New chemical approach to improve the gain properties of a red-emitting molecole for photonic applications

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1. Synthesis of the material

General

Materials and synthesis.

All reagents and solvents were used as received or purified using standard procedures., 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, 2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolane)-9,9-dioctylfluorene, 4,7-dibromo-2,1,3-benzothiadiazole, 2,2'-Bithiophene-5,5'-diboronic acid bis(pinacol) ester, phenylboronic acid pinacol ester, bromobenzene, tetrakis(triphenylphosphine) palladium ((Ph3P)4Pd), distilled toluene, distilled THF, $K_2CO_3$and Aliquat 336 available from Aldrich were used as received. Flash chromatography purifications were carried out using silica gel (200-300 mesh ASTM). Suzuki reactions with conventional heating were carried out under nitrogen atmosphere.

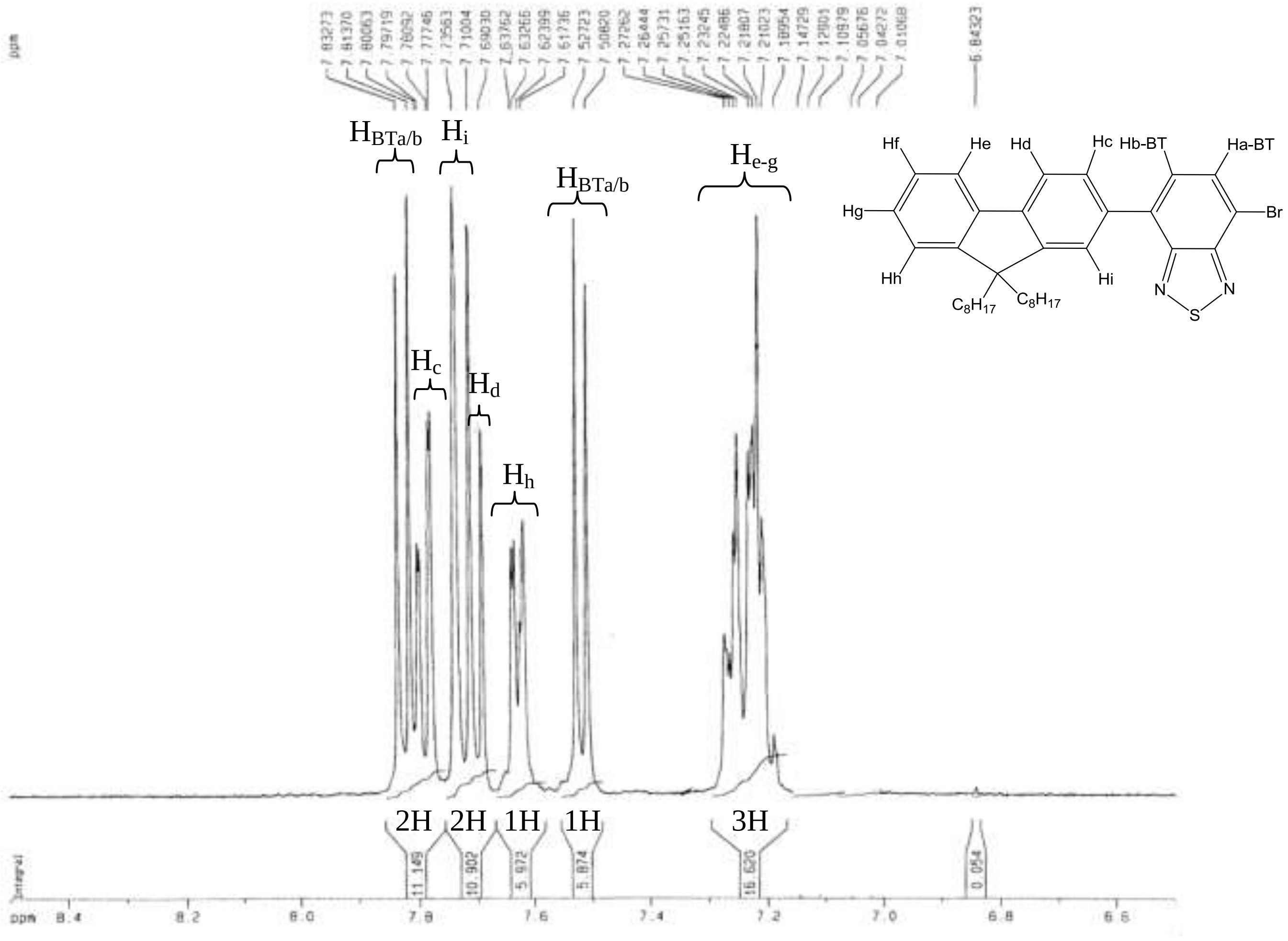
^{1}H and spectra were measured with a Bruker Avance 400MHz instrument. The elemental analyses were performed with a Vario EL elemental analyzer. Mass spectra were collected on an ion trap Finningan Mat GCQ spectrometer operating in electron impact (EI) ionization mode. Each sample was introduced to the ion source region of GCQ via a direct exposure probe (DEP). The melting points were determined with a Bȕchi 510 apparatus. GPC measurements were carried out on a Waters SEC system consisting of a pump, a 410 differential refractometer, and a 490 UV spectrophotometer as detectors. The column was an Ultrastyragel Waters; $CHCl_3$ as solvent and polystyrene as standard were used.

4-Bromo-2,1,3-benzothiadiazole-7-(9,9-dioctylfluorene) and **PF8BT-Br Terminated** were synthesized as reported in ref. 10 and here reported in details

4-Bromo-2,1,3-benzothiadiazole-7-(9,9-dioctylfluorene)

Under inert atmosphere, 250 mg (0.853 mmol) of 4,7-dibromo-2,1,3-benzothiadiazole and 440 mg (0.853 mmol) of 2-(4,4,5,5-tetramethyl-1,3,2-dioxoborolane)-9,9-dioctylfluorene were dissolved in 10 mL of dry toluene, and then 1.6 mL of a degassed aqueous solution of 2 M K2CO3, the phase transfer catalyst Aliquat, and 21 mg (0.02 mmol) of (Ph3P)4Pd were added. The reaction mixture was stirred and heated at reflux under nitrogen for 24 h. The mixture was poured into water and extracted four times with diethyl ether. The combined organic phases were washed with brine, then dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. The product was purified by column chromatography (heptane/CH_2Cl_2 8/2). The yield was 45% (231 mg). 1H NMR ($CDCl_3$, 298 K) δ (ppm): 7.82 (d, 1H, J = 7.6 Hz, BT), 7.79 (dd, 1H, J = 1.37 Hz, J = 7.88 Hz, fluorenyl), 7.73 (s, 1H, fluorenyl), 7.70 (d, 1H, J = 7.89 Hz, fluorenyl), 7.63 (dd br, 1H, fluorenyl), 7.51 (d, 1H, J = 7.61 Hz, BT), 7.27-7.19 (br, 3H, fluorenyl), 1.9 (m, 4H, CH_2), 1.06-0.94 (m, 20H, CH_2), 0.66 (m, 10H, CH_3, CH2).

^{1}H-NMR detail of aromatic part 4-Bromo-2,1,3-benzothiadiazole-7-(9,9-dioctylfluorene)

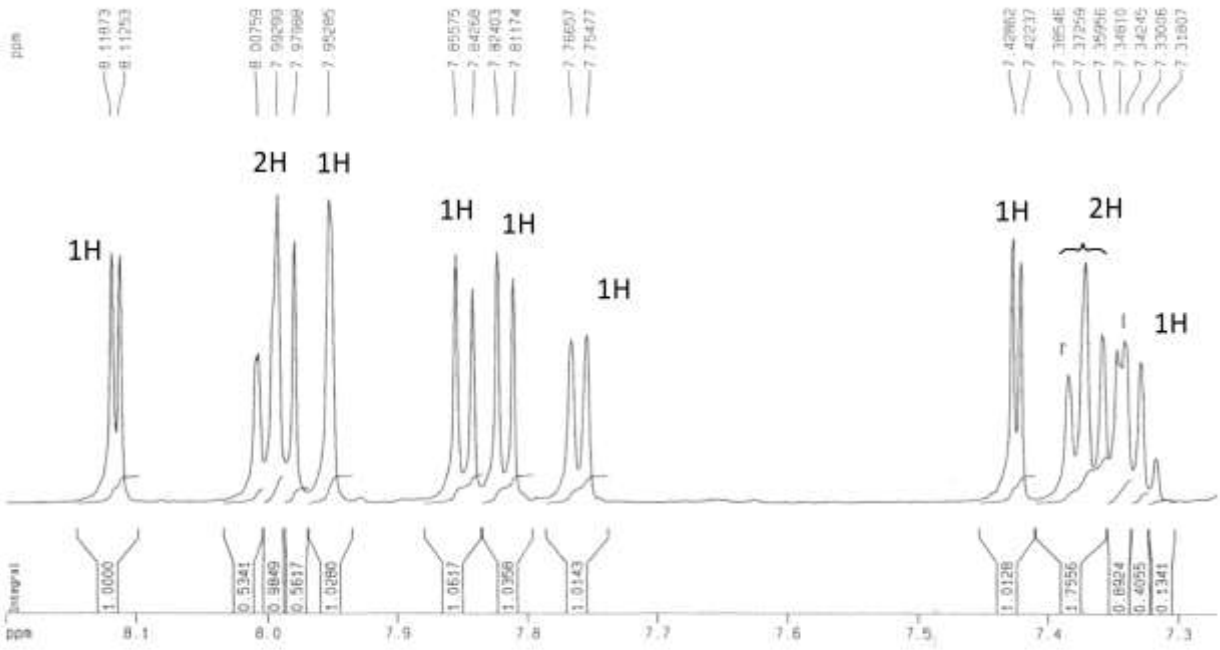


5,5'-bis(7-(9,9-dioctyl-9H-fluoren-2-yl)-2,1,3-benzothiadiazol-4-yl)-2,2'-bithiophene (F-BT-T-)2

Under inert atmosphere, 80 mg (0.13 mmol) of **4-Bromo-2,1,3-benzothiadiazole-7-(9,9-dioctylfluorene)** and 27 mg (0.06 mmol) of 2,2'-Bithiophene-5,5'-diboronic acid bis(pinacol) ester were dissolved in 3 mL of dry toluene, and then 1 mL of a degassed aqueous solution of 2 M

K_2CO_3, the phase transfer catalyst Aliquat, and 1.5 mg (0.001 mmol) of $(Ph_3P)_4Pd$ were added. The reaction mixture was stirred and heated at reflux under nitrogen for 24 h. The mixture was poured into water and extracted four times with diethyl ether. The combined organic phases were washed with brine, then dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. The product was purified by column chromatography (heptane/CH_2Cl_2 7/3). The yield was 75% (72.6 mg). m.p. 181 °C, MS (70 eV, EI): m/z 1210($M^{\cdot +1}$), ^{1}H NMR (CDCl3, 298 K) δ (ppm): 8.11 (d, 2H, J = 3.72 Hz, thienyl), 7.99 (m, 4H, J = 7.86 Hz, J = 7.38 Hz), 7.95 (s, 2H, fluorenyl), 7.84 (d, 2H, J = 7.89 Hz,), 7.82 (d, 2H, J=7.38Hz), 7.76 (d, 2H, J = 7.08 Hz,fluorenyl), 7.42 (d, 2H, J= 3.75 thienyl) 7.38-7.31 (br, 6H, fluorenyl external ring), 2.03 (m, 4H, CH_2), 1.18 (m, 4H, CH_2) 1.15-1.07 (m, 16H, CH_2), 0.79 (t, 6H, J=7.12 CH_3) 0.76 (m, 4H, , CH_2). Anal. calcd for Chemical Formula: $C_{78}H_{90}N_4S_4$, C, 77.31; H, 7.49. Found C, 77.42; H, 7.39

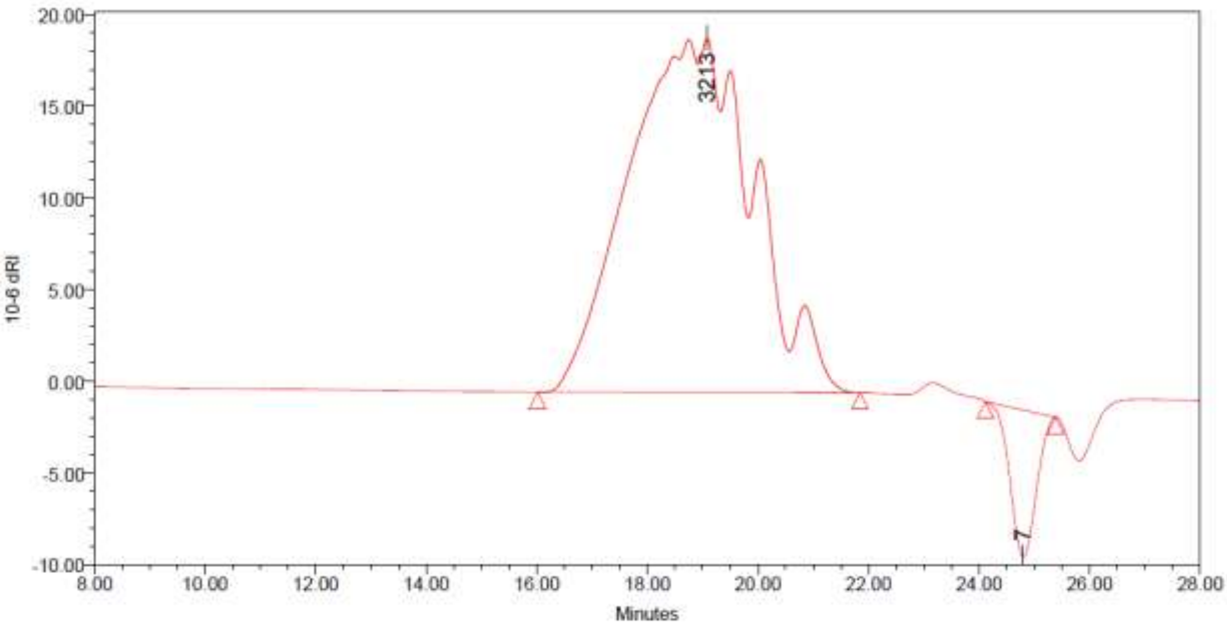
^{1}H-NMR detail of aromatic part of **5,5'-bis(7-(9,9-dioctyl-9H-fluoren-2-yl)-2,1,3-benzothiadiazol-4-yl)-2,2'-bithiophene**



PF8BT-Br Terminated.

To a solution of 150 mg (0.510 mmol) of 4,7-dibromo-2,1,3-benzothiadiazole, 294 mg (0.510 mmol) of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, 12 mg (10.2 μmol) of (Ph_3P)4Pd, and a catalytic amount of Aliquat in 4 mL of toluene, 1 mL (2.2 mmol) of 2 M aqueous solution of K_2CO_3 was added. The reaction was stirred at 100 °C for 3 h then was capped by refluxing for 12 h with an excess of bromobenzene 81 μL (0.76 mmol). The reaction mixture was filtered on Celite and precipitated into methanol (100 mL). The precipitate was collected and extracted with acetone using a Soxhlet apparatus to give a PF8BT-bromine terminated polymer (153 mg, 57% yield). This polymer, soluble in cyclohexane, has been referred to as PF8BT-Br terminated ^{1}H NMR ($CDCl_3$, 298 K) δ (ppm): 8.09-7.92 (m, fluorenyl + BT), 7.71-7.46 (m, Ph), 2.13 (br, 4H, α CH_2 alkyl chain), 1.16 (br, 24H, CH_2), 0.80 (br, 6H, CH_3). *M*n value of 2750 and PDI =2.0. (170 mg, 63% yield). The Mn values were referred to standard of polystyrene

GPC details of the polymeric arm **PF8BT-Br Terminated.**



GPC Relative Calibration Results

	Ret.Time	Mp	Mn	Mw	Mz	Mw/Mn	Mz/Mw
1	19.083	3213	2743	5601	9532	2.04	1.70
2	24.802	7					

PF8BT-T2-PF8BT , R1A core Polymer

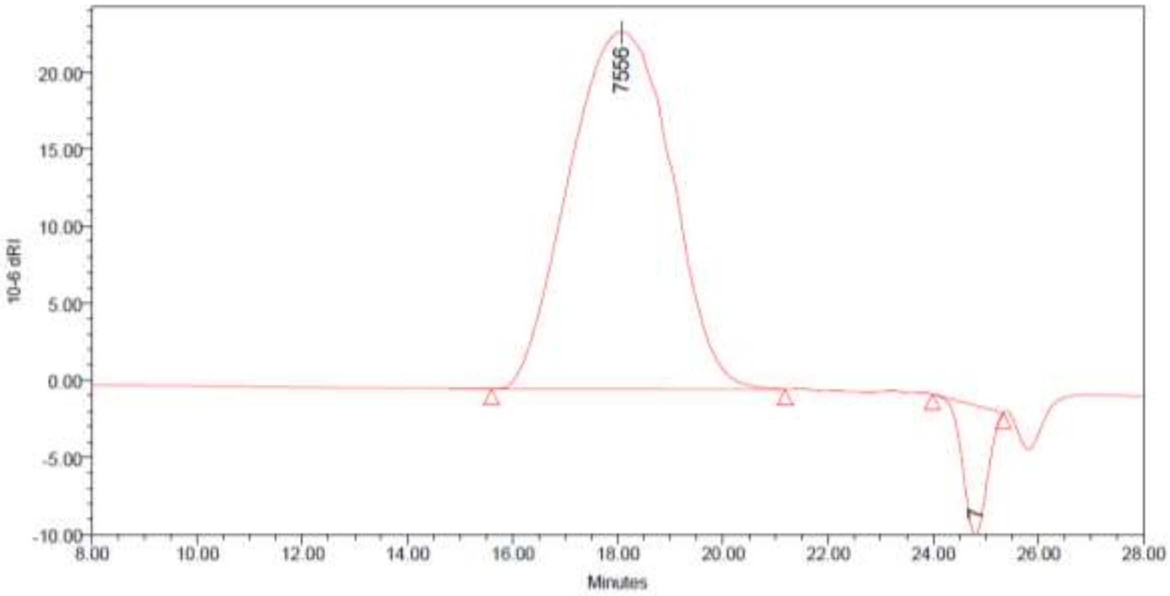
88 mg of PF8BT-Br Terminated was dissolved in toluene and (0.75 mg, 0.65 µmol) of $Pd(Ph_3P)_4$ from a previously prepared toluene solution together with 7.5 ml of [2 M] K_2CO_3 aqueous solution and a drop of Aliquat were added. A toluene solution of 2,2'-Bithiophene-5,5'-diboronic acid bis(pinacol) ester (7.8 mg, 0.019mol in 4.0 ml) to get the core-type polymer was slowly dropped in 3 h maintaining the reaction at 90 °C under stirring. The mixture was further stirred for 15 h. The

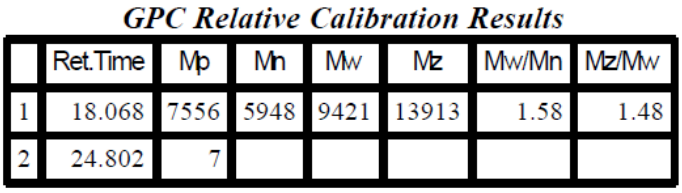
solution was filtered through a Celite column and the polymer was precipitated in methanol. Extraction with cyclohexane was used to remove any residue of unreacted polymer and bithiophene derivative obtaining 50 mg of PF8BT-T2-PF8BT (R1A) core Polymer.

1H NMR (CDCl3, 298 K) δ (ppm): : 8.14-7.82 (br, fluorenyl+BT+T), 7.69–7.6 (m, fluorenyl), 7.49-7.35 (br,terminal fluorenyl and phenyl), , 2.13 (br, CH_2 alkyl chain), 1.14 (br, CH_2), 0.94 (br, CH_2), 0.79 (m, CH_3).

*M*n value of 5900 and PDI =1.6. (65% yield). The Mn values were referred to standard of polystyrene

GPC detail of CORE polymer **PF8BT-T2-PF8BT , R1A**




GPC Relative Calibration Results

	Ret.Time	Mp	Mn	Mw	Mz	Mw/Mn	Mz/Mw
1	18.068	7556	5948	9421	13913	1.58	1.48
2	24.802	7					

2. Experimental setups

The samples were kept in air without encapsulation.

2.1 Pump-probe

In order to temporally resolve the FRET mechanism between the donor and the acceptor, we perform a classical pump-probe measurement as in ref. [6,11]. The laser source is a Ti:Sapphire laser with grating-assisted chirped-pulses amplification, that delivers pulses at 780 nm with 1kHz repetition rate. The beam is then split in two beams, the pump and the probe. This last is focused on a sapphire plate for the white light continuum (WLC) generation (470-770 nm).

For R1A and R48A we used two different pump wavelengths, in order to match the absorption curve of the two materials. For the R1A, the pump beam is focused on a beta-barium borate (BBO) crystal for the second harmonic generation (390 nm). For the R48A we used an optical parametric amplifier (OPA) to tune the pump wavelength at 530 nm. On the pump line, a delay stage controls the temporal delay between the pump and the probe. In both cases the circular spot on the sample has a radius of around 80 μm. The transmission of the probe through the sample is collected, sent in a monochromator and then on a photodiode array. The collected signal is the differential transmission spectra $\Delta T/T(\lambda,t)$ of the probe through the sample.

2.2 Amplified spontaneous emission

For amplified spontaneous emission (ASE) measurements we used a Nd:YAG laser tripled in frequency (355 nm) (BRIO Quantel), that delivers pulses of around 3 ns. The beam is focused orthogonally to the film with a cylindrical lens of focal *f*=50 mm, in order to give a spot of around 1500x100 μm^2. The spectrum is collected at the edge of the film with the help of a spectrograph (Princeton Instruments Acton SP2150, 300 gr/nm) coupled with a CCD camera (Princeton Instruments pixis 256).

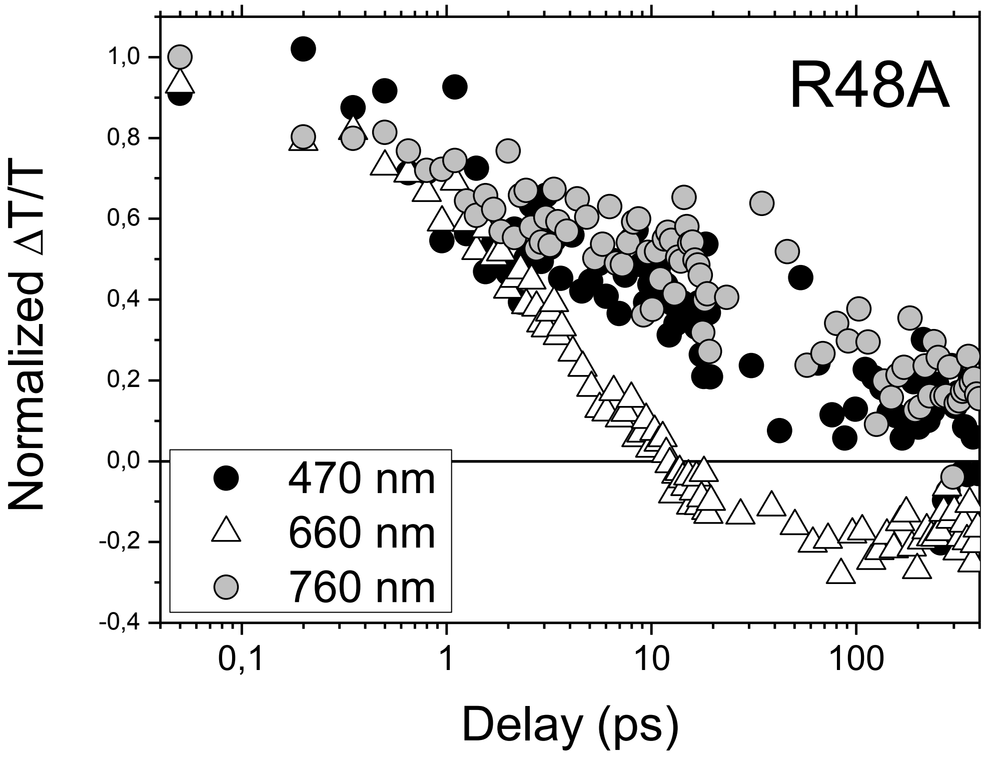


Fig.SI1: Normalized decays at 470nm, 660nm and 760nm(at that wavelength the signal is –ΔT/T).

3. Dynamics of the core R48A

In Fig.2a of the article, we have shown for R48A the presence of a Ground State Bleaching (GSB) band below 530 nm, a Stimulated Emission (SE) band centered at 660 nm and a Photo Induced Absorption band at 760 nm. If we plot the temporal evolution of these three wavelengths (Fig.SI1), we can clearly see that the GSB and PIA have the same evolution, indicating that they arise from the same specie (the singlet state), while the SE shows an additional negative contribution, that we attribute to the charge formation.

4. Mathematical modelling of the copolymer R1A

A mathematical model of the system is given by the set of two coupled equations (1) describing the exciton populations of the donor (N_d) and of the acceptor (N_a), as function of the delay t between the pump and the probe pulse:

$$\begin{cases} \dfrac{dN_d(t)}{dt} = -\dfrac{N_d(t)}{\tau_d} - \dfrac{\gamma_{FRET}}{\sqrt{t}} N_d(t) \\ \dfrac{dN_a(t)}{dt} = \dfrac{\gamma_{FRET}}{\sqrt{t}} N_d(t) - \dfrac{N_a(t)}{\tau_a} - \gamma_{B,a}(t) N_a^2(t) \end{cases} \qquad (1)$$

In this model we take into account the radiative decay path through the monoexponential term of radiative time constant $\tau_{d(a)}$. The term $\gamma_{B,a}(t) = \frac{\gamma_a}{\sqrt{t}}$ models the bimolecular decay [S1,S2] while the term $\gamma_{FRET} = \frac{2}{3}\pi R_0^3 n_a \sqrt{\frac{\pi}{\tau_d}}$ takes into account the FRET mechanism [S1], where R_0 is the so-called Förster radius (the characteristic distance below which the FRET mechanism prevails on the other decay paths as in ref. 13) and n_a is the number of acceptors (i.e. core units) per unit volume. We suppose that in the copolymer we do not have the formation of charges. This last quantity can be calculated starting from the Lambert-Beer law for the absorbance $A(\lambda)$

$$A(\lambda) = \varepsilon(\lambda) l c \qquad (2)$$

and from the relation [S1]

$$N_A \sigma(\lambda) = 1000 \ln(10) \varepsilon(\lambda) \qquad (3)$$

where $\varepsilon(\lambda)$[L/(mol cm)] is the molar decadic absorption coefficient, l is the path of the light in the medium, c[mol/L] is concentration of the absorption sites, N_A is the Avogadro number and $\sigma(\lambda)$ is the absorption cross section.

Coupling these two equations we extract the concentration of a substance

$$c = \frac{A(\lambda) 1000 \ln(10)}{l N_A \sigma(\lambda)} \qquad (4)$$

that in our case is the concentration of absorbing entities at a certain wavelength λ. The sample used for the absorption spectrum was obtained by spin cast technique, it has a thickness l ~ 40 nm and an absorbance $A\big|_{\lambda=470\mathrm{nm}}$ ~ 0.28.

The cross section can be calculated from the pump-probe data through the relation [S3]

$$\sigma(\lambda) = \frac{\frac{\Delta T}{T}(\lambda, t)}{N(t)d} \tag{5}$$

where d~250 nm is the thickness of the sample used for the pump-probe experiment, $\Delta T/T\big|_{\lambda=470\mathrm{nm},t=0\mathrm{ps}}$~0.020 is the differential transmission signal for the maximum absorption wavelength and $N\big|_{t=0\mathrm{ps}}=N_0[\mathrm{cm}^{-3}]$ is the exciton density. The population N_0 can be obtained with the hypothesis that each absorbed photon gives rise to an exciton

$$N_0 = \mathrm{AR}\frac{E_{pulse}}{\hbar\omega}\frac{1}{\pi w_0^2 d} \tag{6}$$

where AR is the absorbed ratio of the incoming pump (~70%), $\hbar$ is the reduced Plank constant, E_{pulse}~20 nJ is the energy per pulse of the pump at frequency ω, w_0 is the radius of the pump spot and d is the thickness of the sample. The obtained initial number of exciton (of the F8BT chains) is N_0~$6\cdot10^{18}$ cm^{-3} and the cross section is $\sigma\big|_{\lambda=470\mathrm{nm}}$~$1.3\cdot10^{-16}$ cm^2.

Substituting the value of the Eq.5 and 6 into the Eq. 4 we obtain the concentration of c = 2 mol/L.

In order to resolve the Eq.1, the pump contribution is taken into account in the initial conditions: from Eq.6 we have for the donor population $N_d(0)= N_0$~$6\cdot10^{18}$ cm^{-3}. Since we are pumping the side chains, the acceptor population starts from zero and the FRET term in the second equation of (1) causes a growth in the core signal.

The value of the donor radiative decay time τ_d~500 ps is taken from previous work as in ref. 14, while the other parameters are found fitting the coupled equations to the experimental data (Tab.S1). The results are shown in Fig.3 of the article, where we report the dynamic at 610 and 470 nm. We choose this wavelength because here the contribution of PIA and SE from F8BT compensate and we have a pure SE dynamic from the N_a population starting from zero. In the other spectral regions we have the contribution of both population and at 470 nm we have the GSB of the donor and of the acceptor (as seen in the previous paragraph). Therefore this wavelength is a linear combination $\alpha N_d + \beta N_a$ of the GSB of the two populations (the values of α and β are reported in Tab.S1). The dynamics at different wavelengths can be fitted varying the parameters α and β.

The values for the bi-molecular interactions are in the range of values for this kind of organic films

[S4, S5] and the value of γ_{FRET} gives a Förster radius R_0 of around 2.65 nm, which is quite small compared to usual organic blend as in ref. 14,17 cited in the article and **[**S4]. Smaller Förster radius corresponds to weaker interaction.

τ_a [ps]	γ_a [cm^3 ps$^{-1/2}$]	γ_{FRET} [ps$^{-1/2}$]	α	β
500	$7{\cdot}10^{-21}$	0.65	0.71	0.29

Table S1. Fitting parameters for Eq. (1).

References:

S1. E. Engel, K. Leo, and M. Hoffmann, *Chem. Phys*., 2006, **325,** 170.

S2**.** B. Greene and R. Millard, *Phys. Rev. Lett.*, 1985, **55**, 1331.

S3. T. Virgili, J. Cabanillas-Gonzales, L. Luer, G. Lanzani “Photophysics of molecular Materials” 2006, Wiley-VCH, ISBN:3-527-40456-2.

S4**.** G. Cerullo, S. Stagira, M. Zavelani-Rossi, S. D. Silvestri, T. Virgili, D. Lidzey, and D. Bradley, *Chem. Phys. Lett*.,2001, **335**, 27.

S5**.** E. Maniloff, V. Klimov, and D. McBranch, *Phys.Rev.B* 1997, **56**, 1876.