Supplementary Information for: Rigidochromic conjugated polymer carrying main-chain molecular rotors

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Methods

Chemicals

All chemicals and solvents were bought from Sigma Aldrich (Merck) Europe, TCI Europe and BIOSOLVE and used as received unless otherwise mentioned. Poly(9,9-di-n-octylfluorenyl-2,7-diyl) from Sigma Alrich was used as a spectroscopy reference. Product number: 571652. Mw $\geq$ 20kg/Mol.

8-[3,5-dibromophenyl]-3,5-diethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (1)

To 50 ml anhydrous and deoxygenated DCM was added 2.64 g (10 mmol) 3,5-dibromobenzaldehyde which was further deoxygenated. To this we added 2.04 ml (1.9 g, 20 mmol) 2-ethyl-1H-pyrrole and 100μl TFA. The reaction is performed for 18 hours under nitrogen atmosphere and light poor conditions at room temperature. To this was added 2.46 g (10 mmol) tetrachloro-1,4-benzoquinone (TCQ) in 30 ml anhydrous DCM, and then stirred for 50 minutes at room temperature. To this 10 ml DiPEA was added followed by stirring for 30 minutes. To this 10 ml BF_3*O(Et)$_2$ was added and stirred for 45 minutes. Solvents were removed under vacuum and the remaining suspension was filtered and washed with DCM. The filtrate was purified by silica column chromatography using DCM as eluent yielding 887 mg (18.3 % mol/mol) product. MS: M+H/z, relative abundance: 481.2, 50; 483.2, 100; 485.2, 50; 1H-NMR (400 MHz, $CDCl_3$, 300 K): (ppm) 7.84 (t, 1H, J=1.8 Hz), 7.59 (d, 2H, J=1.8 Hz), 6.71 (d, 2H, J=4.1 Hz), 6.39 (d, 2H, J=4.2 Hz), 3.08 (q, 4H, J=7.6 Hz), 1.35 (t, 6H, J=7.6 Hz)

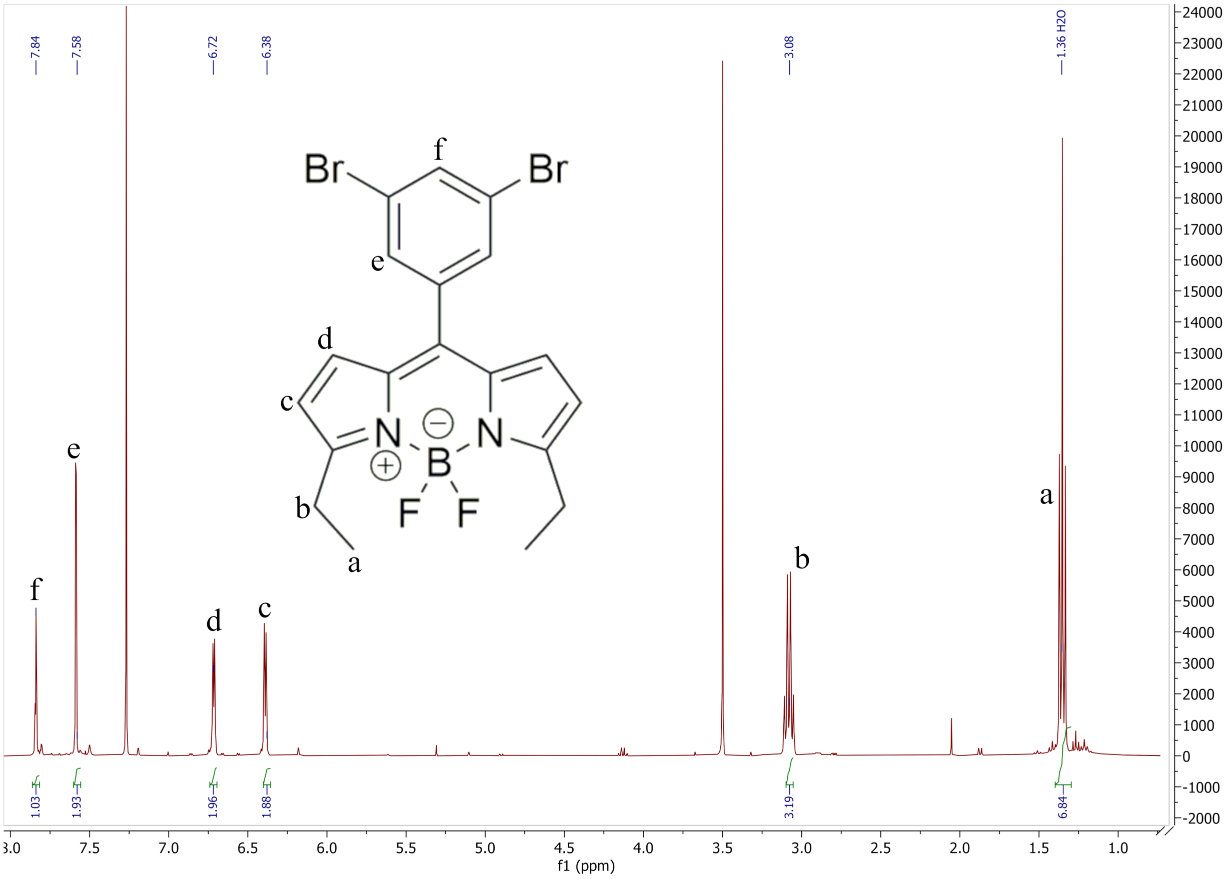


Figure 1: ^{1}HNMR specrum of **1** in $CDCl_3$

8-phenyl-3,5-diethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

As a spectroscopy reference a non-brominated bodipy-rotor was prepared. The same protocol was used as for **1** but with benzaldehyde.

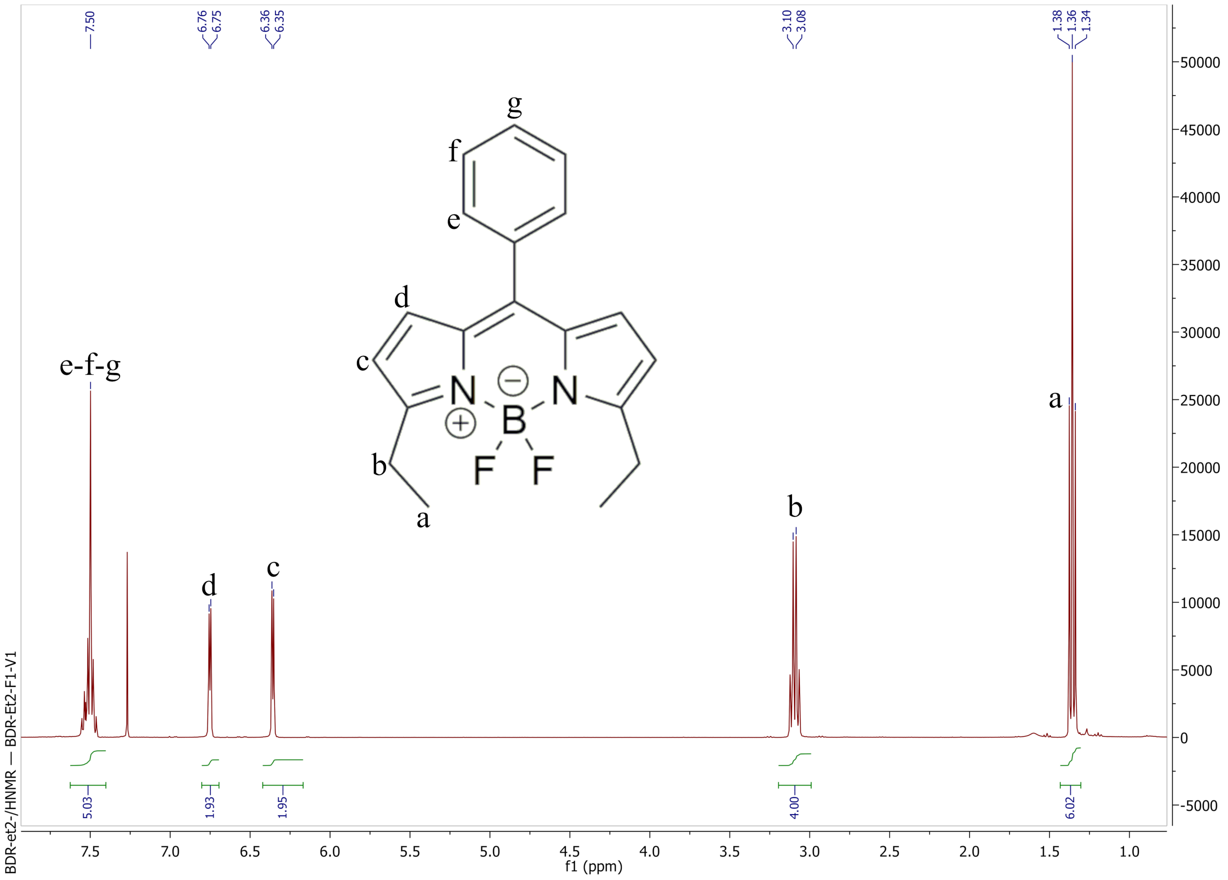
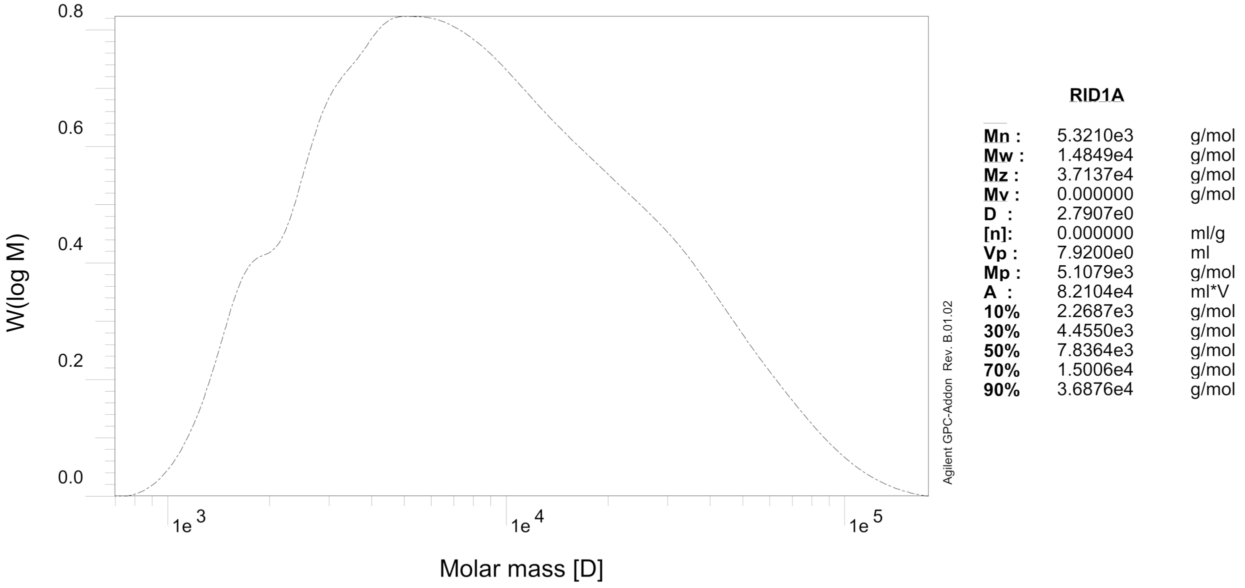


Figure 2: ^{1}HNMR specrum of **8-phenyl-3,5-diethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene** in $CDCl_3$

poly-(9,9-dioctylfluorene-2,7-diyl)-co-(5-[3,5-diethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene-8-yl]-m-phenylene (2a)

Conjugated polymers composed primarily of donor moieties, and doped with a minority fraction of acceptors, are prepared via standard Suzuki-Miyaura polycondensation reactions.[1–3] We dissolve 100 mg (0.2075 mmol) **1**, 341.38 mg (0.6225 mmol) 2,7-dibromo-9,9-dioctyl-fluorene and 463.44 mg (0.8300 mmol) 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-

propanediol) ester in 2 ml toluene, 15 ml 2M K_2CO_3 under nitrogen atmosphere. After thorough deoxygenation, we add 25 mg [1,1-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(DPPF)Cl_2). The reaction is performed for 48 hours at 90°C. The crude product is obtained by precipitation in cold methanol and Soxhlet extraction against ethanol and acetone. Yield: 44.8 mg (7.1%). GPC: Mn: 2.0 kDa, Mw: 5.5 kDa, D: 2.7907; 1H-NMR (400 MHz, $CDCl_3$, 300 K): (ppm) 7.86, (s, 2H), 7.84 (s, 23H), 7.75-7.61 (m, 62H), 3.09 (q (dq?), 4H, J=6.1 Hz), 2.12 (s br, 53H), 1.26-1.14 (m, 341H), 1.35 (t), 6H, J=6.1 Hz), 0.82 (m, 172H)



RID1A

Mn :	5.3210e3	g/mol
Mw :	1.4849e4	g/mol
Mz :	3.7137e4	g/mol
Mv :	0.000000	g/mol
D :	2.7907e0	
[n]:	0.000000	ml/g
Vp :	7.9200e0	ml
Mp :	5.1079e3	g/mol
A :	8.2104e4	ml*V
10%	2.2687e3	g/mol
30%	4.4550e3	g/mol
50%	7.8364e3	g/mol
70%	1.5006e4	g/mol
90%	3.6876e4	g/mol

Figure 3: GPC trace and calculated mass against polystyrene reference standards for **2a** measured in $CHCl_3$ at 35°C.

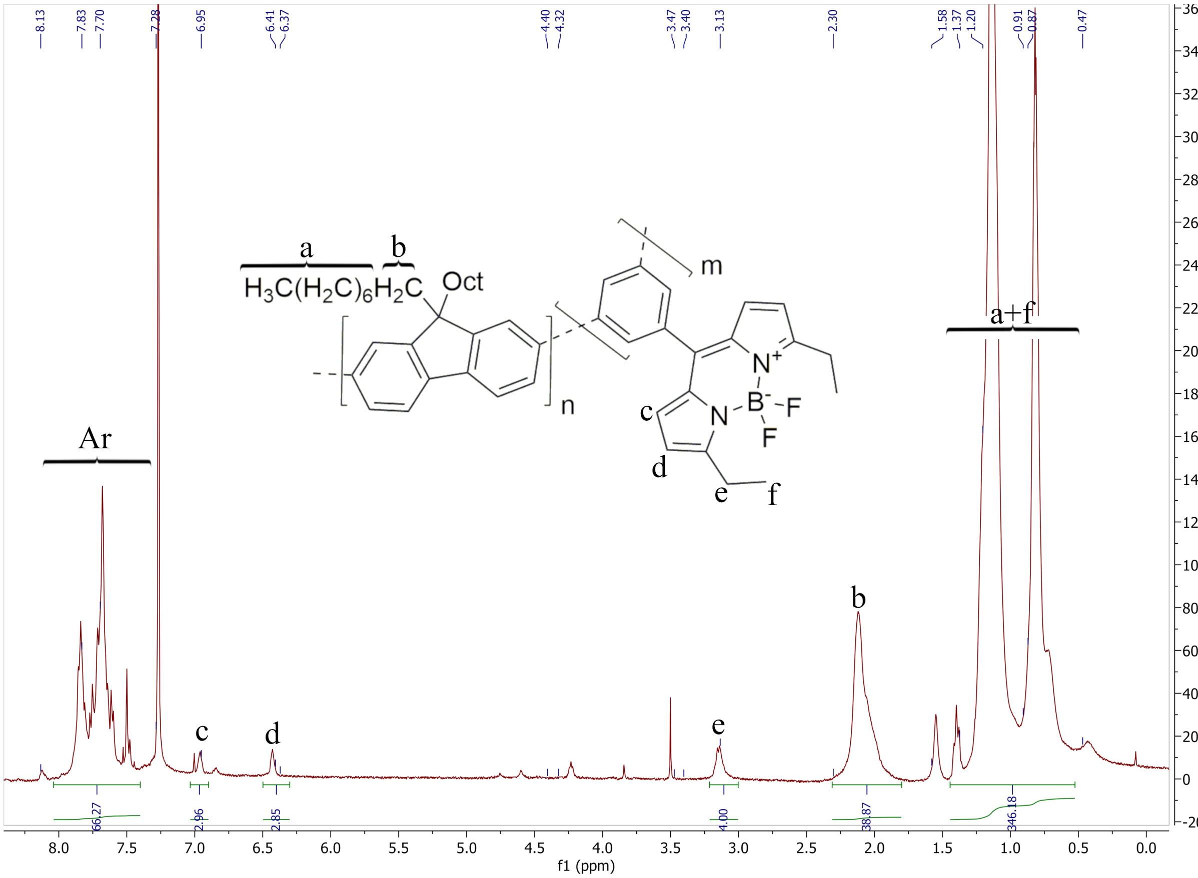
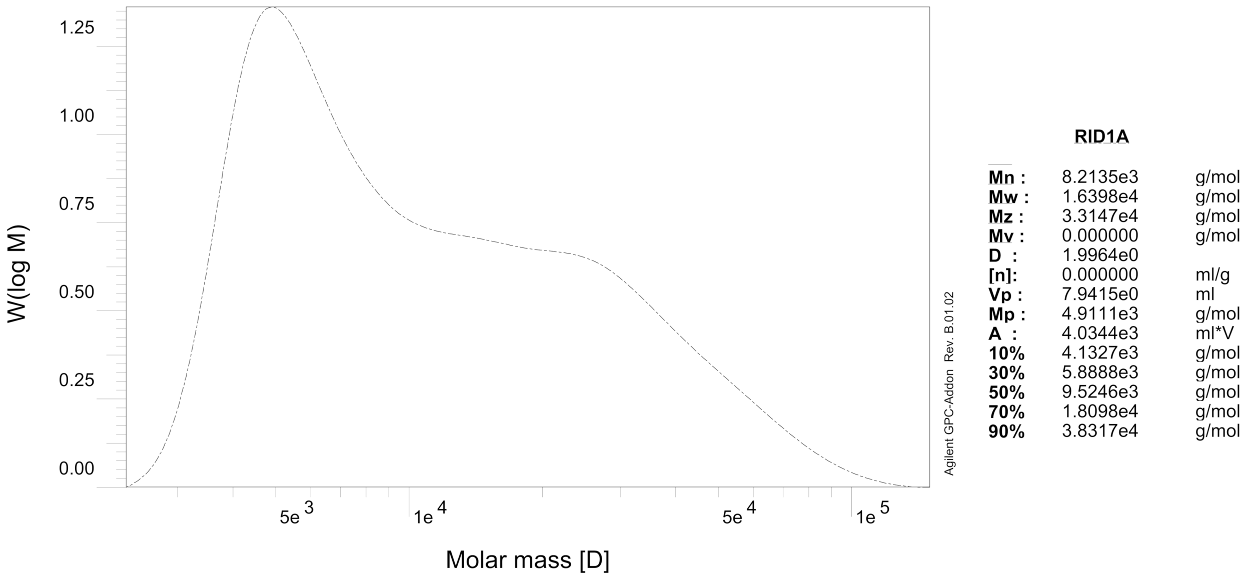


Figure 4: ^{1}HNMR specrum of **2a** in $CDCl_3$

poly-(9,9-dioctylfluorene-2,7-diyl)-alt-(5-[3,5-diethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene-8-yl]-m-phenylene (2b)

Using the same protocol we **2b** using the following amounts: 200 mg (0.4150 mmol) **1** and 231.72 mg (0.4150 mmol) 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester & 12.5 mg Pd(DPPF)Cl_2. Yield: 69.5 mg (23.5%). GPC: Mn: 3.0, Mw: 6.1 kDa, D: 1.9964; 1H-NMR (400 MHz, $CDCl_3$, 300 K): (ppm) 8.10-7.5 (13H, m), 6.95 (2H, s), 6.43(2H, s), 3.13 (4H, m), 2.10(5H, s), 1.37-0.6(75H,m)



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RID1A

Mn :     8.2135e3       g/mol
Mw :     1.6398e4       g/mol
Mz :     3.3147e4       g/mol
Mv :     0.000000       g/mol
D  :     1.9964e0
[n]:     0.000000       ml/g
Vp :     7.9415e0       ml
Mp :     4.9111e3       g/mol
A  :     4.0344e3       ml*V
10%      4.1327e3       g/mol
30%      5.8888e3       g/mol
50%      9.5246e3       g/mol
70%      1.8098e4       g/mol
90%      3.8317e4       g/mol
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Figure 5: GPC trace and calculated mass against polystyrene reference standards for **2b** measured in $CHCl_3$ at 35°C.

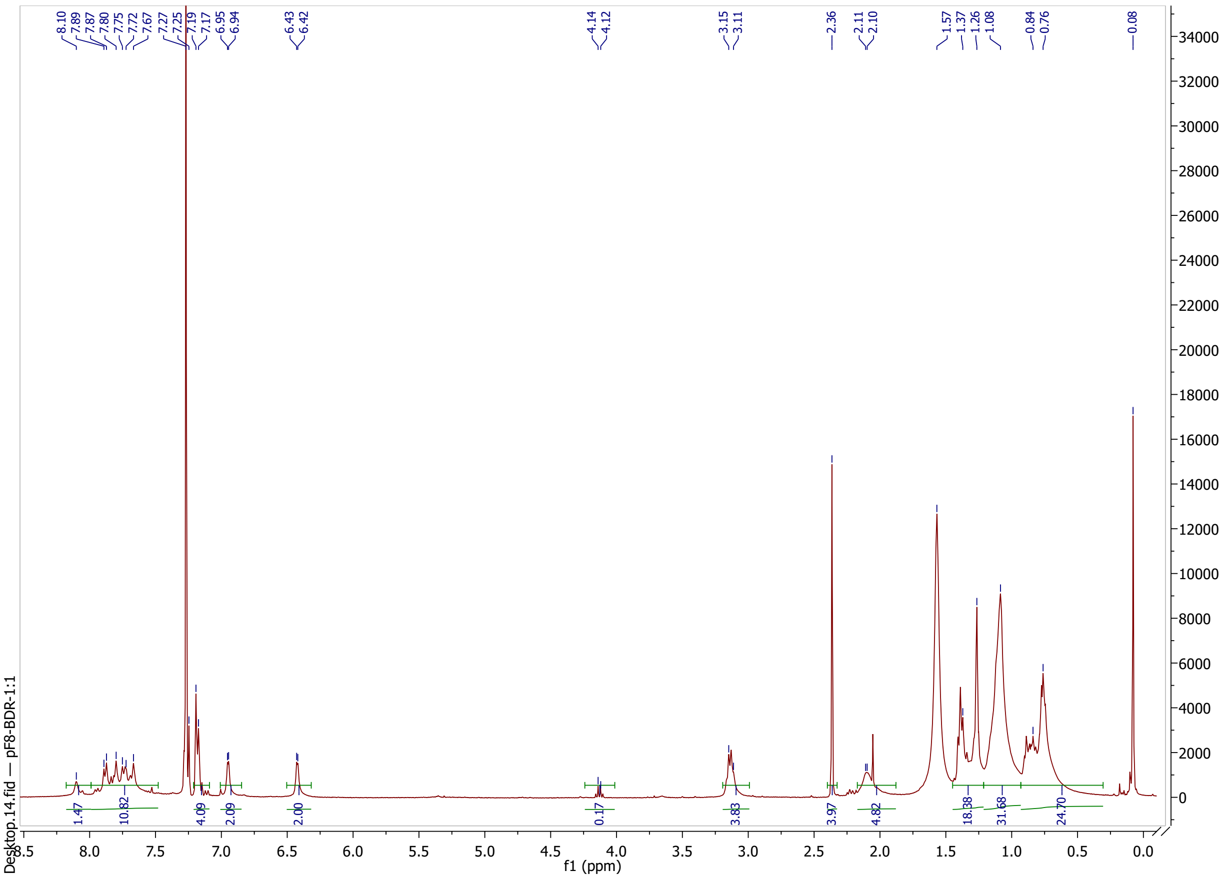
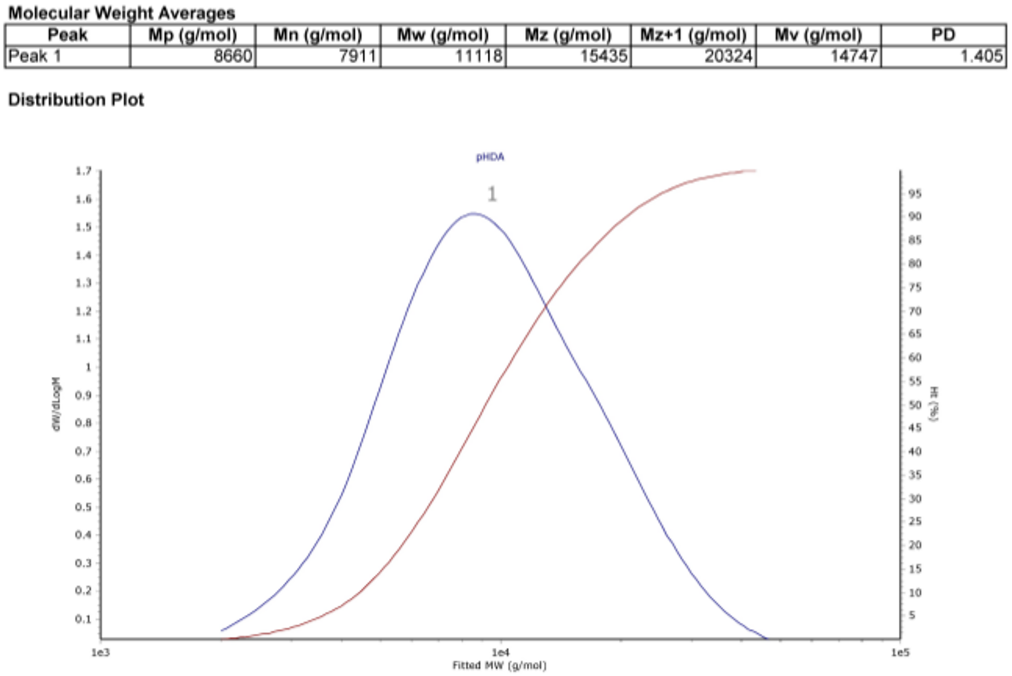


Figure 6: ^{1}HNMR specrum of **2b** in CDCl$_3$

Synthesis of poly(hexadecyl acrylate

In 40 ml Toluene 12.5g (42.2mmmol) octadecyl acrylate and 18mg 2,2'-dimethyl-2,2'-azodipropiononitril (AIBN) were dissolved. In a roundbottom flask fitted with reflux condensor 10ml of Toluene was stirred and heated to 140°C for 5 minutes. The octadecyl acrylate solution was added via a dropping funnel over the course of 1 hour and this was reacted at 140°C for 24 hours. The product was cleaned by precipitating in cold methanol three times.



Molecular Weight Averages

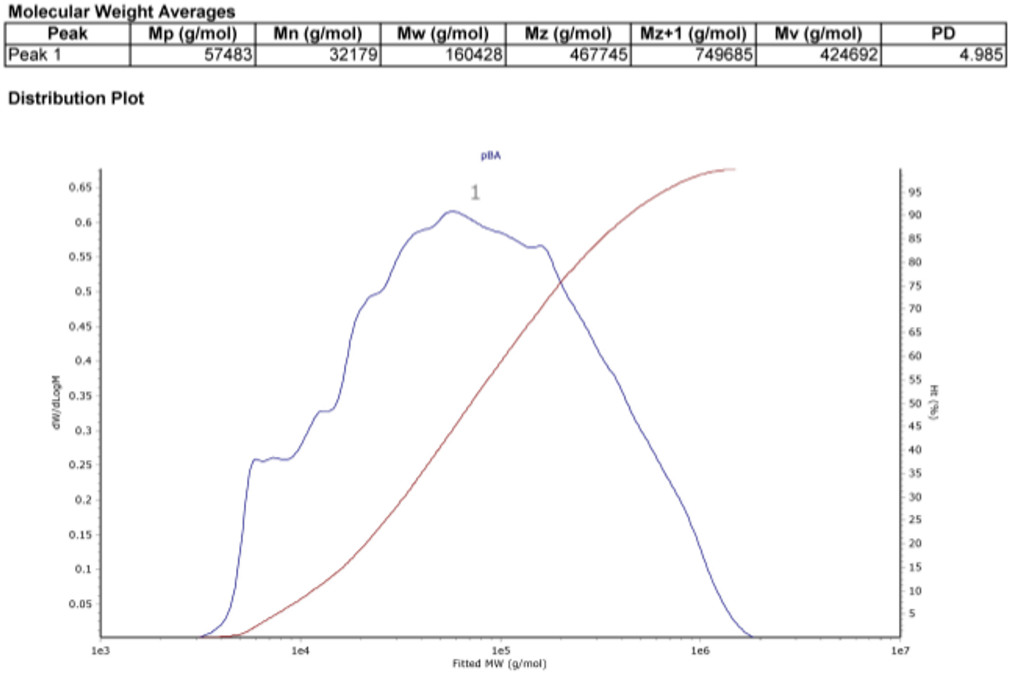
Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	8660	7911	11118	15435	20324	14747	1.405

Distribution Plot

Figure 7: GPC trace and calculated mass against polystyrene reference standards for pHDA measured in $CHCl_3$ at 35°C.

Synthesis of poly(butyl acrylate

Inhibitor was removed from 30g (0.24 mol) butyl acrylate by running over an alumina plug. To this 0.5%(mol/mol) AIBN and 30 ml Toluene were added. The mixture was deoxegynated and reacted at 70°C for 18 hours under oxygen free conditions. The product was precipitated into cold methanol.



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	57483	32179	160428	467745	749685	424692	4.985

Distribution Plot

Figure 8: GPC trace and calculated mass against polystyrene reference standards for pBA measured in $CHCl_3$ at 35°C.

Optical Spectroscopy

All optical spectroscopy experiments are performed in toluene, containing ≤ 5 μg/ml of polymer, in a quartz cuvette after filtering over a 0.2 micron PTFE syringe filter. Absorption spectra are recorded on a Shimadzu UV-2600. All fluorescence excitation, emission and lifetime measurements were performed on an Edinburgh FS5, equipped with a 372nm pulsed laser and Time-Correlated Single-Photon Counting module for lifetime measurements. All depicted spectra are an average of two consecutive measurements. Lifetime decay curves were obtained with 10^4 counts, 4095 channels in a 50ns window. Fluorescent lifetimes were obtained from a lifetime-distribution fitting procedure performed in DecayFit 1.4 from FluoroTools.

Table 1: Absorption and emission maxima for sensor 1 & 2

Sensor	λ_{abs}(nm)	λ_{emm}(nm)
1	366, 516	412, 529
2	340, 516	417, 555

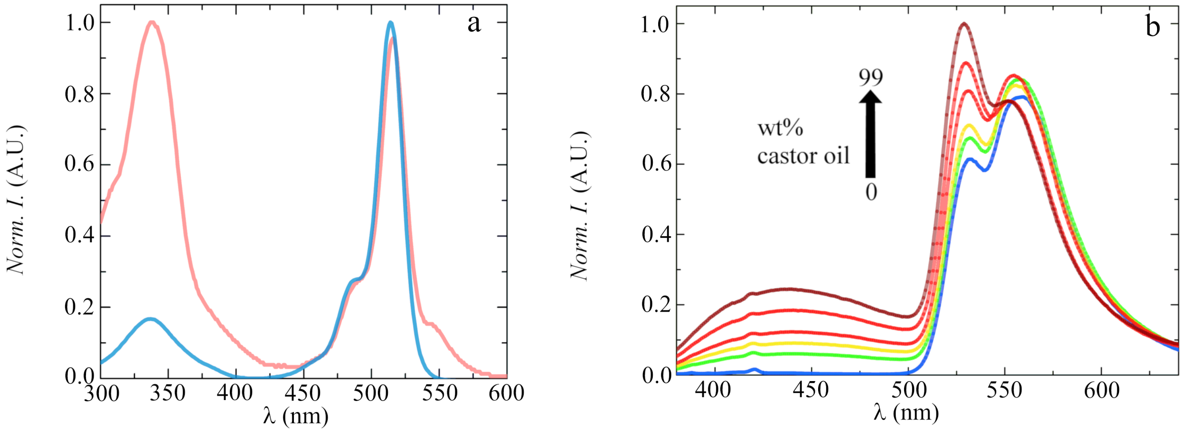


Figure 9: a) Normalized absorption spectra of non-brominated **1** (blue) and **2b** (red) in toluene. In the absorption spectrum of **2b** there is a red-shifted shoulder present which is indicative of aggregation. and b) fluorescence emission spectra ($\lambda_{ex} = 372nm$) in different wt % of castor oil in toluene (0, 30, 45, 60, 83, 99 wt %) normalized to the highest peak. The first peak of the acceptor emission is slightly responsive to the increasing viscosity whereas the second peak shows little response to viscosity. This supports the idea that the shoulder is cause by aggregation resulting in an unresponsive acceptor emisison peak. The donor emission features of the **2b** have broadened with those in the **2a** and show a response in intensity to the viscosity. Rendering its use as an internal reference innefective.

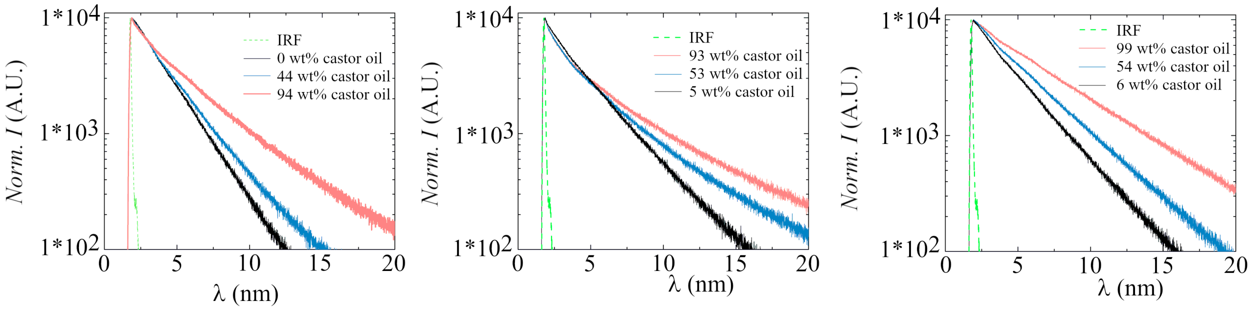


Figure 10: Representive lifetime decay traces (λ_{em} = 580nm and 540nm respectively) of non-brominated **1**, **2b** and **2a** in different mixtures of castor oil and toluene. Where **1** and **2a** show single-exponential decays the **2b** shows bi-exponential decays at higher viscosity which could be attributed to the unresponsive red-shifted emission band thought to be caused by aggregation.

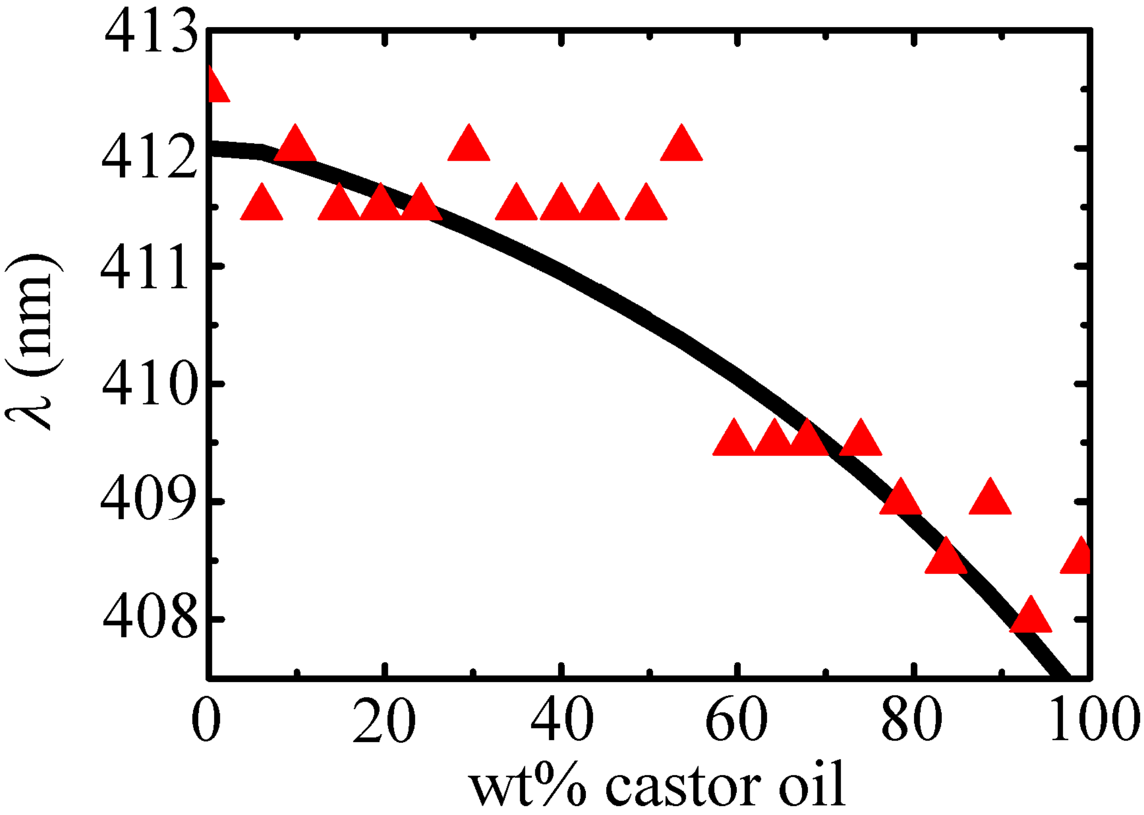


Figure 11: Maximum emission wavelength as a function of wt% castor oil for **2a** obtained from the emission spectra of Fig.4a in the main text.

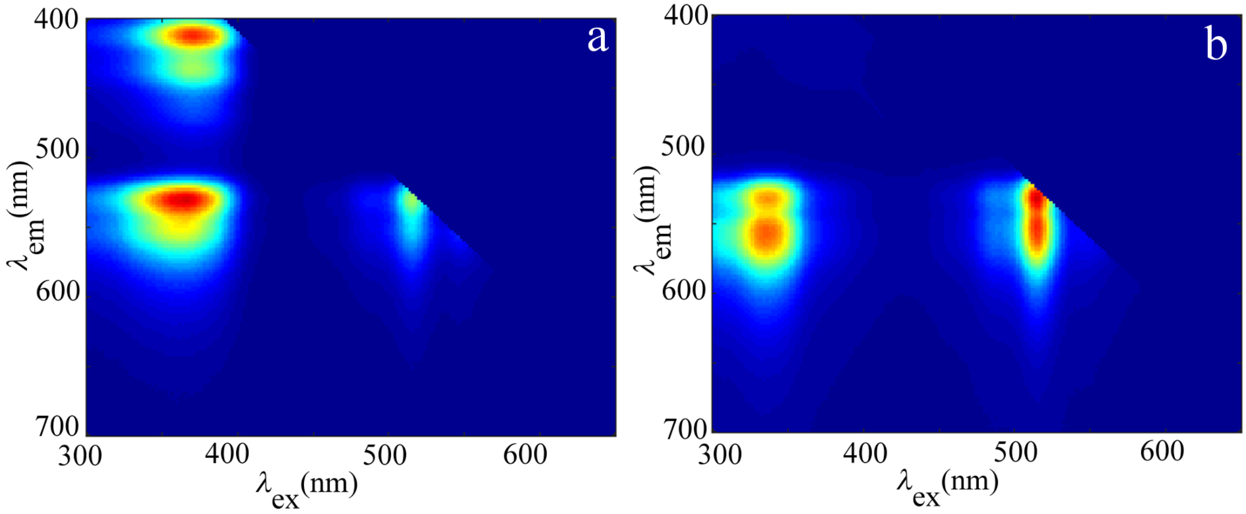


Figure 12: 2D excitation-emission scan of **2a** and **2b** in chloroform.

Confocal fluorescence microscopy

We prepared a solution of 10wt% pHDA and 10 wt% pBA in chloroform. To this 0.5 wt% of rigidochromic sensor **2a** was added, with respect to total polymer mass. The polymer solution was spincoated onto a coverslip at 2000 rpm. Solvent was removed by placing the sample in a vacuum stove at 40°C for 3 days. Imaging experiments were performed on a Nikon C2 confocal scanning laser microscope, with an excitation source at 405 nm. The donor and acceptor emission, upon donor excitation, were detected on two spectrally-split PMT detectors, recorded through a 60x/1.40 oil immersion objective.

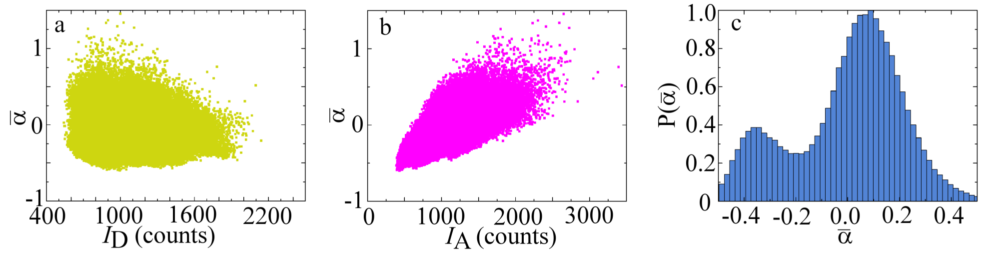


Figure 13: Correlation analysis shows the normalised ratio per pixel as a function of donor intensity (a) and acceptor intensity (b). Histogram of normalised ratios shows two distinct mechanical populations, corresponding to the two domains (c).

References

1. Miyaura, N.; Yanagi, T.; Suzuki, A. The Palladium-Catalyzed Cross-Coupling Reaction of Phenylboronic Acid with Haloarenes in the Presence of Bases. *Synthetic Communications* **1981**, *11*, 513–519.

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3. Cingil, H. E.; Storm, I. M.; Yorulmaz, Y.; te Brake, D. W.; de Vries, R.; Cohen Stuart, M. A.; Sprakel, J. Monitoring Protein Capsid Assembly with a Conjugated Polymer

Strain Sensor. *Journal of the American Chemical Society* **2015**, *137*, 9800–9803, PMID: 26230158.