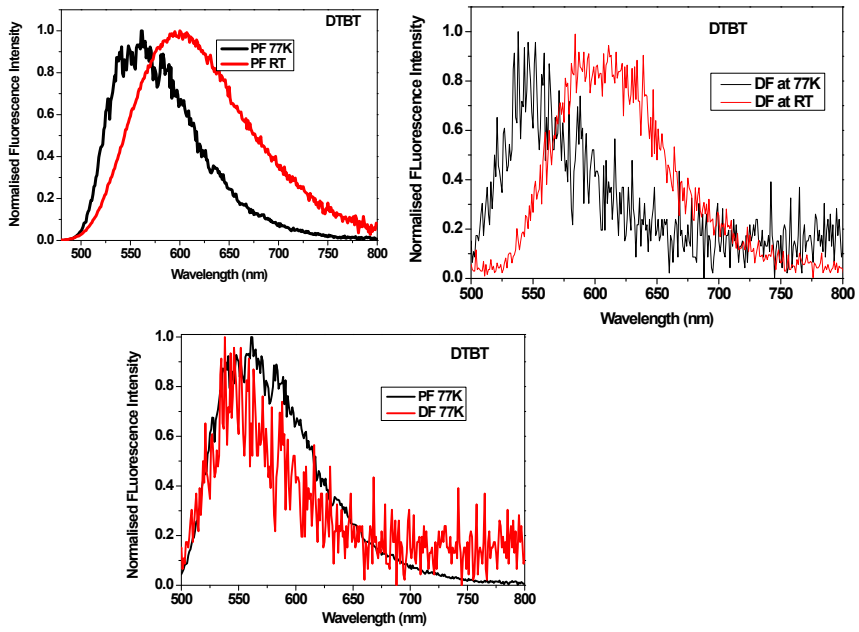


Fig. S3: Delayed fluorescence (DF) spectra of DTBT in ethanol and methanol mixtures (1:1) at room temperature and 77k. All phosphorescence measurements at RT and 77K were carried out in 1:1 ethanol-methanol solutions.

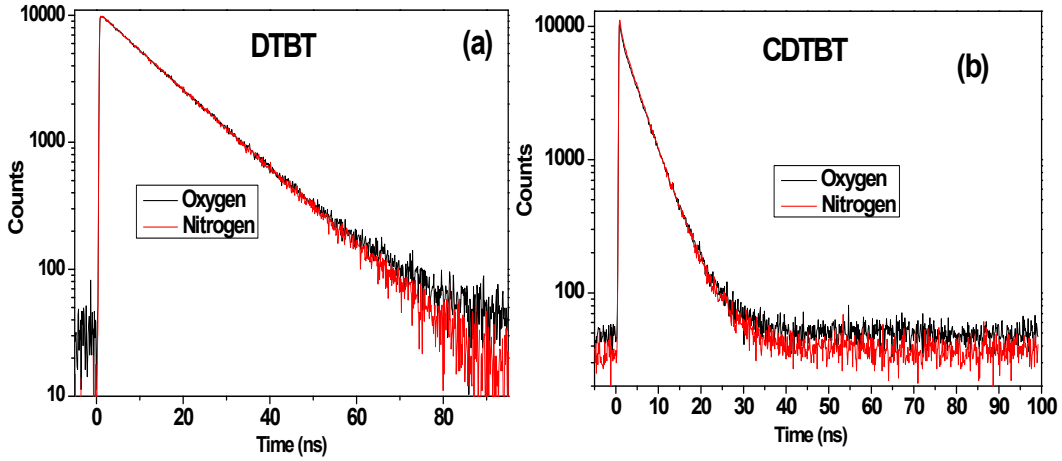


Fig. S4: TCSPC measurements of (a) DTBT and (b) CDTBT in oxygen and nitrogen