Supporting Information

Thermoresponsive fluorescent polymers based on a quaterthiophene-containing boron dipyrromethene (Bodipy) dyad dispersed in silicone rubber

Andrew C. Benniston, Graeme Copley, Anthony Harriman and Ruth Ryan

$^1H/^{13}C$ NMR Assignment

The most upfield shifted signal (at $\delta = 7.12$) in the aromatic region is assigned to H_2 (ring a) since the pattern corresponds to a doublet of doublets. By a combination of the COSY spectrum and the *J* coupling constants the other two protons H_1 and H_3 can now be assigned. Using the HMQC spectrum, the proton bearing carbon resonances corresponding to the four thiophene groups are identified, and confirmed (where possible) by the ^1J coupling constants in the HMBC spectrum. By careful inspection of the HMBC spectrum it is possible to identify all the quaternary carbons for the Bodipy group, and in particular the meso carbon (δ= 134.4 ppm) connecting it to the first thiophene group. This meso carbon in the HMBC spectrum shows a clear correlation (^3J) to the proton signal at $\delta = 7.19$ ppm, and is hence consistent with this proton being H_{15} on the thiophene (ring d). The COSY spectrum confirms this proton is coupled to the resonance at $\delta = 7.48$ ppm (i.e., H_{14}). Having identified the proton and carbon resonances for rings a and d, assignment of $^1H/^{13}C$ signals for the other two rings is performed by working outwards and finding correlations between quaternary carbons and ring protons. The only complication is the inability to completely assign protons H_7 and H_{10} since there is, even at 800 MHz, accidental equivalence of the proton signals.

Thiophene Ring Rotation

It is worth noting that there was no appreciable change in the shape or shift of the aromatic proton signals for **BD-T4** in D_6- DMSO over the limited temperature range of 298 to 313 K. There has been a number of NMR spectroscopic studies carried out on oligothiophenes,[1] and some controversy exists over the size of the rotation barrier. Muguruma and co-workers[2] showed for a quaterthiophene derivative containing bulky groups at either end that rotation was slow enough to be seen by NMR spectroscopy. However, recent work by Holdcroft *et al.*[3] concluded that rotational barriers for di- and tetra-thiophenes are low, and that NMR spectra reflect a system in the so-called fast exchange regime. In light of these findings, we assume that the three thiophenes (rings a-c) for T4 are free to rotate in solution. This notion is in keeping with the comparability of the high and low temperature NMR spectra. A remaining question concerns the relative rotational freedom of thiophene ring d which might be restricted by the two methyl groups on the Bodipy core. The lack of alteration in the proton signals for H_{14} and H_{15} in

DMSO with increasing temperature suggests that fast rotation takes place. However, molecular dynamics simulations (MDS) run in a solvent matrix suggest that the thiophene group rocks from side to side and does not spin round freely as needed from the NMR interpretation.

In related work, it was shown that a quinone group attached directly to the meso position of Bodipy is sufficiently bulky to hinder rotation about its axis.[4] The molar volume[5] of thiophene is less than that of benzo-1,4-quinone by ca. 13 cm^3 mol^{-1}, and this might permit easier rotation on the NMR timescale. The major overlap of aromatic signals for the dyad in other common NMR solvents meant that low temperature studies were not possible.

References

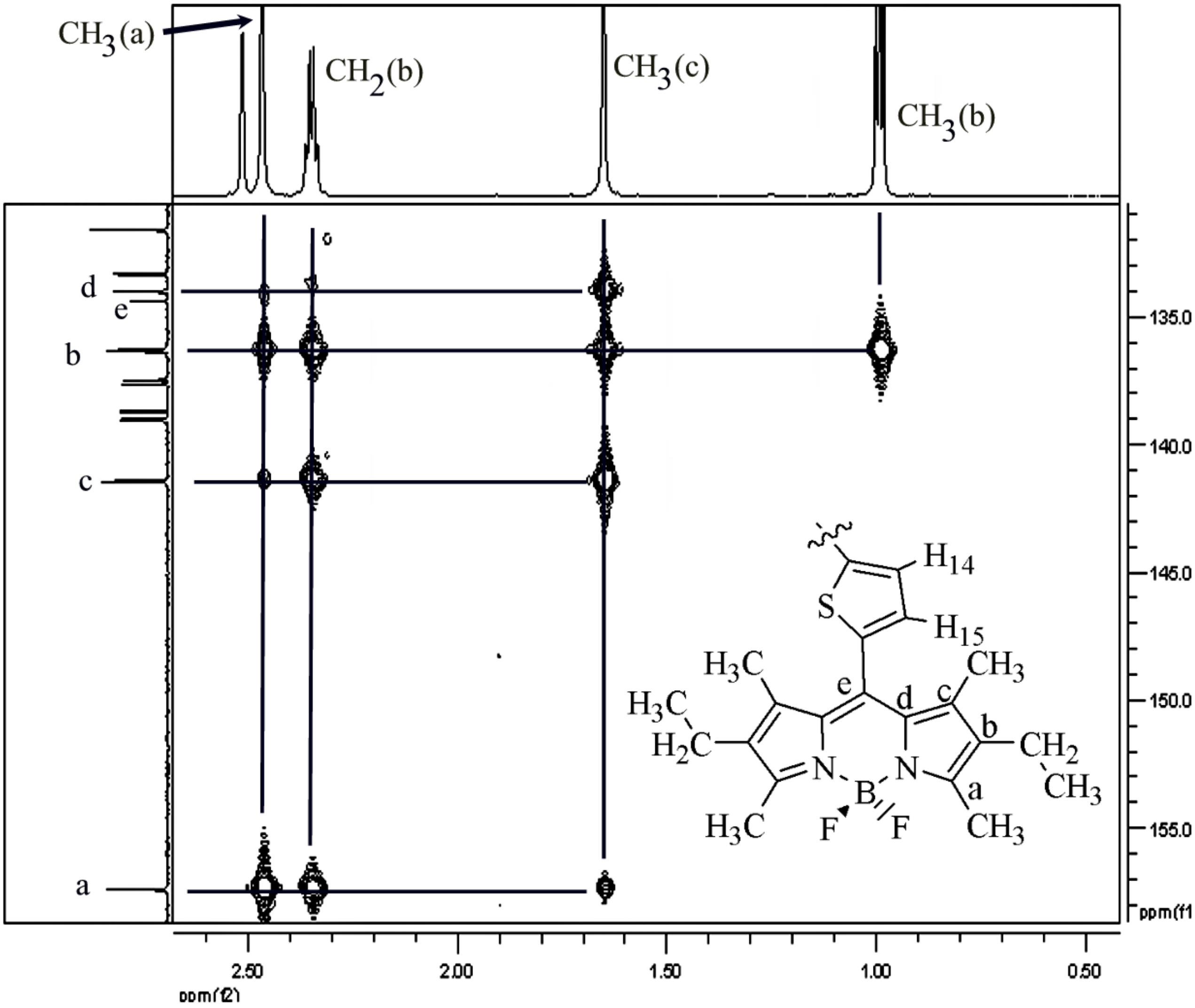
1: (a) L. DeWitt, G. J. Blanchard, E. LeGoff, M. E. Benz, J. H. Liao, M. G. Kanatzidis, *J. Am. Chem. Soc.* 1993, **115**, 12158-12164. (b) J. C. Horne, G. J. Blanchard, E. LeGoff, *J. Am. Chem. Soc.* 1995, **117**, 9551-9558.

2: H. Muguruma, K. Kobiro, S. Hotta, *Chem. Mater.* 1998, **10**, 1459-1467.

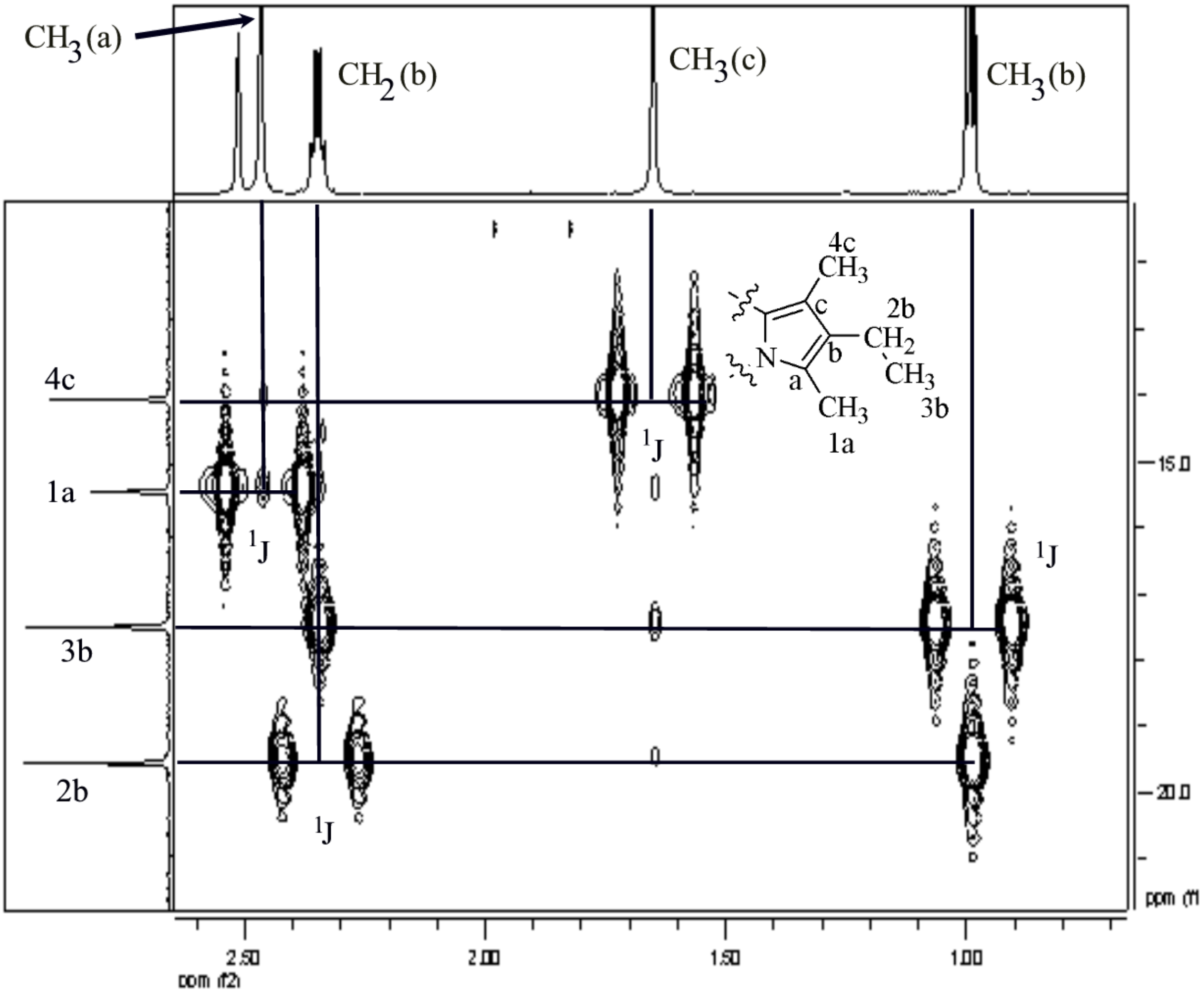
3: G. A. Diaz-Quijada, N. Weinberg, S. Holdcroft, B. M. Pinto, *J. Phys. Chem. A* 2002, **106**, 1266-1276.

4: A. C. Benniston, G. Copley, K. J. Elliott, R. W. Harrington, W. Clegg, *Eur. J. Org. Chem*. 2008, 2705-2713.

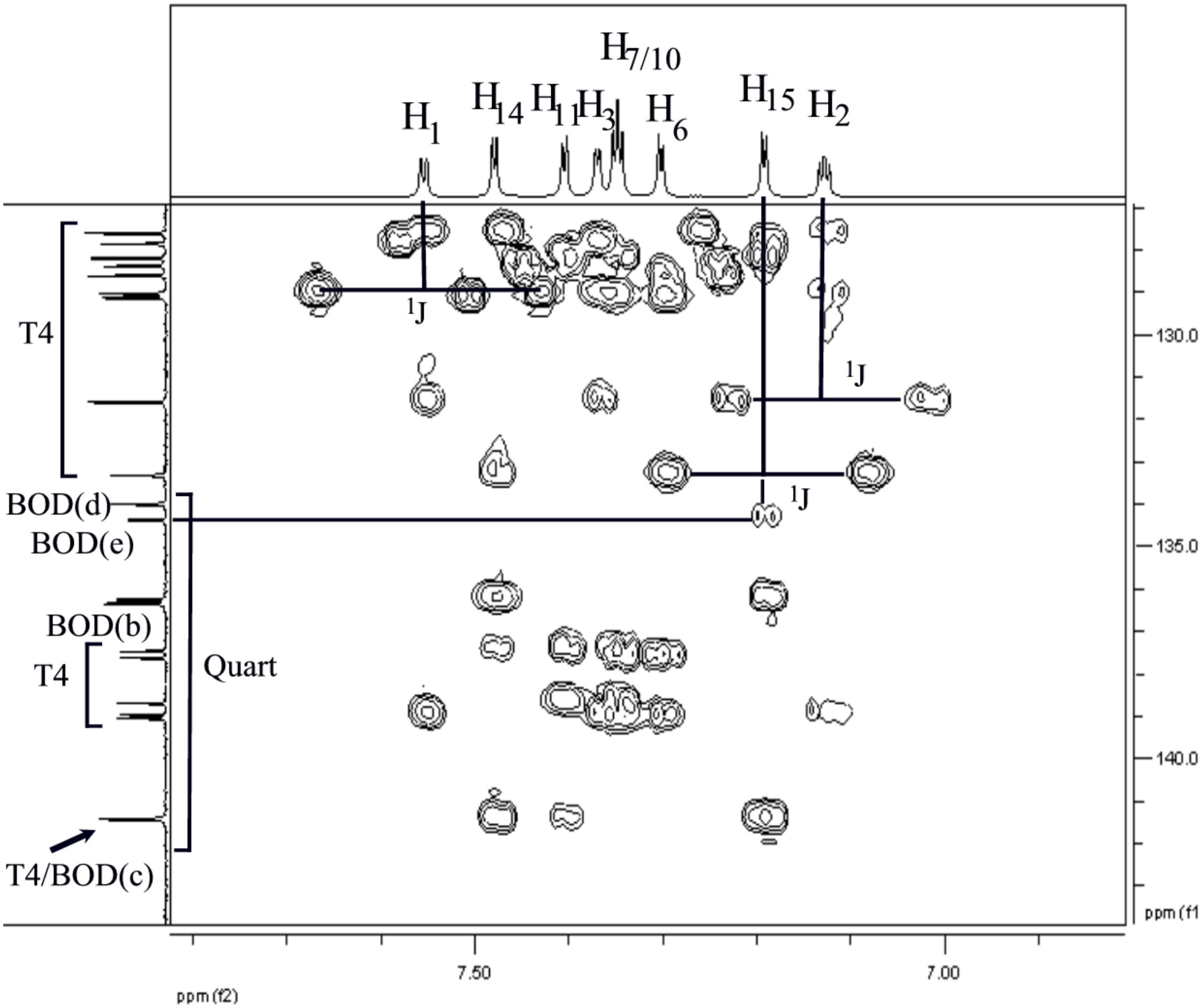
5: A. Bondi, *J. Phys. Chem*. 1964, **68**, 441-451.



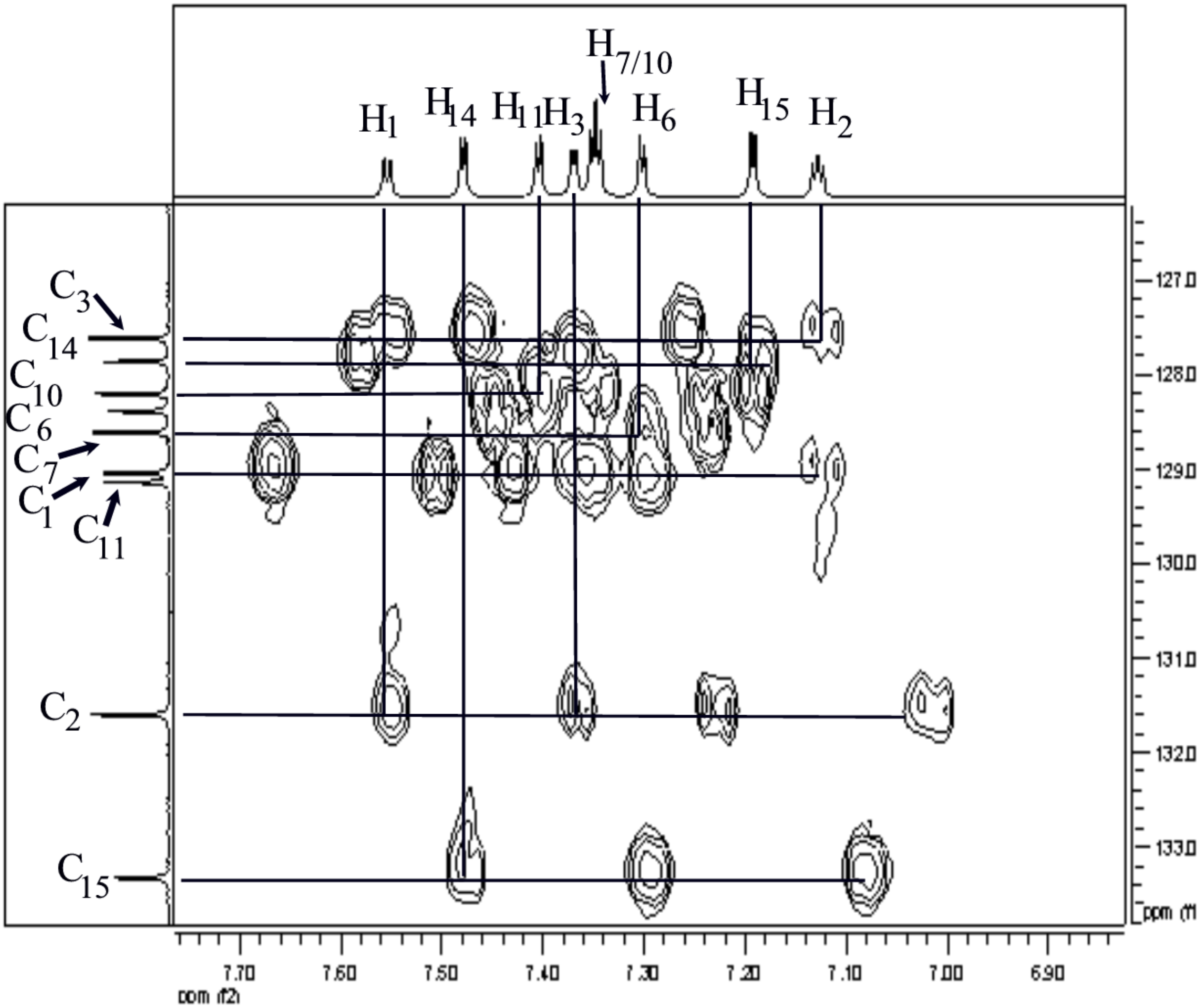
S1. Partial HMBC spectrum of **BD-T4** in D_6-DMSO showing the assignment of the Bodipy carbon resonances.



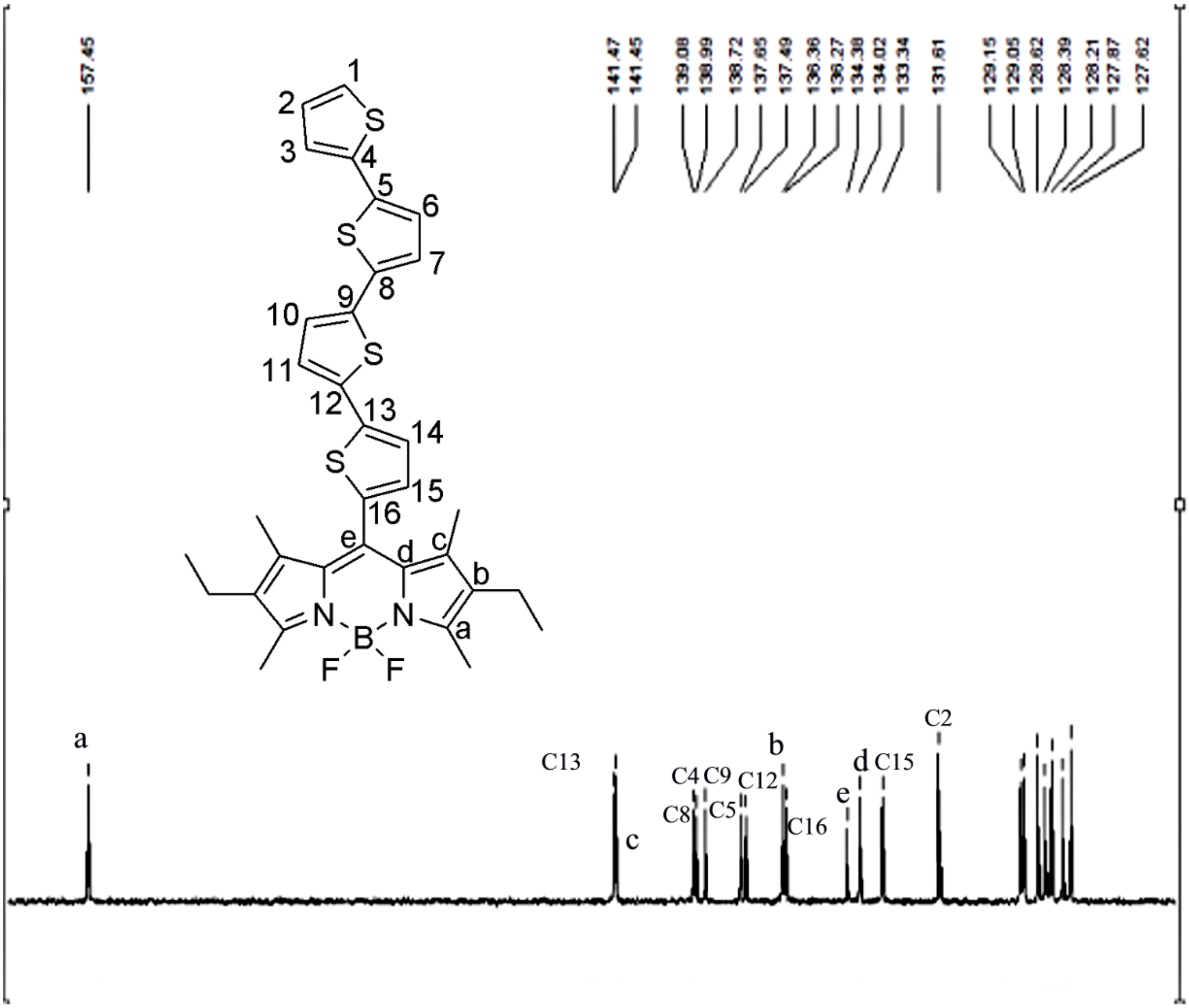
S2. Partial HMBC spectrum of **BD-T4** in D_6-DMSO showing assignment of the alkyl group carbon resonances for the Bodipy group.



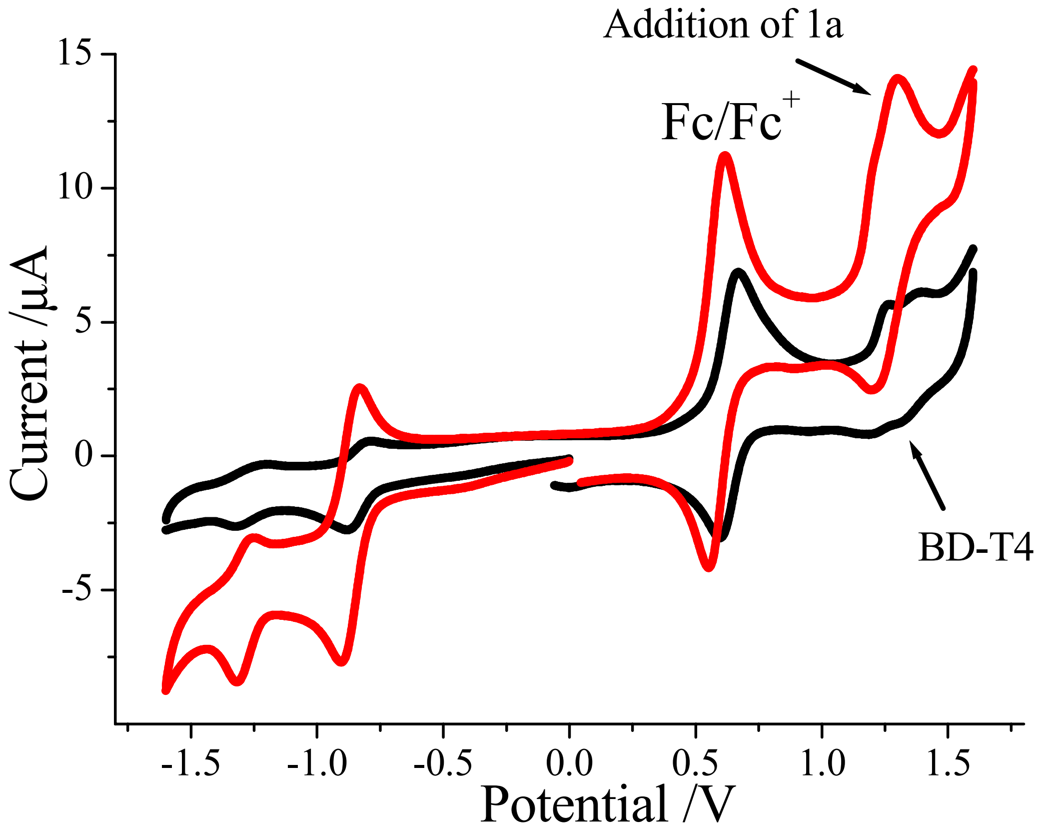
S3. Partial HMBC spectrum of **BD-T4** in D_6-DMSO showing partial assignment of the Bodipy and oligothiophene carbon resonances.



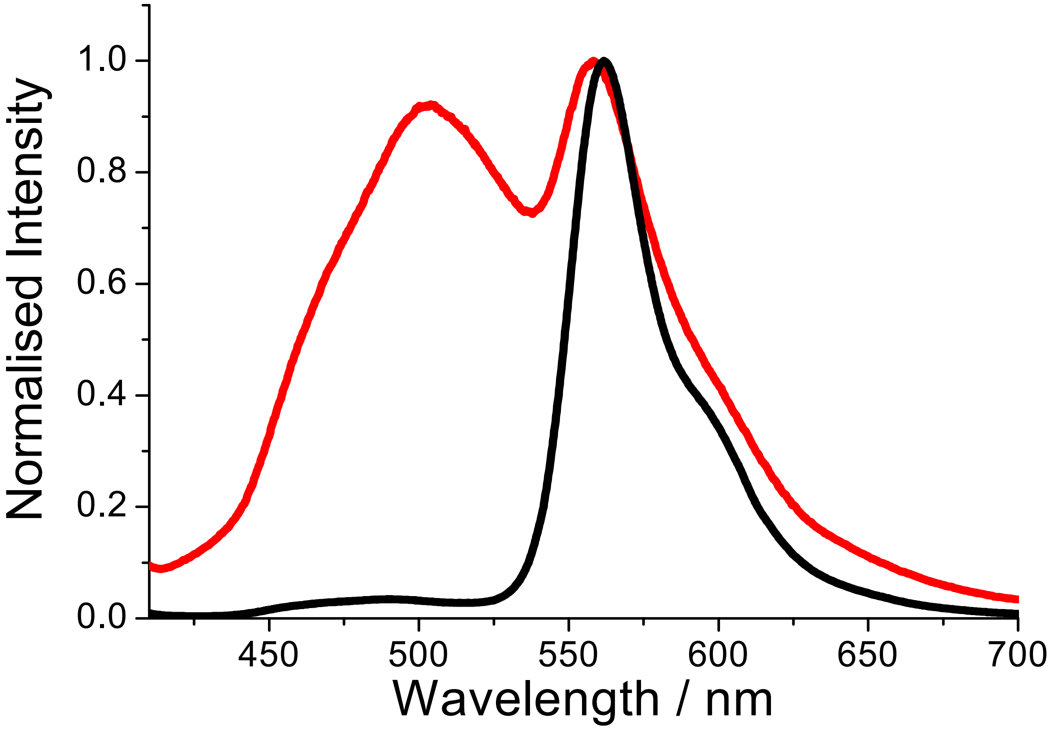
S4. Partial HMBC spectrum of **BD-T4** in D_6-DMSO showing the assignment of the oligothiophene carbon resonances.



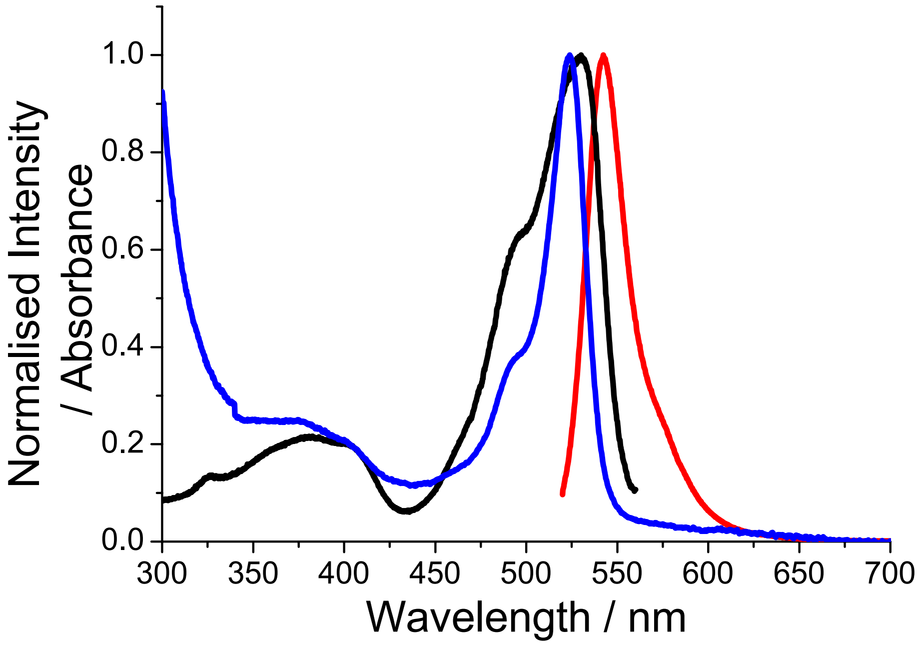
S5. ^{13}C {^{1}H} NMR spectrum of **BD-T4** in D_6-DMSO showing the partial assignment of the Bodipy and oligothiophene carbon resonances.



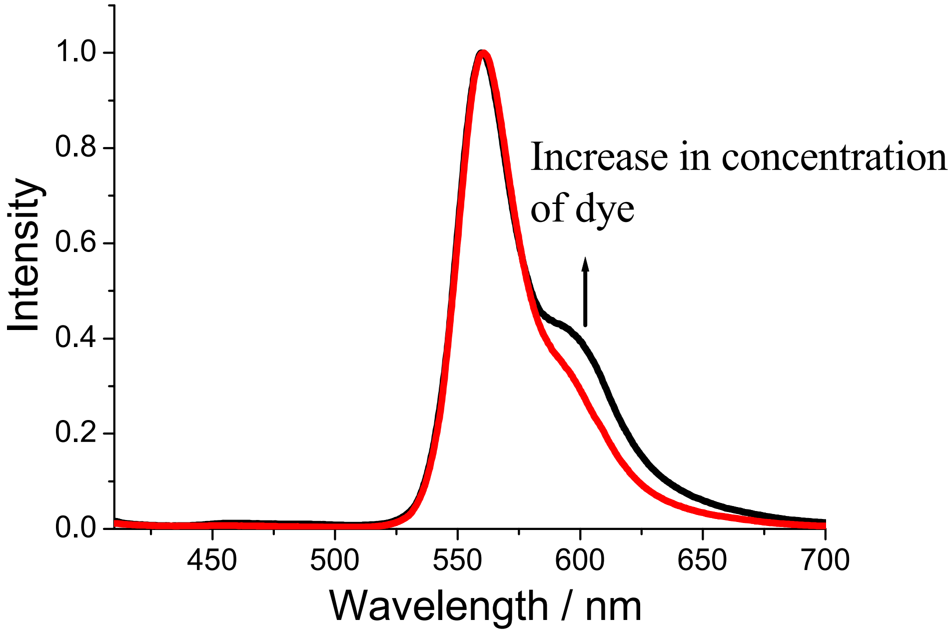
S6. Cyclic voltammograms for **BD-T4** (dark) and in the presence of **1a** (red) in dry N_2-purged CH_3CN (0.2 M TBATFB) at a Pt working electrode and Ag wire reference. Scan rate = 100 mVs^{-1}.



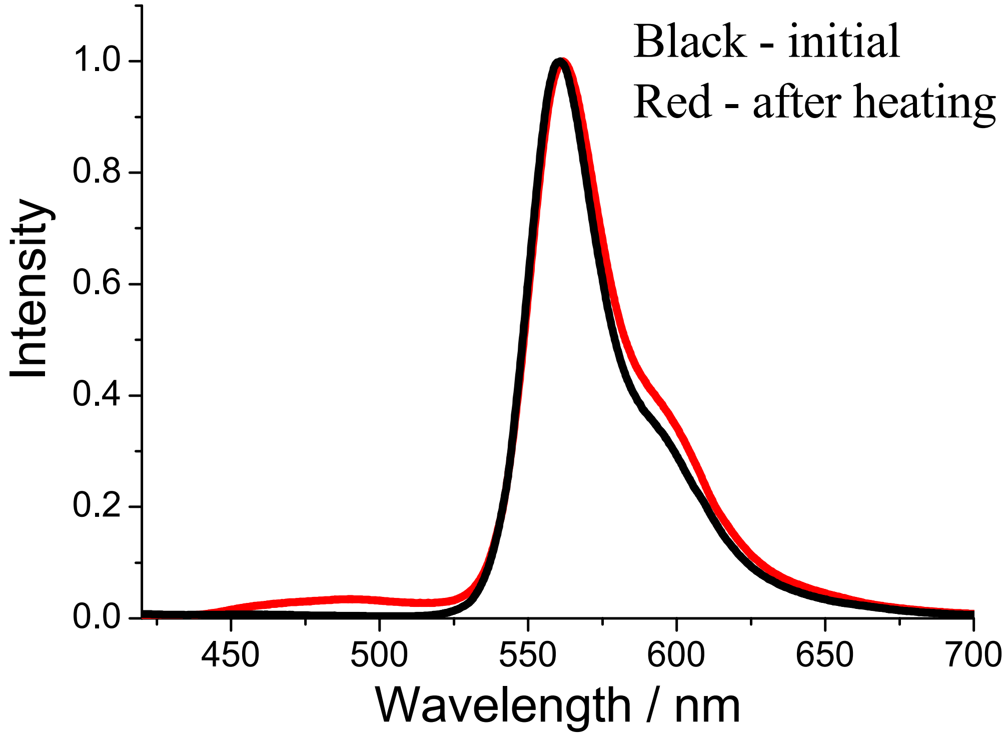
S7. Comparison of the emission spectra for **BD-T4** dispersed in silicone rubber before (black) and after (red) exposure to sunlight for 48 hrs. Excitation wavelength = 400 nm.



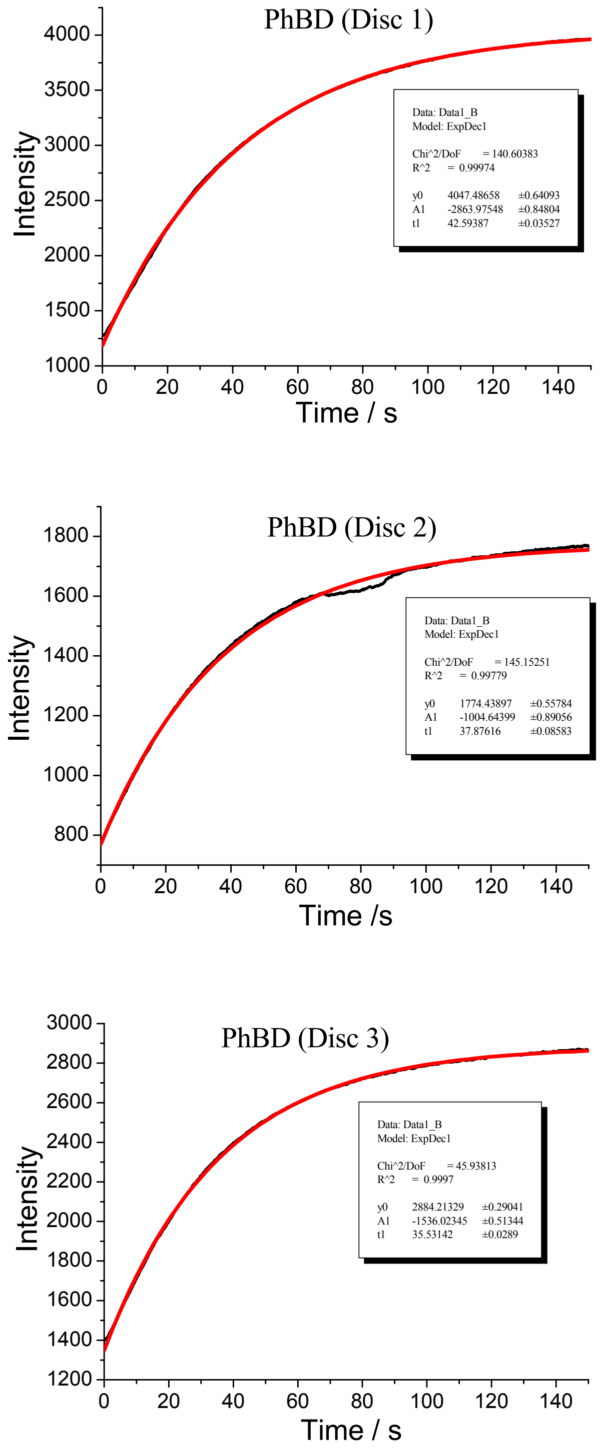
S8. Absorption spectrum (blue), emission spectrum (red) and fluorescence excitation spectrum (black) for **PhBD** dispersed in silicone rubber under optimised conditions. Excitation wavelength = 510 nm.



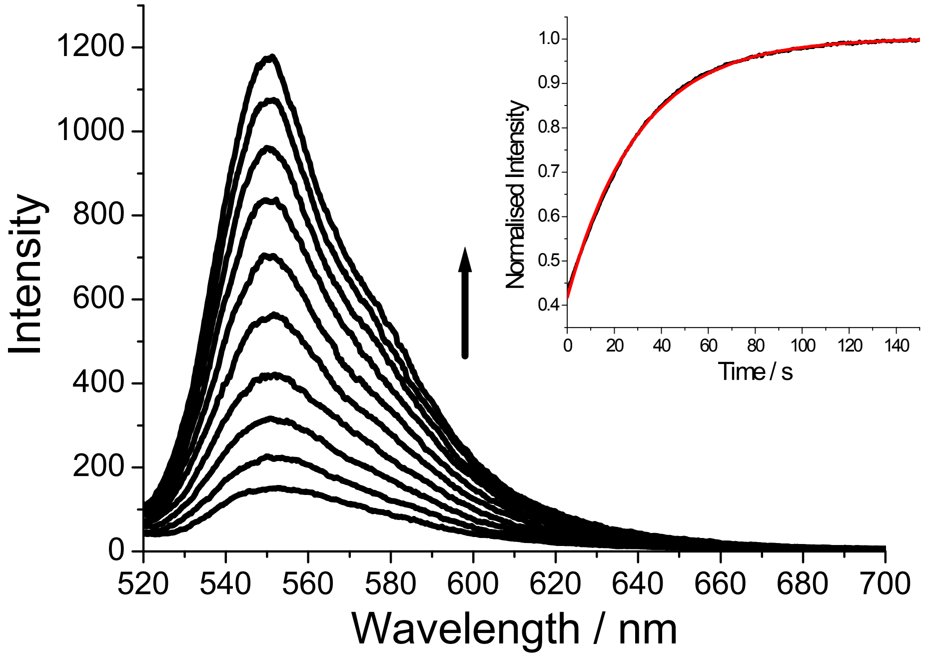
S9. Comparison of the fluorescence emission spectra for **BD-T4** dispersed in silicone rubber at two different concentrations. Excitation wavelength = 400 nm.



S10. Emission spectra for **BD-T4** dispersed in silicone rubber before and after heating. The dye concentration is ca. 5 fold lower than that shown in Figure 6. Excitation wavelength = 400 nm.



S11. Recovery in fluorescence intensity with time for **PhBD** dispersed in silicone rubber after heating. The concentration of dye dispersed in the silicone rubber decreases from disc 1 to disc 3. (Disc 3: 2.6 x10^{-7} moles in 0.95 g of silicone; disc 2: 2.6 x10^{-7} in 0.38 g silicone; disc 1: 1.1 x 10^{-6} moles in 0.44 g of silicone)



S12. Recovery in fluorescence intensity with time for **PhBD** dispersed in silicone rubber after heating. The concentration of the dye is approximately half that shown for Figure 5 in the text.