

Supporting Information
for
Synthesis and photophysical characteristics of
polyfluorene polyrotaxanes

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Characterization data of the compounds: The stability constant, FTIR, ¹H NMR and ¹³C NMR spectra of the investigated copolymers

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S1. The stability constant (K_s) of **1**-TM- β CD inclusion complex

Figure S1 shows the changes in the absolute optical density (OD) at 321 nm with increasing concentration of TM- β CD to a 2 μ M solution of **1** in CHCl_3 . The data were obtained by using a direct binding equation, according to a 1:1 host–guest complexation stoichiometry in ProFit 6.2 (QuantumSoft) [1]. The determined value was found to be 580 (± 100) M^{-1} for **1**-TM- β CD inclusion complex. The value is in good accordance with the reported stability constants of CDs with different guest molecules in organic solvents [2]. To our knowledge, K_s of monomer **1** encapsulated inside of TM- β CD or TM- γ CD has not been studied yet.

S2. The stability constant (K_s) of **1**-TM- γ CD inclusion complex

K_s was determined by measuring the change in the absolute optical density (OD) at 321 nm with increasing concentration of TM- γ CD and the fitting, according to a 1:1

host-guest complexation stoichiometry, Figure S2. The determined value was found to be $160 \pm 30 \text{ M}^{-1}$ lower than that of **1-TM- β CD** inclusion complex, due to its larger cavity which allows better dethreading of the guest **1**. This part of our studies provided us the unexpected better results concerning the binding affinity of monomer **1** compared to 5,5'-dibromo-2,2'-bithiophene, as previously reported [3,4].

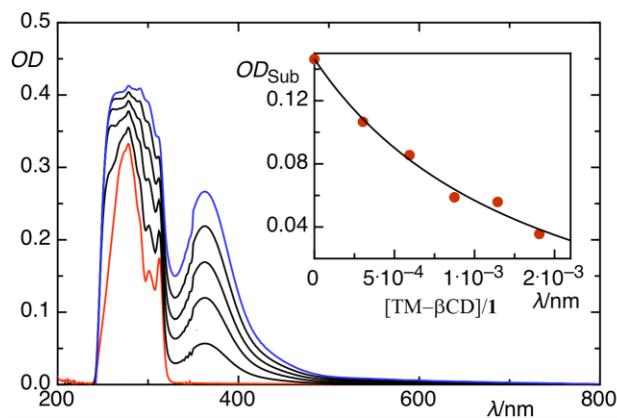


Figure S1: The change in the absorption spectra upon addition of TM- β CD to a 2 μM solution of **1** in CHCl₃ at $\lambda_{\text{ex}} = 321 \text{ nm}$. The fitted binding constant curve (according to a 1:1 host-guest complexation stoichiometry) is shown in the inset.

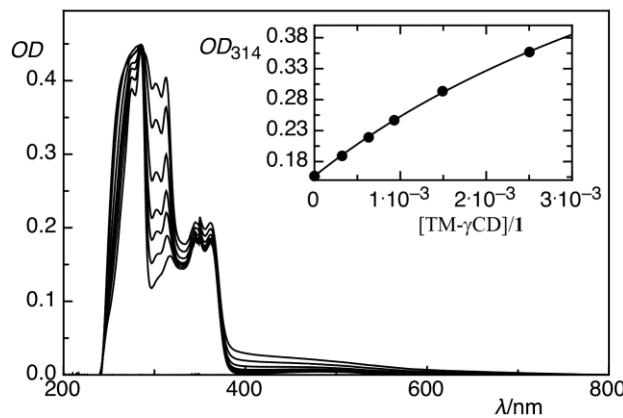


Figure S2: The change in the absorption spectra upon addition of TM- γ CD to a 3 μM solution of **1** in CHCl₃ at $\lambda_{\text{ex}} = 321 \text{ nm}$. The fitted binding constant curve (according to a 1:1 host-guest complexation stoichiometry) is shown in the inset.

S3. FTIR spectra of the reference **3, **3-TM- β CD** and **3-TM- γ CD** polyrotaxane copolymers**

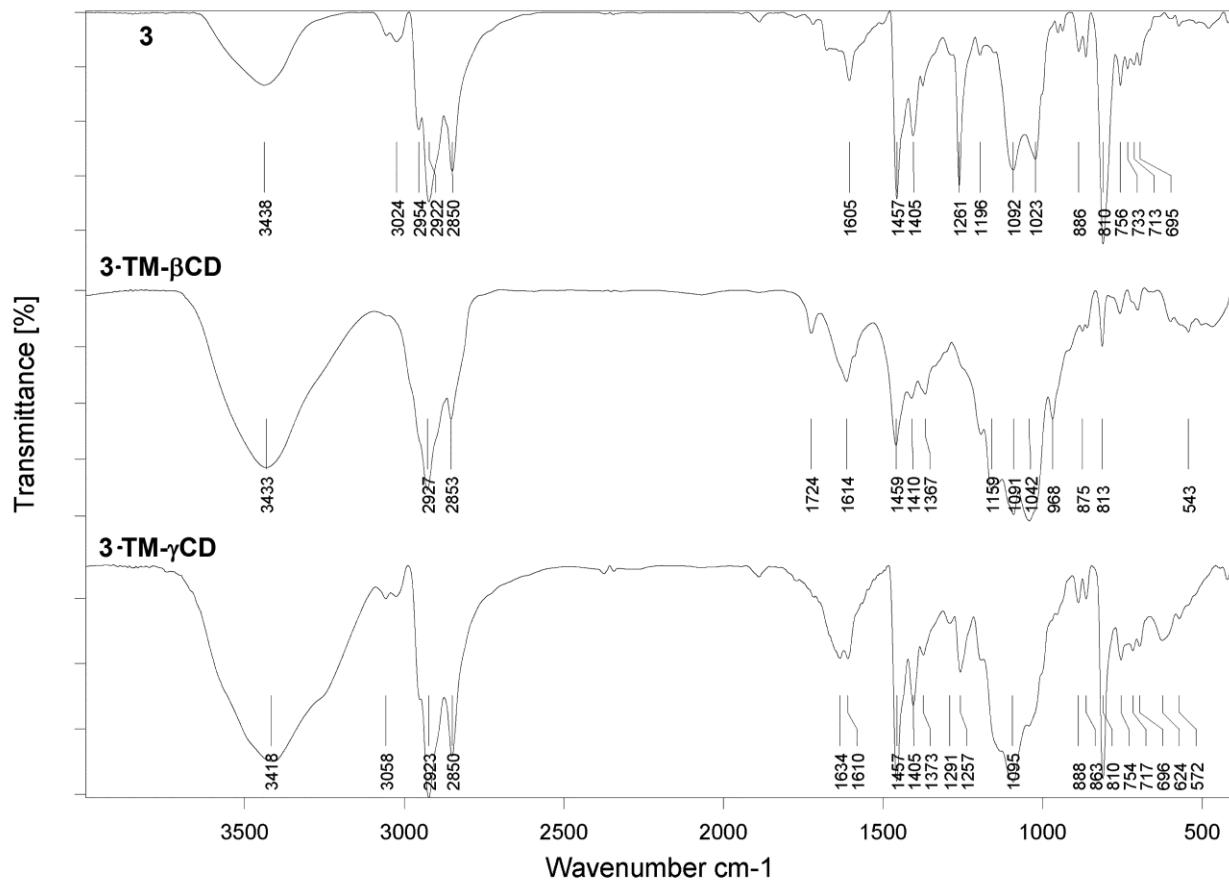


Figure S3: FTIR spectra of the reference **3**, **3-TM- β CD** and **3-TM- γ CD** polyrotaxane copolymers

Figure S3 compares the FTIR spectra of **3**, **3-TM- β CD** and **3-TM- γ CD** polyrotaxane copolymers. FTIR spectrum of the non-rotaxane **3** exhibited characteristic stretching vibrations in the 2954–2850 cm⁻¹ region (aromatic β C–H and ϕ C–H stretching) that are shifted towards lower frequency in the spectra of **3-TM- β CD** and **3-TM- γ CD** polyrotaxanes. FTIR spectra of **3-TM- β CD** and **3-TM- γ CD** show all the characteristic bands of **3** and additional bands located in the 1159–1042 cm⁻¹ region corresponding to TM- β CD and TM- γ CD.

S4. ^1H NMR spectrum of the non-rotaxane **3** copolymer

The ^1H NMR and ^{13}C NMR spectra, with resonance peak assignments of the non-rotaxane **3** confirmed its chemical structure, Figures S4 and S5.

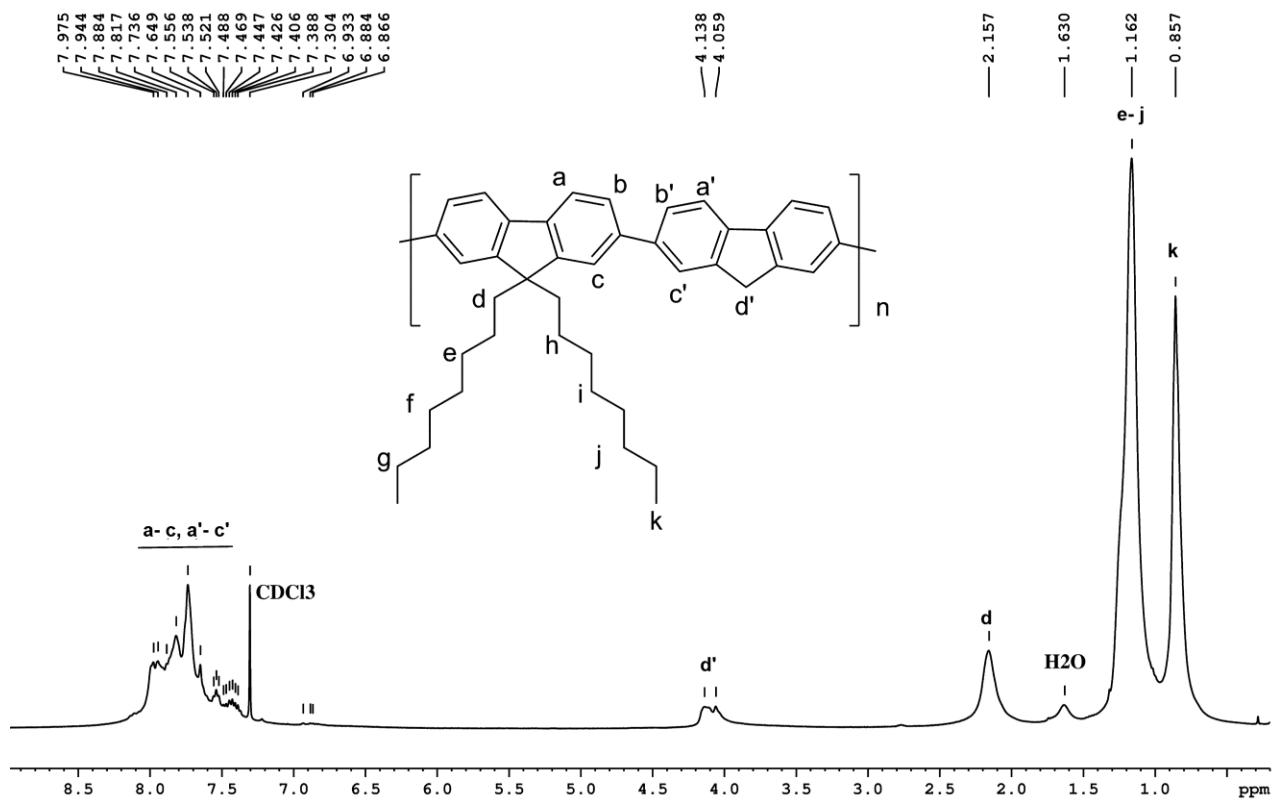


Figure S4: ^1H NMR spectrum of the non-rotaxane **3** copolymer with assignments of the resonance peaks in CDCl_3 .

S5. ^{13}C NMR of the non-rotaxane **3** copolymer

As shown in Figure S4, all typical proton resonance peaks of the non-rotaxane copolymer are visible in the spectrum in CDCl_3 .

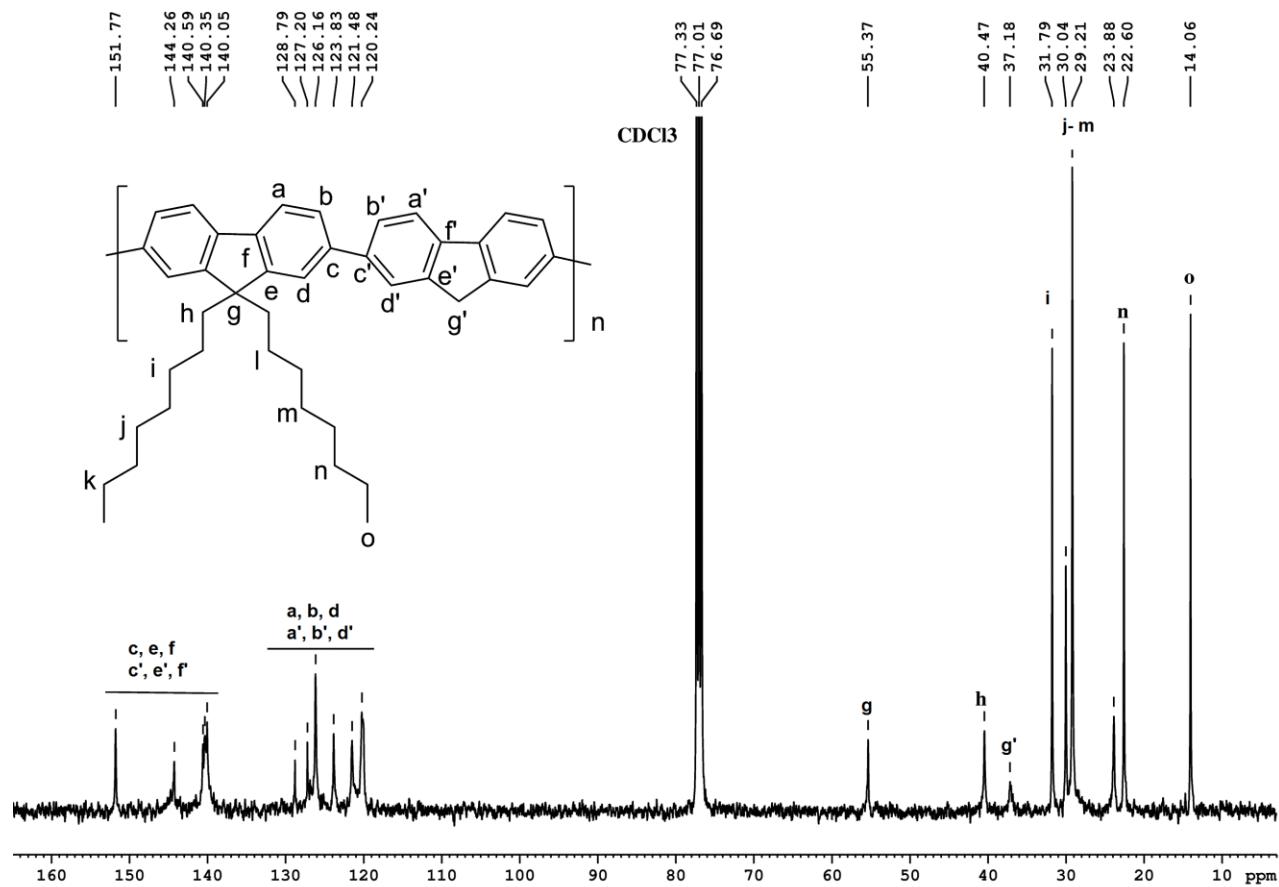


Figure S5: ^{13}C NMR spectrum of the non-rotaxane **3** copolymer with assignments of the resonance peaks in CDCl_3 .

S6. ^1H NMR spectrum of the polyrotaxane **3-TM- γ CD** copolymer

The ^1H NMR analysis was used to determine the coverage of the rotaxane with macrocycle, i.e., the average number of TM- γ CD macrocycles per repeating unit, which has been calculated using the ratio of the integrated area of the peak assigned to the aromatic protons labeled “d” in Figure S6 (2.106 ppm, I_d) and the anomeric H-1 proton of TM- γ CD (5.18–5.26 ppm, I_{H^1}); $(I_d \text{H}^d/4)/(I_{\text{H}^1}/8)$. The average number of TM- γ CD macrocycles per monomer **1** repeat unit has been found to be 0.11 (i.e., 11% coverage). It should be noted that the determined coverage is in accordance with the reported value

of the stability constant, and suggested that much more dethreading or equilibration had occurred compared with TM- β CD under the conditions of the polycondensation reaction.

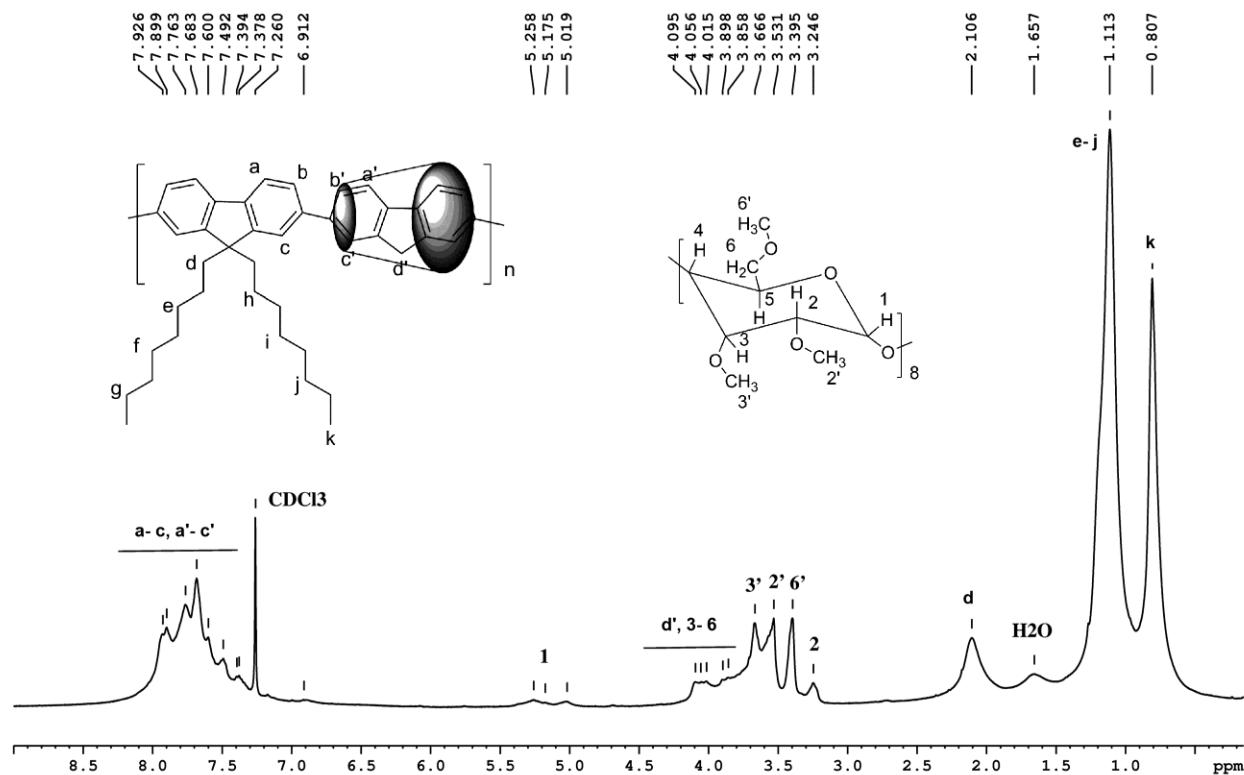


Figure S6: ^1H NMR spectrum of the polyrotaxane **3**-TM- γ CD copolymer in CDCl_3 with assignments of the resonance peaks.

S7. ^{13}C NMR of the non-rotaxane **3·TM- γ CD polyrotaxane**

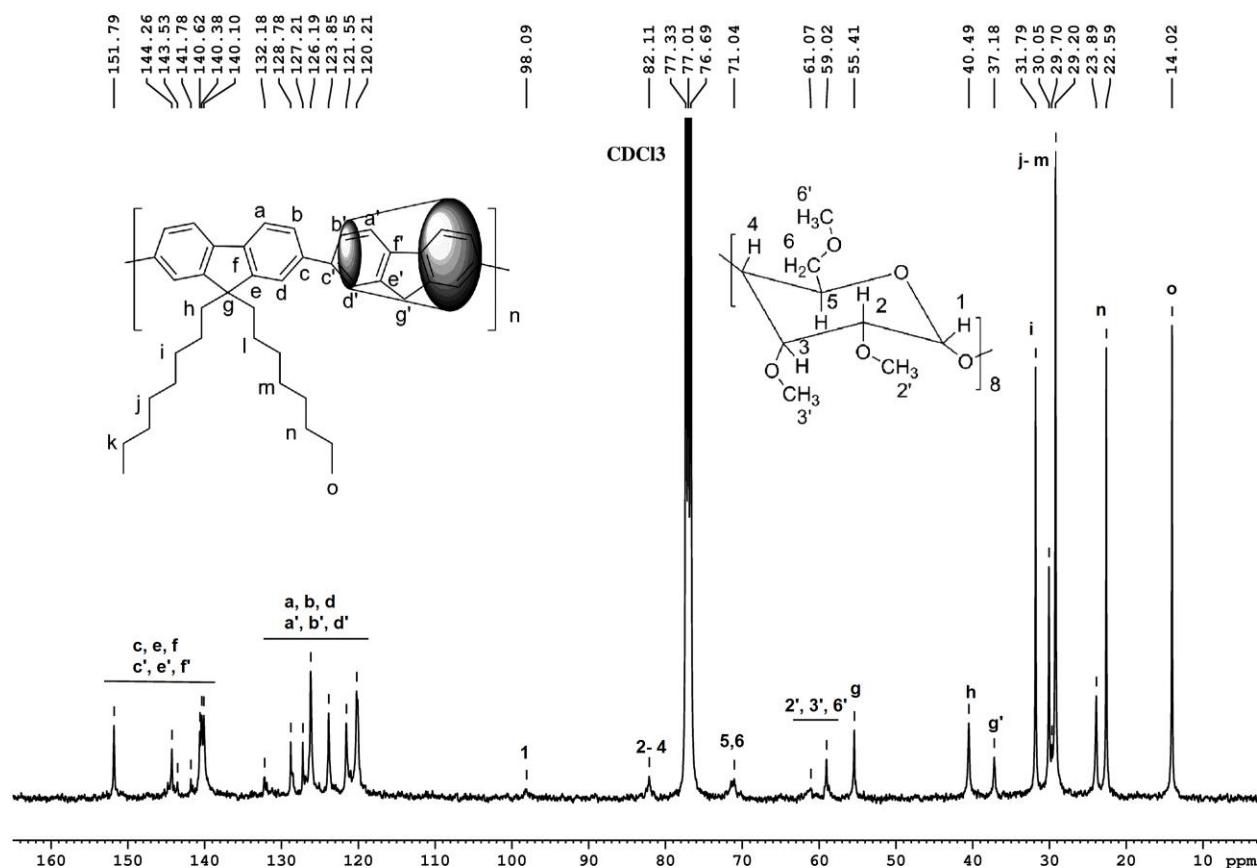


Figure S7: ^{13}C NMR spectrum of the non-rotaxane **3**·TM- γ CD copolymer with assignments of the resonance peaks in CDCl_3 .

References

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