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SUPPLEMENTARY MATERIAL

Confinement effect on the photophysics of ESIPT fluorophores

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1. Materials and Methods

The octaacid (OA) and the fluorophores were synthesized by following the literature procedure.[1,2] ^{1}H and ^{13}C NMR spectra for the fluorophores were recorded on a Varian VNMRs 300 MHz spectrometer. The chemical shifts were expressed as δ (ppm) relative to tetramethylsilane (TMS) as the internal standard and using DMSO-d_6 as the solvent.

^{1}H NMR titration: The ^{1}H NMR titration experiments were carried out on a Bruker 500 MHz NMR spectrometer at 25^{o}C. To 0,6 mL of octaacid solution 1 mM (in 10 mM $Na_2B_4O_7$ in D_2O) taken in a NMR tube, 0.25 equivalent increments of the guest (2.5 μL of 60 mM in DMSO-d_6) were added till it reached host:guest ratio of 1:1. After shaking the NMR tube for 2 min after each addition the spectra were recorded.

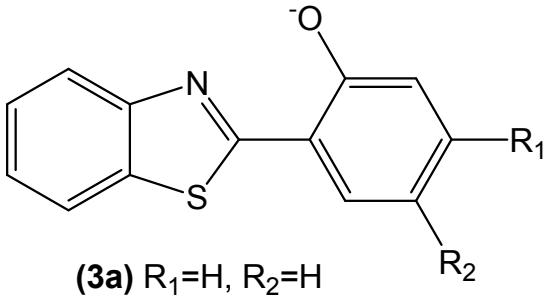
Solution Concentration: The fluorophores in solution were studied at a concentration of 10^{-5} M in acetonitrile, ethanol, dichloromethane, benzene and buffered water (10 mM $Na_2B_4O_7$ water solution, pH 9).

Inclusion complexes 2:1 (G:H) were studied and prepared by adding 5.0 μL of 60 mM DMSO-d_6 solution of the fluorophores (guest) to 0.6 mL of 1 mM OA in 10 mM $Na_2B_4O_7$ water solution and diluted using the latter $Na_2B_4O_7$ buffer.

Photophysics study: UV-Vis absorption spectra were recorded by using a Shimadzu UV-2101PC spectrophotometer. The steady-state luminescence spectra were recorded using the absorption maxima as excitation wavelength in a FS920CDT fluorimeter (Edinburgh Analytical Instruments). Fluorescence lifetime was measured by time-correlated single photon counting using a nF920 fluorimeter (Edinburgh Analytical Instruments). EPLED-330 (330 nm), EPLED-360 (360 nm) and EPL 405 (405 nm) were used as excitation source for guest:host complexes and free guests. All measurements were performed at room temperature (25^{o}C). To the lifetime measurements, a monochromator was used to set a particular wavelength in despite of the total fluorescence. The fluorescence decay curves were analyzed using the software F900 (Analysis of Lifetime Data). A mono ($Fit=A+B_1\exp(-t/\tau_1)$) and bi-exponential ($Fit=A+B_1\exp(-t/\tau_1)+B_2\exp(-t/\tau_2)$) approximations were used. A nonlinear least square method was employed to fit the decay to a sum of exponentials. The value of χ^2 and a

visual inspection of the residuals and the autocorrelation function were used to determine the quality of the fit. The quantum yield of fluorescence (Φ_{FL}) was calculated at 25°C using quinine sulfate (Riedel) in H_2SO_4 0.5 M and coumarin-153 (Aldrich) in ethanol as standards.[3,4]

2. Structure of the ionic species



(3a) R_1=H, R_2=H
(3b) R_1=NH_2, R_2=H
(3c) R_1=H, R_2=NH_2

Figure S23. Structure of the ionic species of **3a-c**, where the counterion is sodium.

3. Chemical structure and schematic representation of the host OA

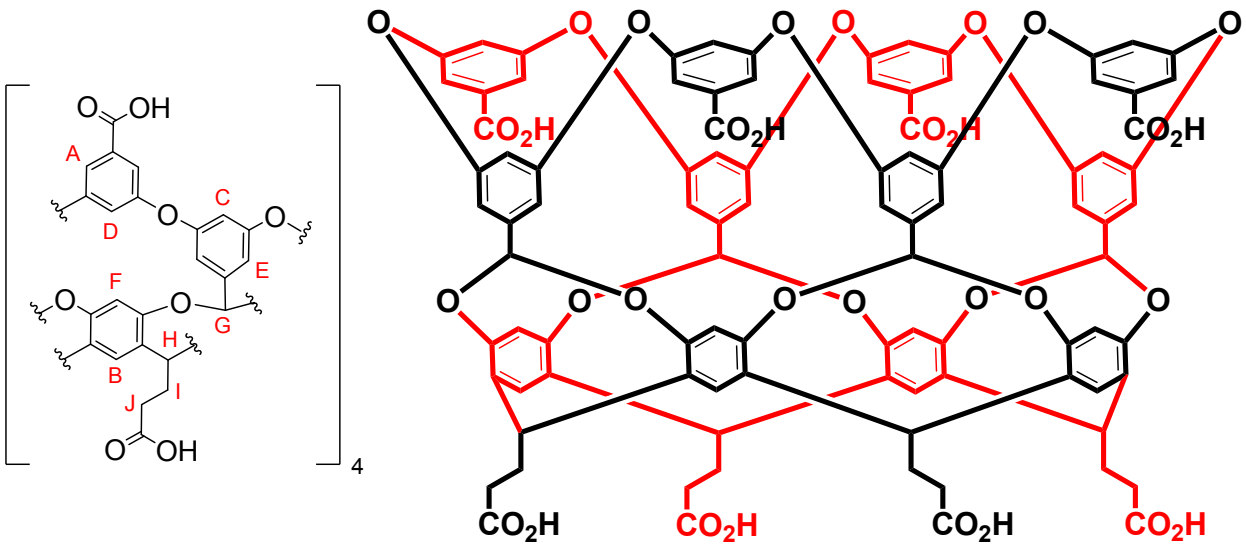


Figure S27. Chemical structure and schematic representation of the host OA protons A-J used to examine the ^{1}H NMR spectra.

4. Titration Experiments

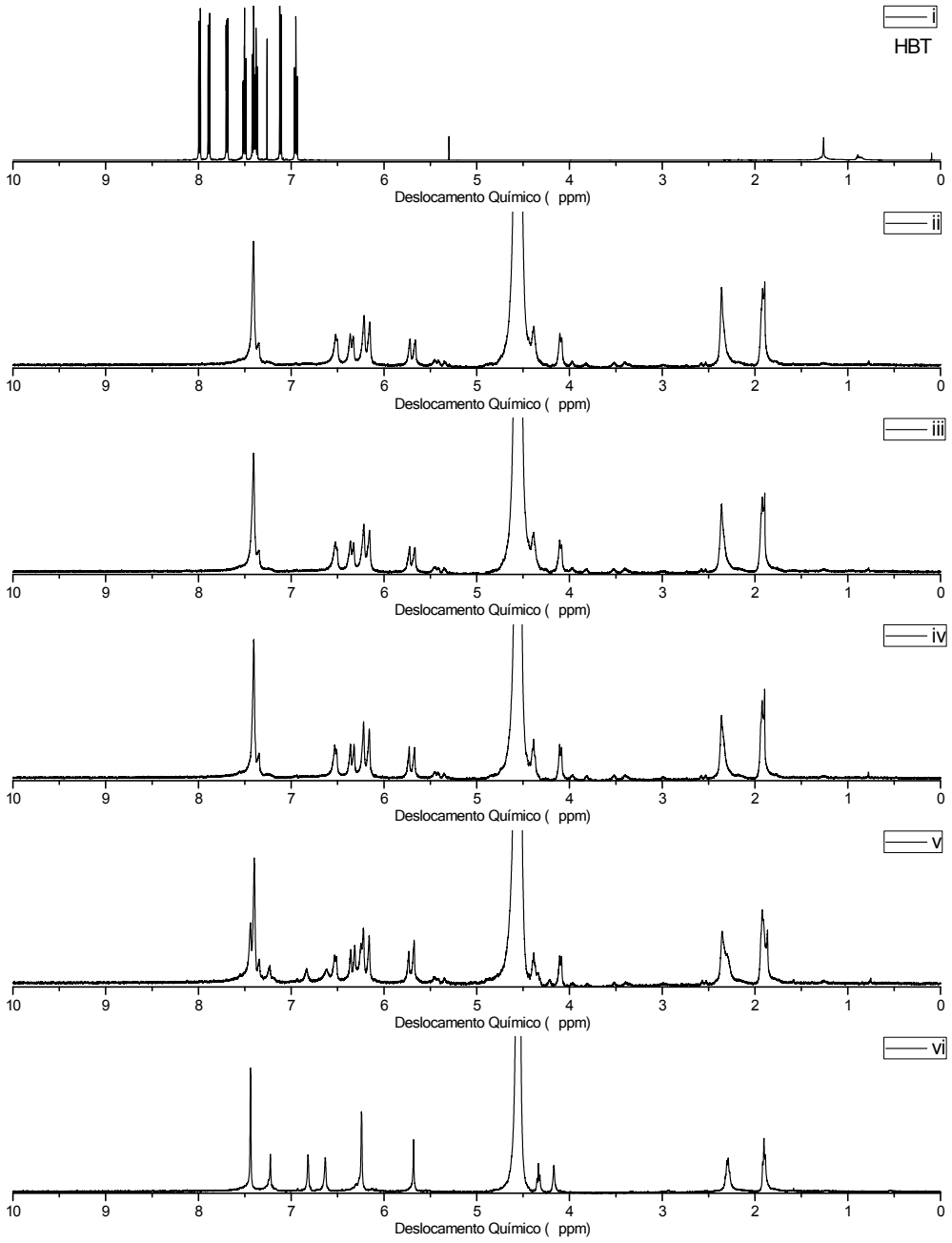


Figure S28. ^{1}H NMR spectra of (i) **HBT** in $CDCl_3$; (ii-v) **HBT** (60 mM DMSO-d_6 solution) in presence of OA at different guest:host (**1**:OA) molar ratio by fixing the host concentration and increasing the guest volume stepwise. (ii) 10.0 µL, (iii) 7.5 µL, (iv) 5.0 µL, (v) 2.5 µL and (v) 0.6 mL of 1 mM OA in 10 mM $Na_2B_4O_7$ D_2O solution.[5] A-J represents the uncomplexed OA proton signals; a'-j' represent complexed OA proton signals, and * represents the guest proton signals.

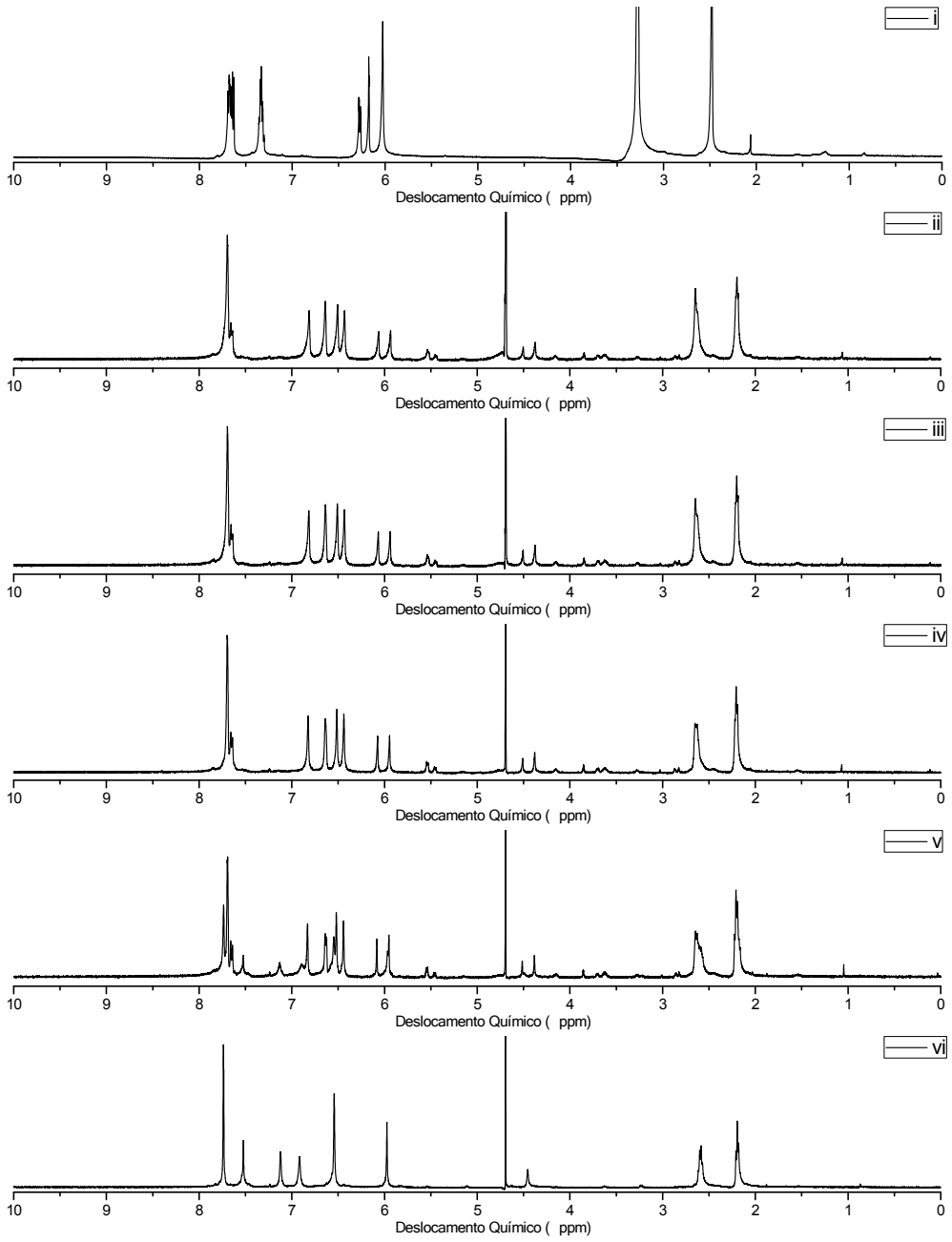


Figure S29. ^{1}H NMR spectra of (i) **4AHBT** in DMSO-d_6; (ii-v) **4AHBT** (60 mM DMSO-d_6 solution) in presence of OA at different guest:host (**1**:OA) molar ratio by fixing the host concentration and increasing the guest volume stepwise. (ii) 10.0 µL, (iii) 7.5 µL, (iv) 5.0 µL, (v) 2.5 µL and (v) 0.6 mL of 1 mM OA in 10 mM $Na_2B_4O_7$ D_2O solution.[6] A-J represents the uncomplexed OA proton signals; a'-j' represent complexed OA proton signals, and * represents the guest proton signals.

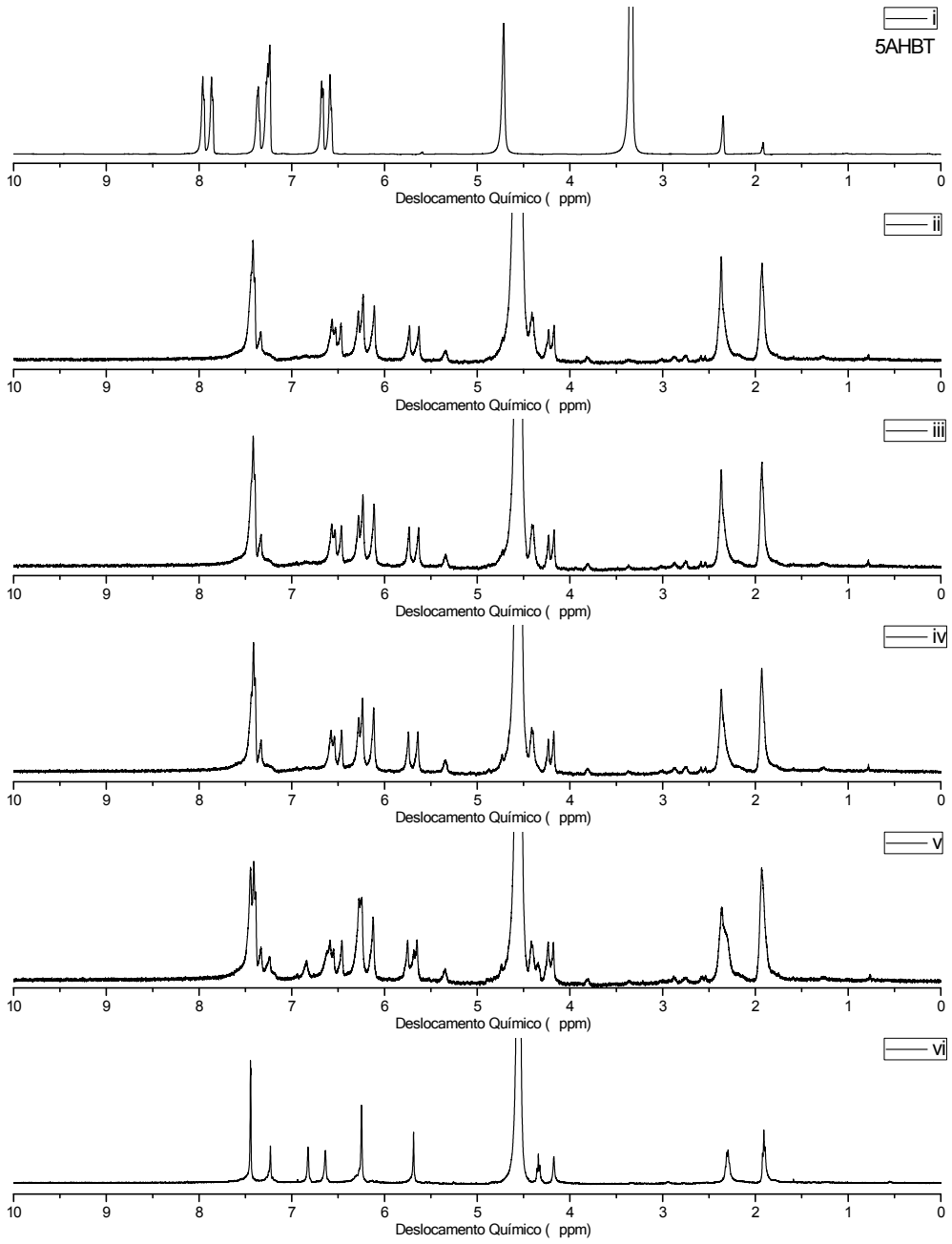


Figure S30. ^{1}H NMR spectra of (i) **5AHBT** in DMSO-d_6; (ii-v) **5AHBT** (60 mM DMSO-d_6 solution) in presence of OA at different guest:host (**1**:OA) molar ratio by fixing the host concentration and increasing the guest volume stepwise. (ii) 10.0 µL, (iii) 7.5 µL, (iv) 5.0 µL, (v) 2.5 µL and (v) 0.6 mL of 1 mM OA in 10 mM $Na_2B_4O_7$ D_2O solution.[7] A-J represents the uncomplexed OA proton signals; a'-j' represent complexed OA proton signals, and * represents the guest proton signals.

5. Photophysical data

Table S4. Relevant data from the time resolved fluorescence spectroscopy from **HBT-4AHBT-5AHBT** and the respective inclusion complexes within OA, where λ_{em} is the analyzed emission wavelength, λ_{ex} is the excitation source in nanometers, B is the pre-exponential factor, τ is the fluorescence lifetime, *Rel.* is relative contribution and χ^2 is the chi-square of the fit.

Environment[a)]	λ_{ex} (nm)	λ_{em} (nm)	A	B_1	τ_1 (ns)	Rel. %	B_2	τ_2 (ns)	Rel. %	χ^2
HBT										
Ethanol	330	507	6.886	678.971	3.204	100	-	-	-	1.106
	330	374	-1.235	66.586	2.717	100	-	-	-	1.108
DCM	330	530	3.085	88.536	2.579	100	-	-	-	1.096
Benzene	330	536	1.921	116.149	2.724	100	-	-	-	1.098
@$(OA)_2$	330	451	37.069	2446.018	3.558	100	-	-	-	1.101
	330	529	34.027	4245.108	1.794	58.93	1086.122	4.887	41.07	1.118
4AHBT										
Ethanol	330	404	48.127	20819.852	1.768	100	-	-	-	1.127
DCM	330	398	57.156	1067.650	1.519	100	-	-	-	1.114
	330	503	11.442	116.665	2.247	100	-	-	-	1.069
Benzene	360	395	13.955	525.473	1.478	100	-	-	-	1.144
	360	509	44.903	247.551	2.230	100	-	-	-	1.198
@$(OA)_2$	360	505	37.488	1954.279	2.165	100	-	-	-	1.146
	360	432	33.663	5516.392	2.345	100	-	-	-	1.119
5AHBT										
Ethanol	360	521	66.778	10530.253	3.134	100	-	-	-	1.110
DCM	360	470	197.384	7023.738	2.585	13.37	15077.892	7.800	86.63	1.039
	360	624	43.436	274.445	2.950	100	-	-	-	1.118
Benzene	360	467	32.627	2352.718	2.493	23.73	2463.696	7.650	76.27	1.102
	360	624	46.739	293.629	4.190	100	-	-	-	1.216
@$(OA)_2$	405	619	17.118	410.521	2.783	100	-	-	-	1.116
		498	8.767	4391.830	2.913	70.00	862.577	6.357	30	1.104

[a)] DCM=Dichloromethane

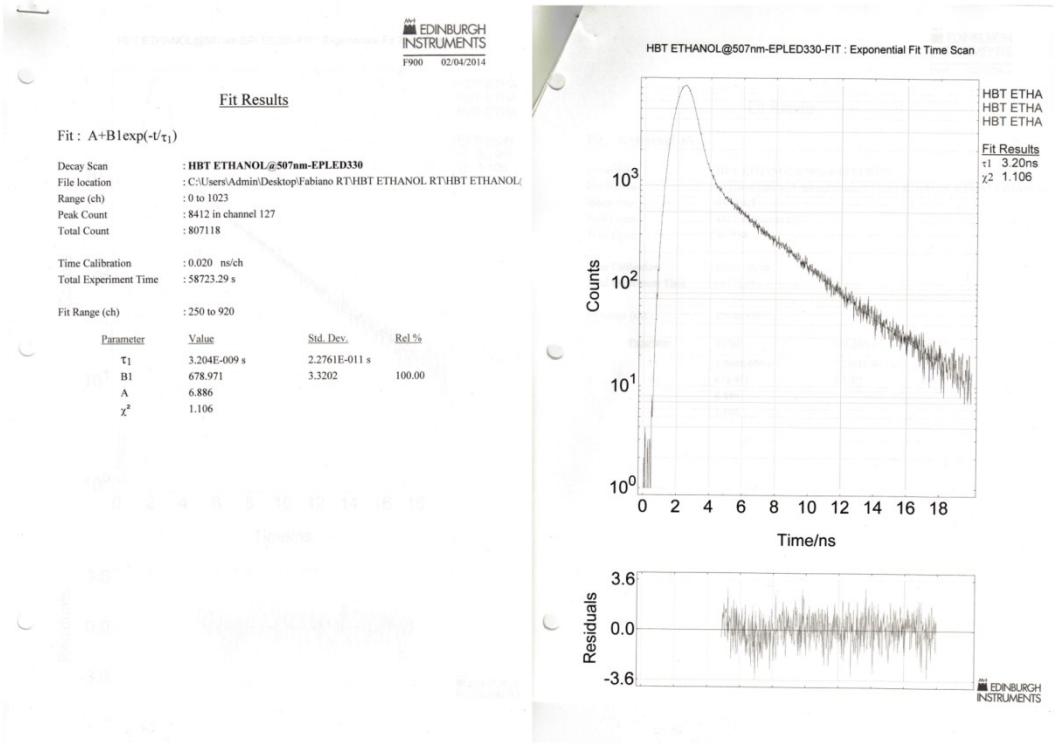


Fig. S31. Fit results of the HBT in ethanol @507 nm EPLED 330 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

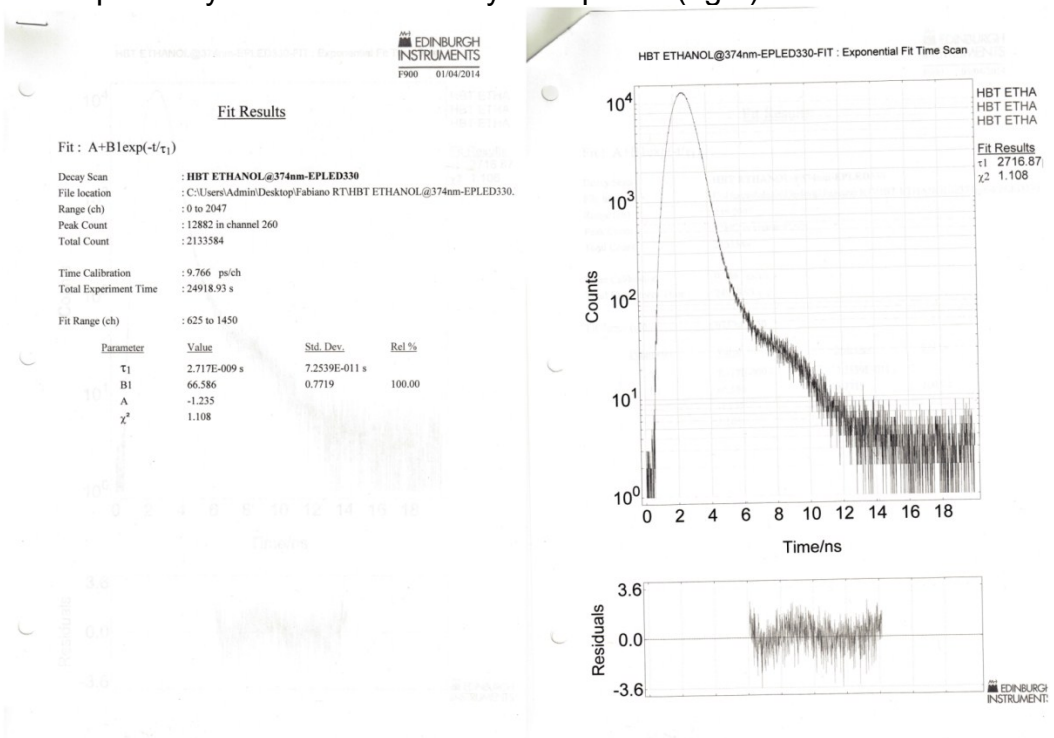


Fig. S32. Fit results of the HBT in ethanol @374 nm EPLED 330 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

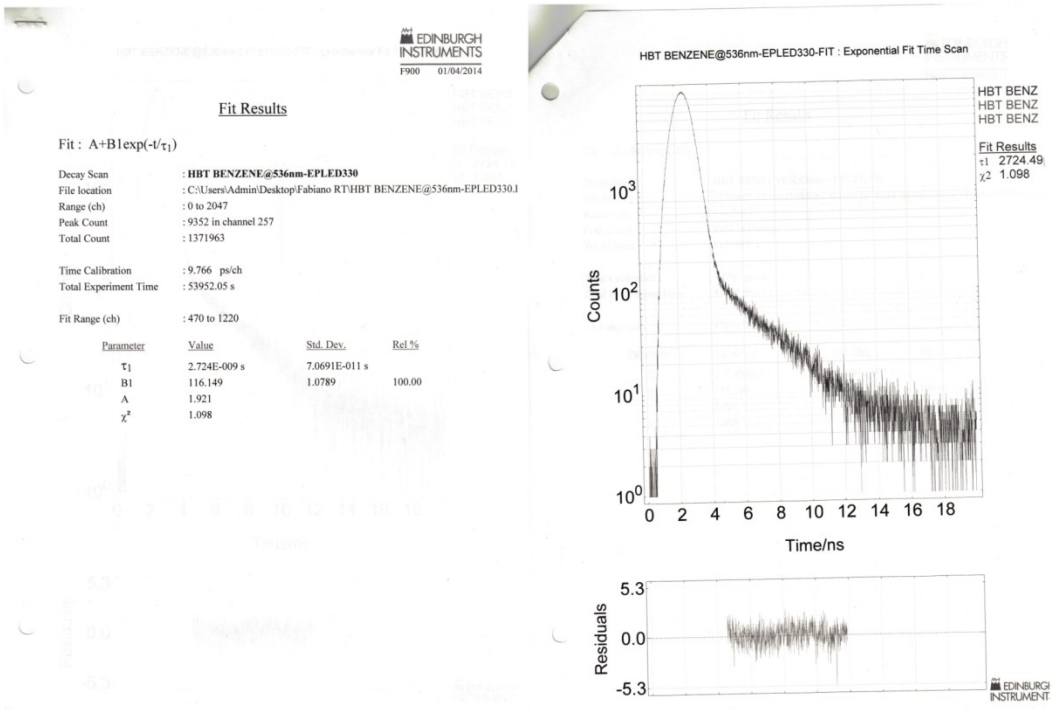


Fig. S33. Fit results of the HBT in benzene @536 nm EPLED 330 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

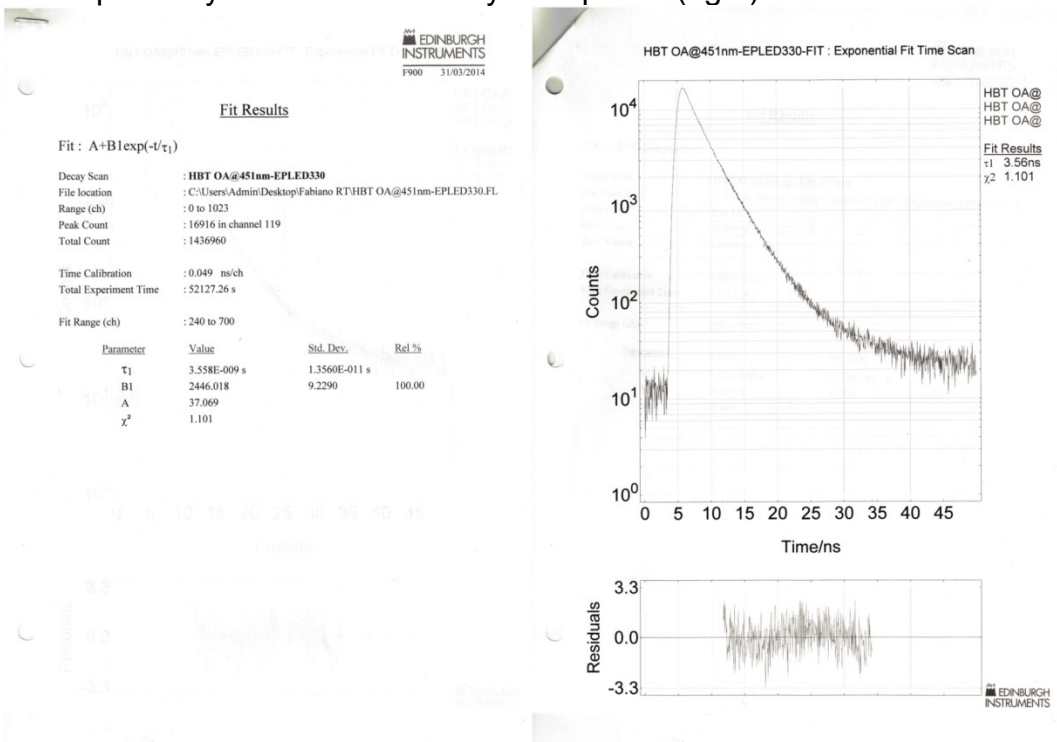


Fig. S34. Fit results of the HBT@$(OA)_2$ @451 nm EPLED 330 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

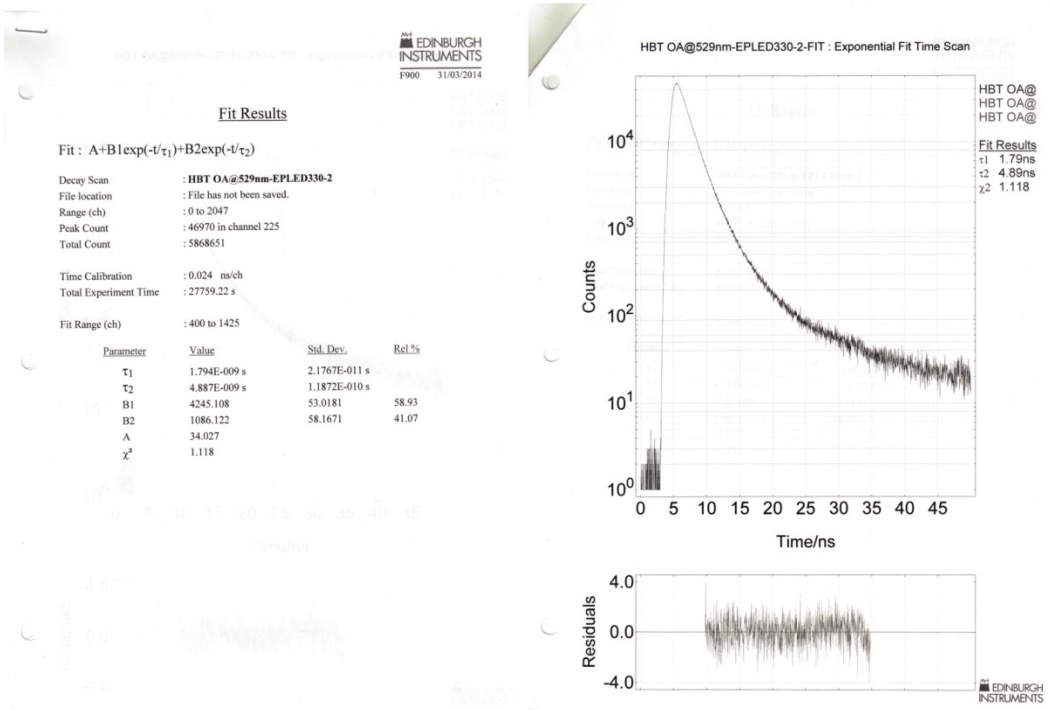


Fig. S35. Fit results of the HBT@$(OA)_2$ @529 nm EPLED 330 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

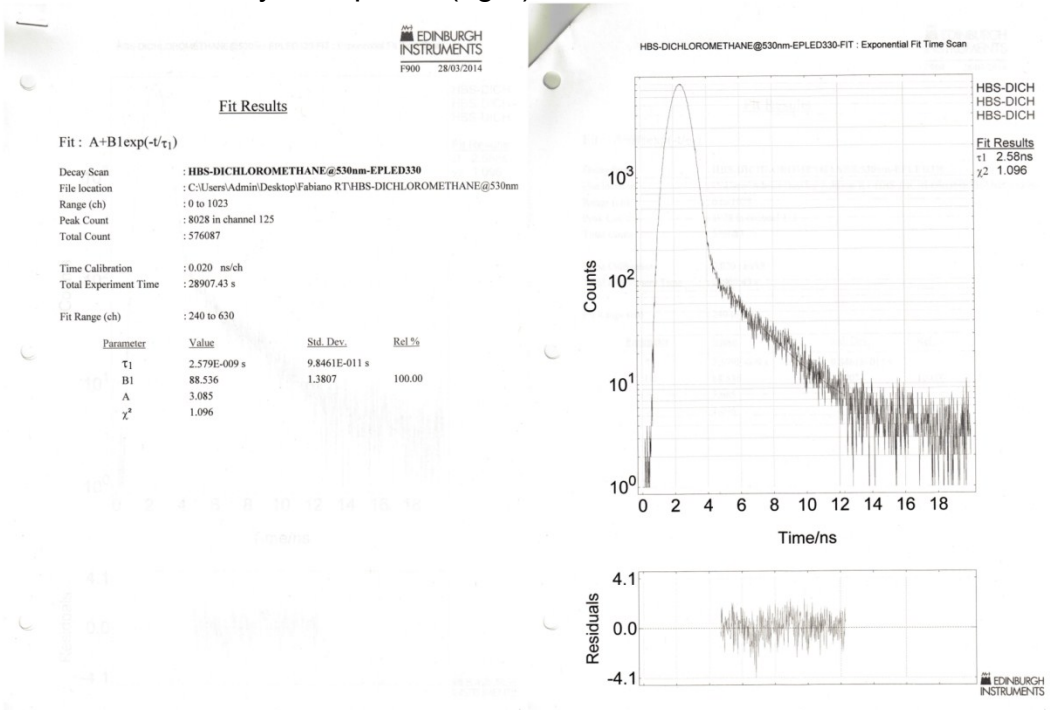


Fig. S36. Fit results of the HBT in dichloromethane @530 nm EPLED 330 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

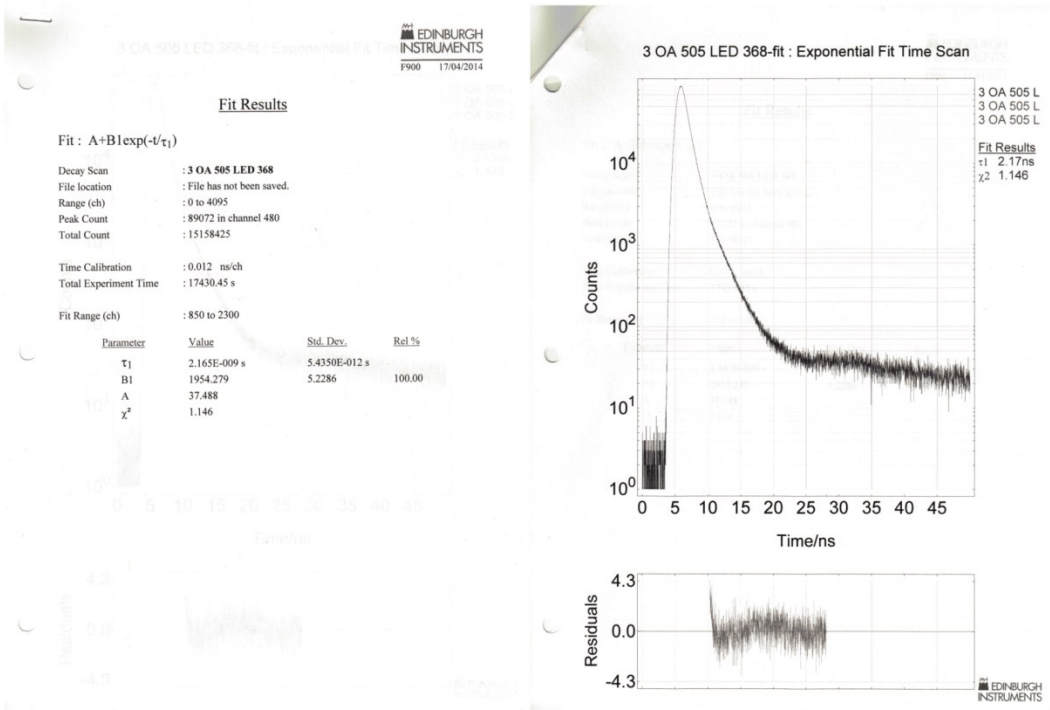


Fig. S37. Fit results of the 4AHBT@$(OA)_2$ @505 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

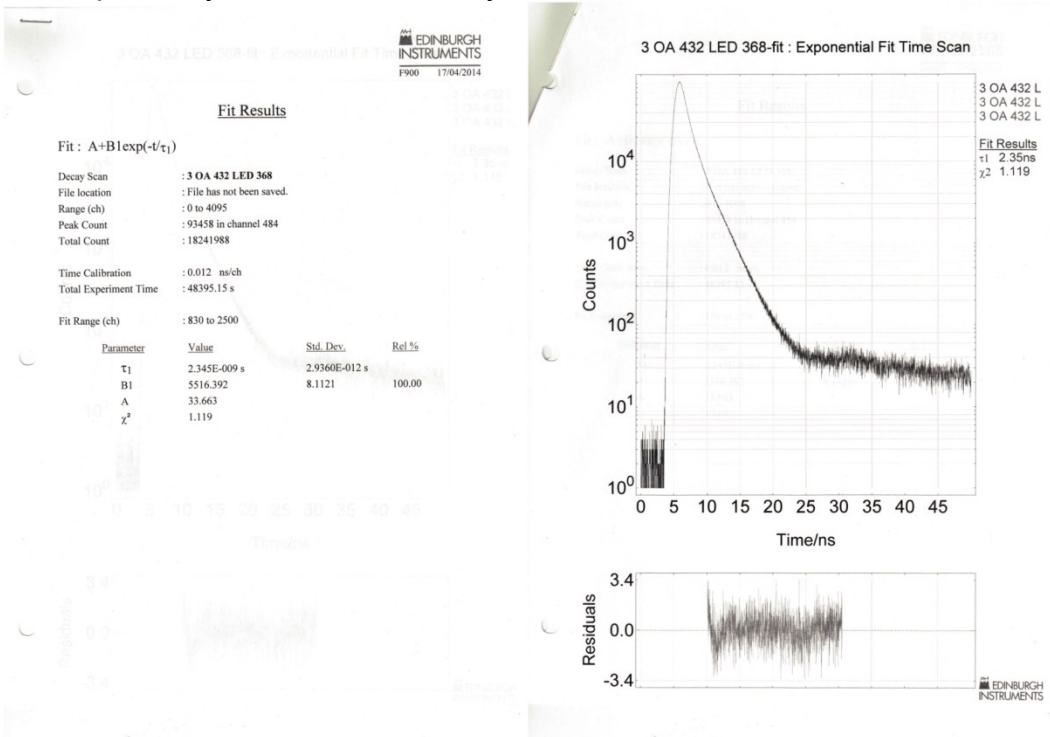


Fig. S38. Fit results of the 4AHBT@$(OA)_2$ @432 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

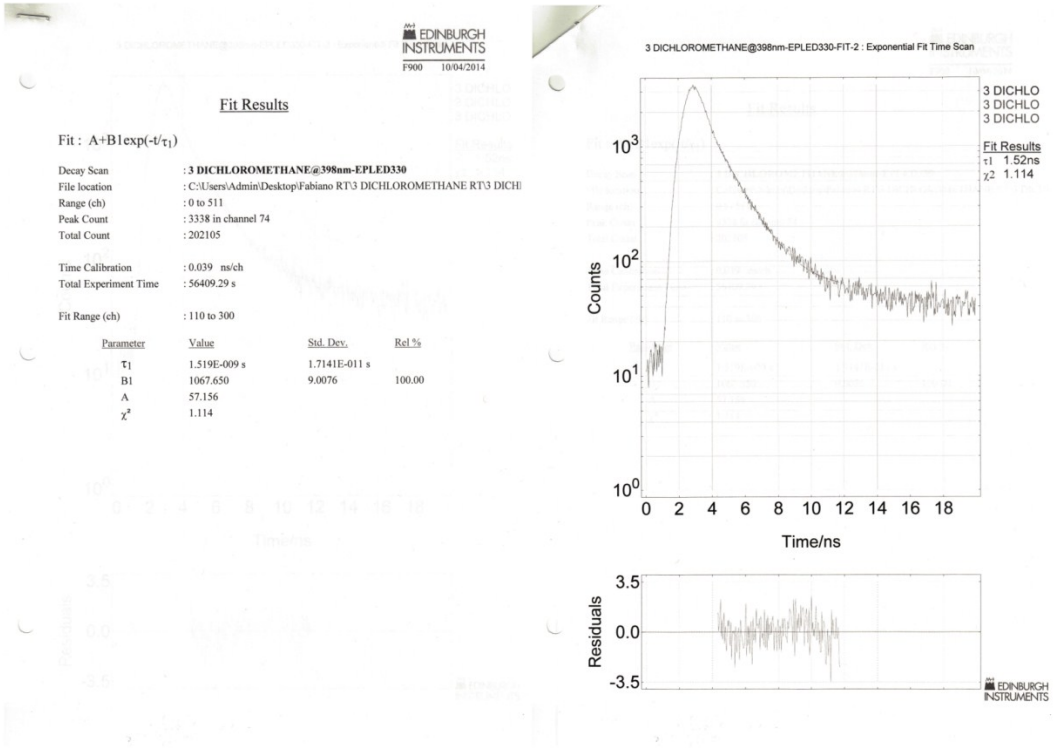


Fig. S39. Fit results of the 4AHBT in dichloromethane @398 nm EPLED 330 nm (lef). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

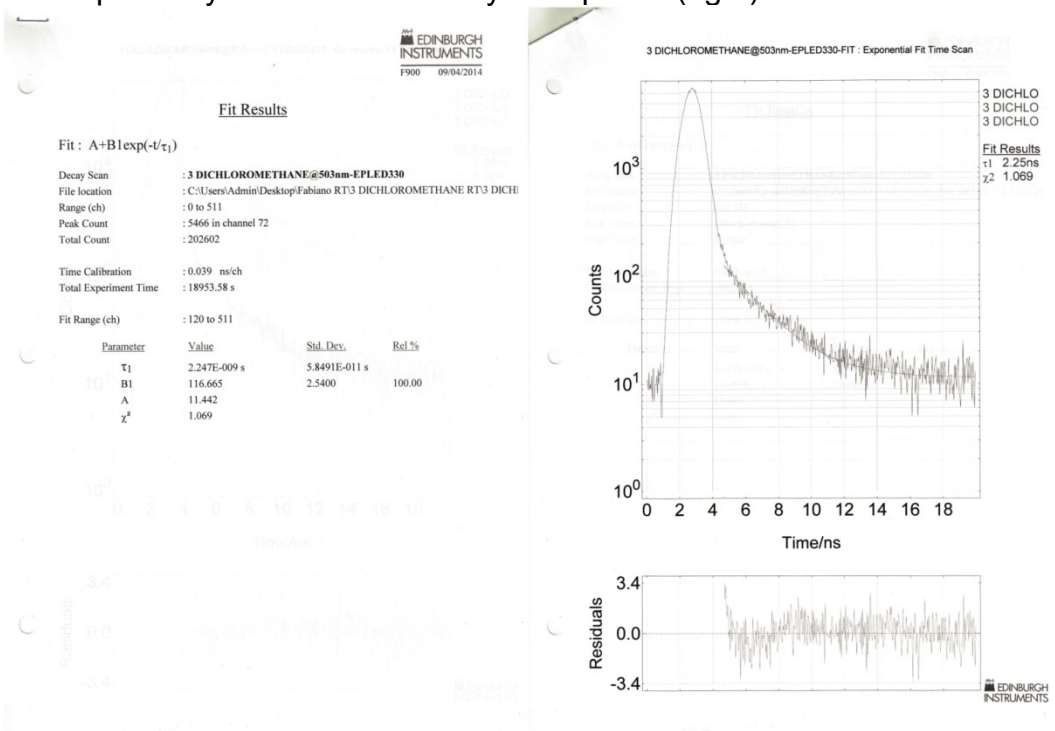


Fig. S40. Fit results of the 4AHBT in dichloromethane @503 nm EPLED 330 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

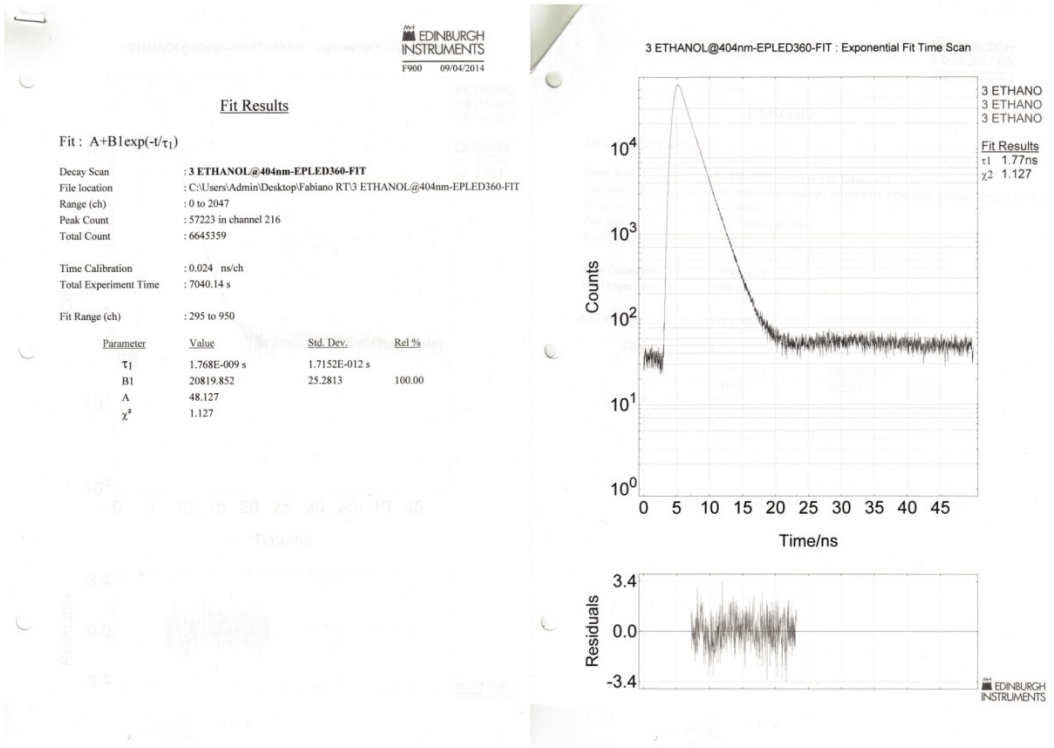


Fig. S41. Fit results of the 4AHBT in ethanol @404 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

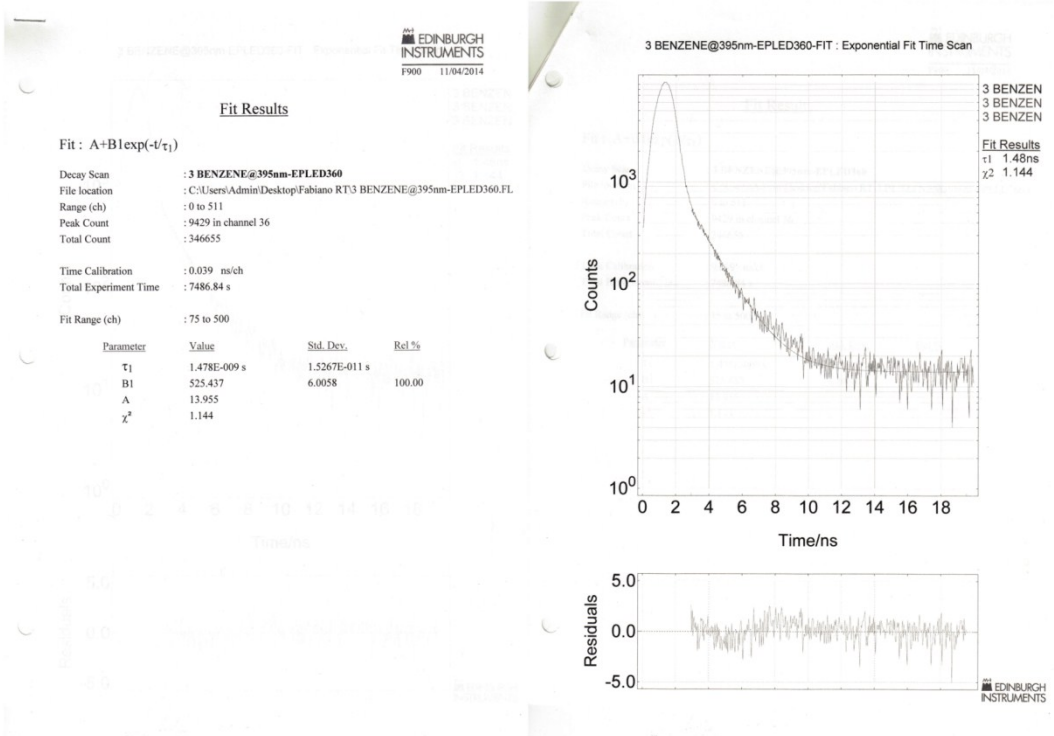


Fig. S42. Fit results of the 4AHBT in benzene @395 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

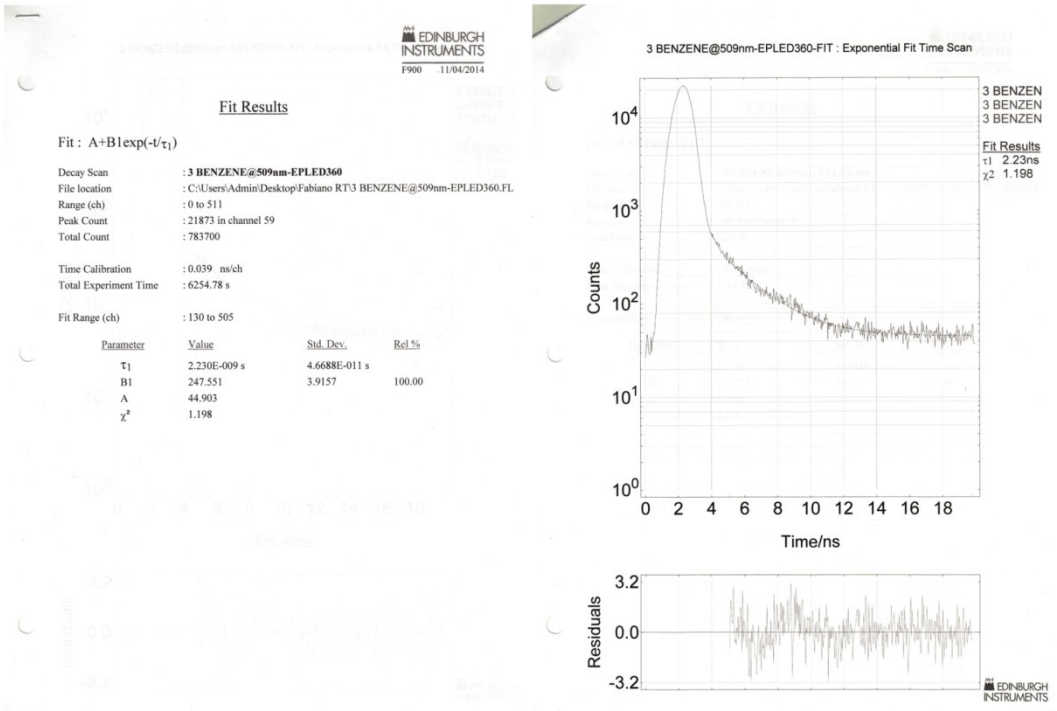


Fig. S43. Fit results of the 4AHBT in benzene @509 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

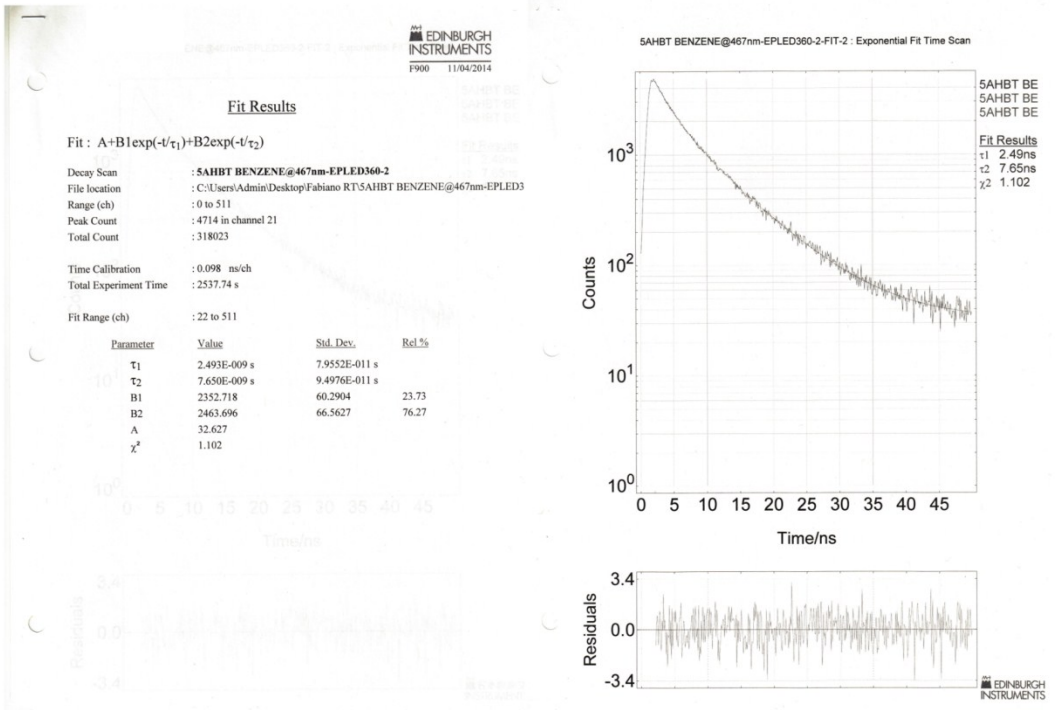


Fig. S44. Fit results of the 5AHBT in benzene @467 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

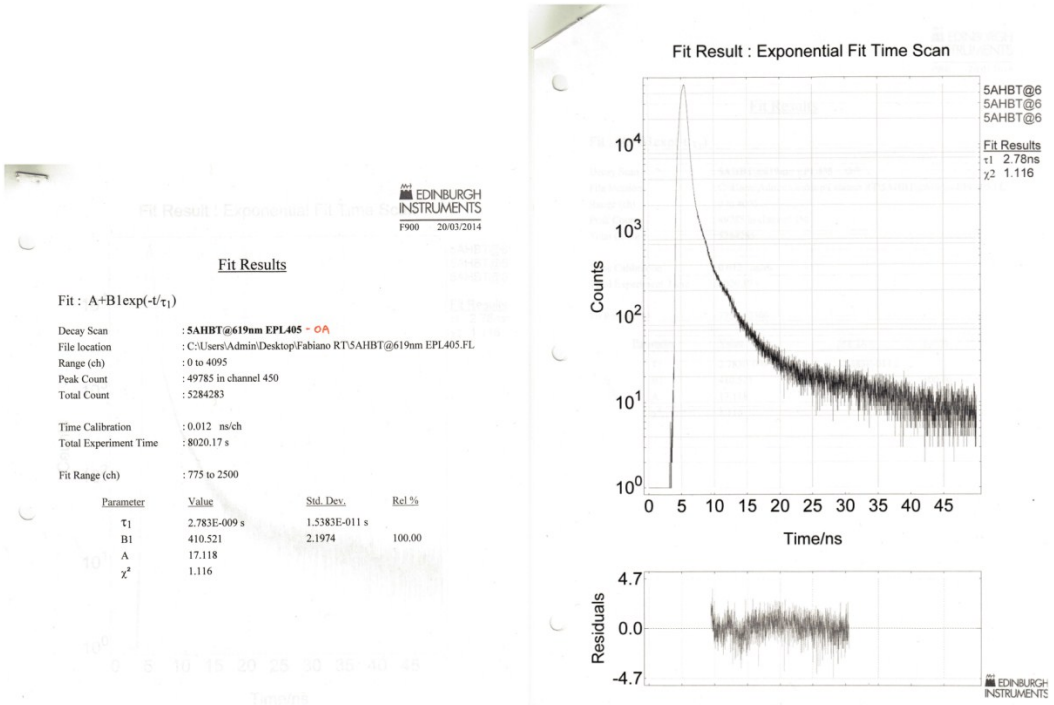


Fig. S45. Fit results of the 5AHBT@$(OA)_2$ @467 nm EPL 405 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

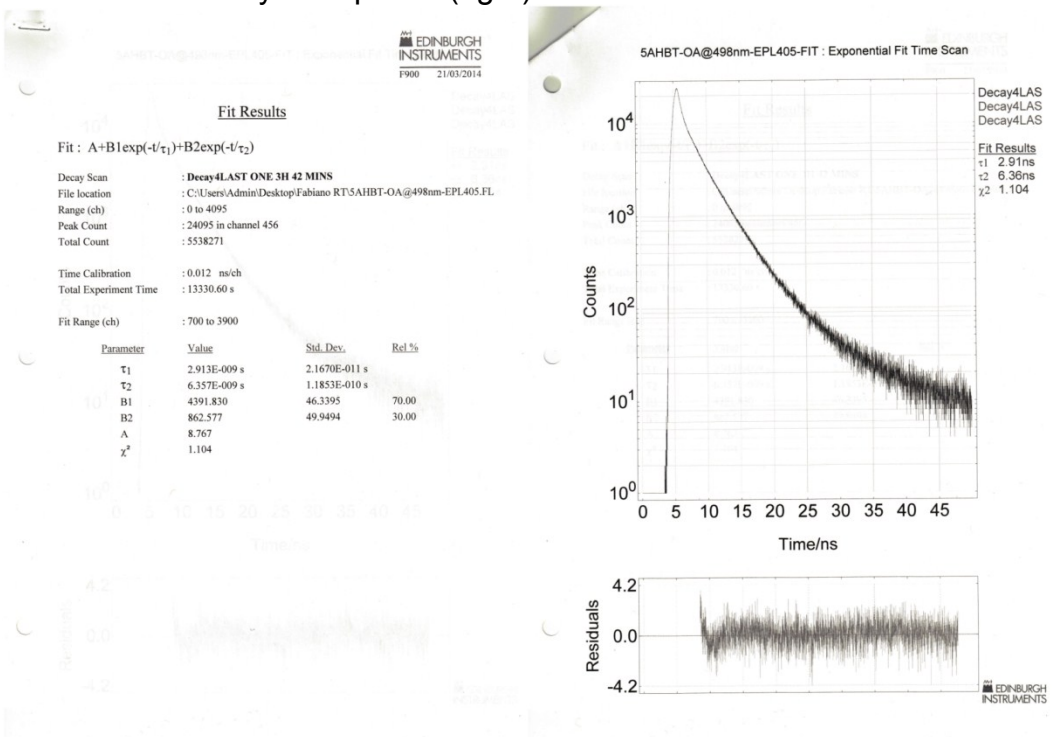


Fig. S46. Fit results of the 5AHBT@OA @498 nm EPL 405 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

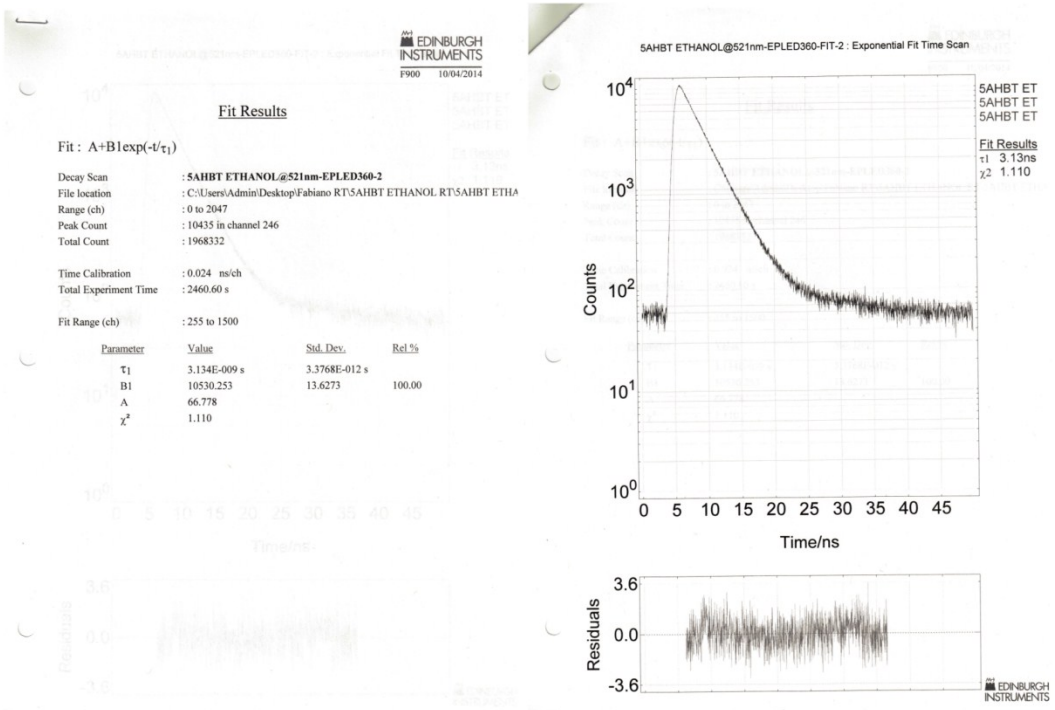


Fig. S47. Fit results of the 5AHBT in ethanol @521 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

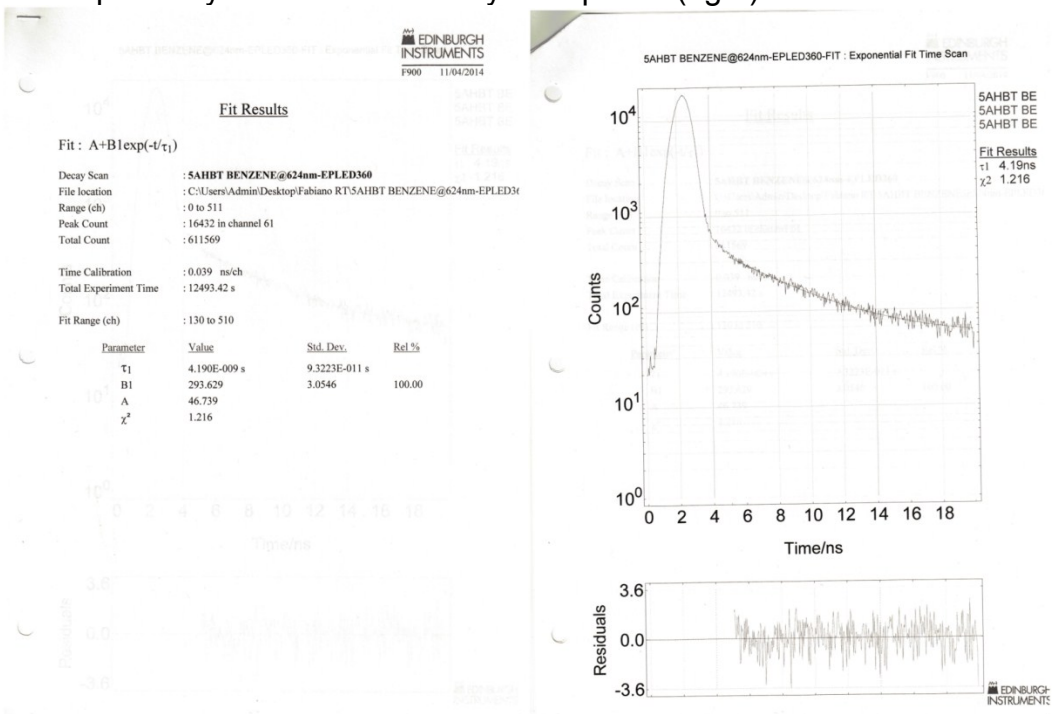


Fig. S48. Fit results of the 5AHBT in benzene @624 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

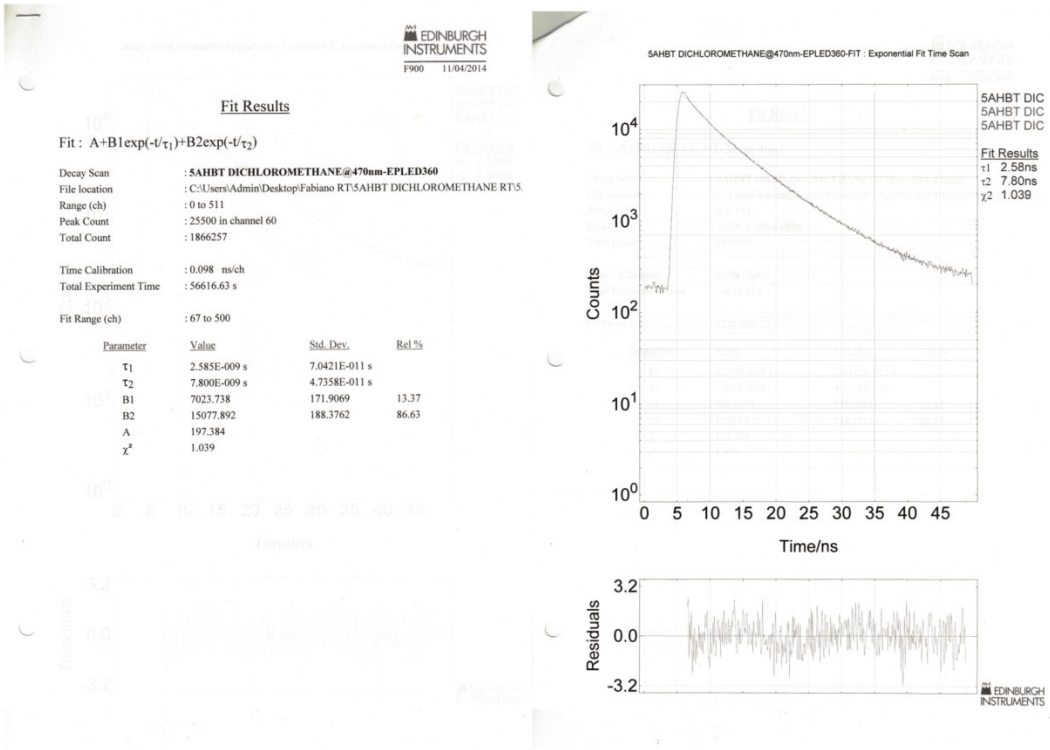


Fig. S49. Fit results of the 5AHBT in dichloromthane @470 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

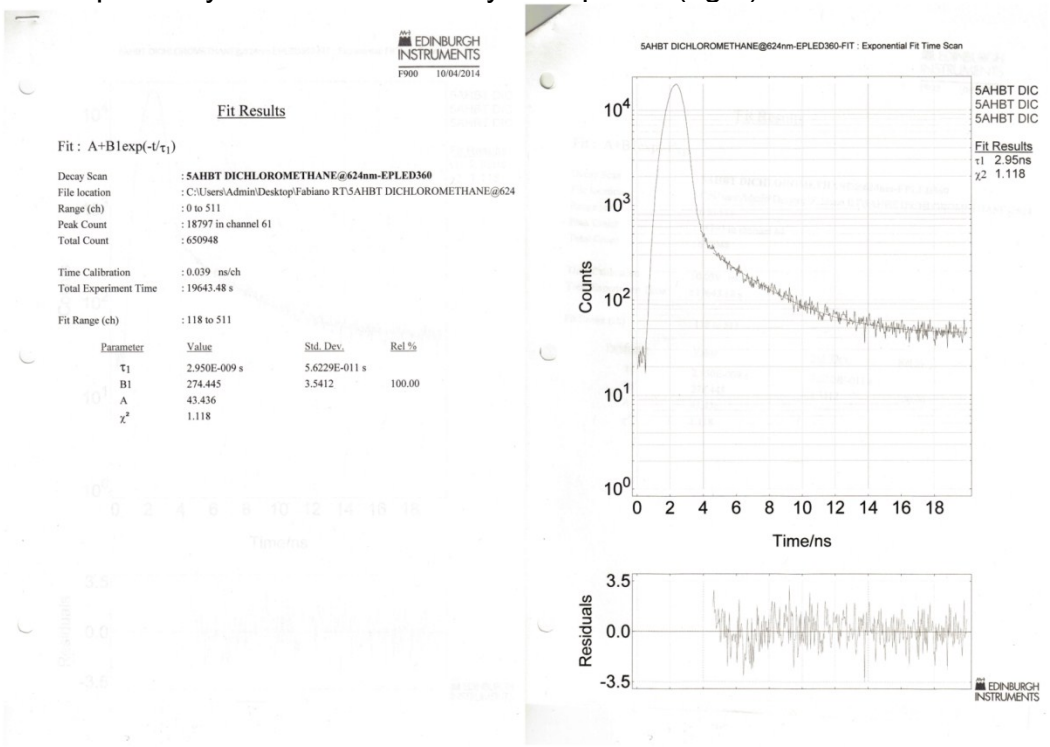


Fig. S50. Fit results of the 5AHBT in dichloromethane @624 nm EPLED 360 nm (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

6. References

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6. R. Kulasekharan, N. Jayaraj, M. Porel, R. Choudhury, A.K. Sundaresan, A. Parthasarathy, M.F. Ottaviani, S. Jockusch, N.J. Turro, V. Ramamurthy, Guest rotations within a capsuleplex probed by NMR and EPR techniques, Langmuir 26 (2010) 6943-6953.

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