# **Supporting Information**

# Synthesis, photophysics and Langmuir films of polyfluorene/permodified cyclodextrin polyrotaxanes

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#### **1. Experimental Section**

**1.1. Reagents**. 2,7-dibromofluorene (97%) (DBF), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (97%) (DOF), tetrakis(triphenylphosphine) palladium (99%) (Ph<sub>3</sub>P)<sub>4</sub>Pd(0), bromobenzene (99%) (Br-Ph), and ferrocene (Fc) were purchased from Sigma-Aldrich and used as received. Tetrabutylammonium perchlorate (TBACIO<sub>4</sub>) for electrochemical analysis (99.0%) (Fluka) was used without further purification. Acetonitrile (ACN) (Fischer), methylene chloride (DCM), petroleum ether, toluene, tetrahydrofuran (THF) and all other solvents were purchased from commercial sources (Sigma-Aldrich, Fisher) and used without further purification. All reactions were monitored by thin layer chromatography, using aluminum sheets coated with silica gel 60 F254.

#### **1.2.** Materials Synthesis

# **1.2.1.** Synthesis of 2,3,6-tri-O-trimethylsilyl β-CD (TMS·β-CD) and 2,3,6-tri-O-trimethylsilyl γ-CD (TMS·γ-CD)

TMS· $\beta$ -CD and TMS· $\gamma$ -CD host molecules were synthesized by the silulation reaction of native  $\beta$ -CD or  $\gamma$ -CD with 1-trimethylsilylimidazole according to a literature procedure.<sup>1,2</sup>

## **1.2.2. Synthesis of DBF·TMS·β-CD** and DBF·TMS·γ-CD inclusion complexes

To a solution of TMS· $\beta$ -CD (1.1 g, 0.41 mmol) in DCM (5.0 mL) was added DBF (0.072 g, 0.22 mmol) and water as a competitive molecule (2.0  $\mu$ L). The solution was stirred at ambient temperature for 24 h. Then, the DCM was removed by evaporation and the white solid was used for the preparation of **PF·TMS·\beta-CD** polyrotaxane. The DBF·TMS· $\gamma$ -CD inclusion complex was synthesized under similar experimental conditions except (1.25 g, 0.41 mmol) of TMS· $\gamma$ -CD was used instead of TMS· $\beta$ -CD.

# 1.2.3. Synthesis of PF·TMS·β-CD and PF·TMS·γ-CD polyrotaxanes

The synthesis procedure was as follows: Degassed toluene (6 mL) was added to a DBF·TMS· $\beta$ -CD solid followed by the addition of DOF (0.123g, 0.22 mmol), and subsequently 2 mL of 3M sodium carbonate aqueous solution. The mixture was stirred for 3 h at ambient temperature and then 5.1 mg (0.44 × 10<sup>-2</sup> mmol) of ((Ph<sub>3</sub>P)<sub>4</sub>Pd(0) dissolved in 5 mL of degassed toluene was added. The mixture was protected in the dark and nitrogen (N<sub>2</sub>) atmosphere and vigorously stirred at 85-90 °C for three days. An excess of 0.015 g (0.027 mmol) of DOF dissolved in 4 mL of toluene was then added and the reaction was continued overnight. Finally, 2.0 µL of Br-Ph as a monofunctional end-capping reagent and the reaction was continued for 6 h.<sup>3,4</sup> After cooling, the mixture was poured into water and extracted with toluene (20 mL), washed with water (3 x 25 mL), dried over MgSO<sub>4</sub>, concentrated under

reduced pressure and precipitated with methanol. The precipitate was filtered, washed with water and acetone and dried. The resulting compound was dissolved in petroleum ether and the insoluble part was filtered. The soluble part in petroleum ether was collected and concentrated, precipitated in hexane and the solid was filtered. The soluble fraction in hexane was concentrated by vacuum evaporation and, finally, recovered as a yellow solid. 0.32 g, yield = 26.5 % of **PF·TMS·β-CD** polyrotaxane compound was obtained.

<sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ,  $\delta$ , ppm): 7.91-7.34 (aromatic H), 4.10 (CH<sub>2</sub> from fluorene), 4.10-3.58 (H1-H6 from TMS· $\beta$ -CD), 2.10 (CH<sub>2</sub> from dioctyl units), 1.24-0.77 (CH<sub>2</sub> and CH<sub>3</sub> from dioctyl units), 0.12 (Si-CH<sub>3</sub> from TMS· $\beta$ -CD).

IR (KBr, cm<sup>-1</sup>): 3436, 2963, 2924, 2853, 1712, 1649, 1459, 1262, 1099, 1024, 966, 865, 696.

GPC (THF, Pst standard):  $M_n \sim 23\ 000\ g \cdot mol^{-1}$ ,  $M_w/M_n = 2.37$ .

**PF·TMS·γ-CD** was synthesized by similar experimental conditions with those used for the preparation of **PF·TMS·β-CD**, except that TMS·γ-CD was used instead of TMS·β-CD. **PF·TMS·γ-CD** was also obtained as a yellow solid in a 21.6 % yield.

<sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ,  $\delta$ , ppm): 7.99-7.38 (aromatic H), 4.15 (CH<sub>2</sub> from fluorene), 4.02-3.55 (H1-H6 from TMS·γ-CD), 2.19 (CH<sub>2</sub> from dioctyl units), 1.24-0.79 (CH<sub>2</sub> and CH<sub>3</sub> from dioctyl units), 0.14 (Si-CH<sub>3</sub> from TMS·γ-CD).

IR (KBr, cm<sup>-1</sup>): 3438, 2965, 2924, 2851, 1712, 1644, 1458, 1261, 1097, 1021, 871, 723.

GPC (THF, Pst standard):  $M_n \sim 25\ 000\ g \cdot mol^{-1}$ ,  $M_w/M_n = 2.24$ .

# 1.2.4. Synthesis of the reference PF copolymer

The non-rotaxane **PF** counterpart was prepared from DBF and DOF under similar experimental conditions as described above, except that free monomer DBF was used instead of TMS· $\beta$ -CD or TMS· $\gamma$ -CD. The toluene solution was concentrated by rotary evaporation and precipitated in CH<sub>3</sub>OH. The precipitate was filtered, washed with water and acetone and dried. Further, the solid was redissolved in CHCl<sub>3</sub>, precipitated with methanol, collected by filtration and dried. The copolymer was obtained as an orange solid in yield of 41.3 %.

IR (KBr, cm<sup>-1</sup>): 3421, 3053, 2923, 2850, 1734, 1610, 1457, 1291, 986, 810, 695.

<sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ,  $\delta$ , ppm): 7.91-7.35 (aromatic H), 4.09 (CH<sub>2</sub> from fluorene), 2.16 (CH<sub>2</sub> from dioctyl units), 1.39-0.77 (CH<sub>2</sub> and CH<sub>3</sub> from dioctyl units).

GPC (THF, Pst standard):  $M_n \sim 28\ 000\ g\cdot\ mol^{-1}$ ,  $M_w/M_n = 1.83$ .

#### **1.3.** Materials Characterizations

MALDI mass spectrometry (MALDI MS) spectra of TMS $\beta$ -CD and TMS $\gamma$ -CD were obtained using a RapifleX TOF-TOF instrument (Bruker, Germany). The mass spectrometer was operated by FlexControl 4.0 and acquired spectra were processed by FlexAnalysis 4.0 software. The ionization laser power was adjusted just above the threshold in order to produce charged species. 6000 spectra were averaged for each sample analysis. The MS theoretical isotopic profiles of the TMS CDs were obtained using enviPat Web 2.4 software (https://www.envipat.eawag.ch/index.php). The method used to prepare the samples was dried droplet. Samples were dissolved in THF (10 mg·mL<sup>-1</sup>) and mixed by vibration. 20 µL of trans-2-(3-(4-tert-butylphenyl)-2methyl-2-propenylidene) malononitrile (DCTB) matrix solution (20 mg·mL<sup>-1</sup> in THF) was mixed with 2 µL of sample. 2 µL of NaI solution (5 mg·mL<sup>-1</sup> in THF) was added to the sample and matrix mixture. 1  $\mu$ L of the final mixture was deposited on the MALDI steel plate. <sup>1</sup>H NMR spectra have been recorded on a Bruker Avance NEO 400 MHz instrument equipped with a 5 mm QNP direct detection probe and z-gradients. The spectra were recorded using  $CD_2Cl_2$  as solvent, at ambient temperature. The chemical shifts are reported as  $\delta$  values (ppm) relative to the solvent residual peak (5.3 ppm). The IR (KBr pellets) spectra were obtained on a Bruker Vertex 70 spectrophotometer. The binding affinity ( $K_s$ ) values were determined by UV-vis absorption titration of TMS· $\beta$ -CD or TMS· $\gamma$ -CD into a 5 µM solution of DBF in DCM. Gel permeation chromatography (GPC) was performed with a PL-EMD 950 Evaporative Mass Detector instrument using THF as eluent at a flow rate of 1 mL min<sup>-1</sup>. The thermal properties were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC was performed with a Mettler Toledo DSC-1 calorimeter with two repeated heating-cooling cycles at a heating rate of 10 °·min<sup>-1</sup> under N<sub>2</sub> atmosphere. TGA analysis was performed under constant N<sub>2</sub> flow (20 mL·min<sup>-1</sup>) with a heating rate of 10 °C·min<sup>-1</sup> from 25 to 600 °C using a Mettler Toledo TGA/SDTA 851 balance. UV-vis absorption spectra were recorded on a SPECORD 200 Analytik Jena spectrometer with 10 mm guartz cells. Fluorescence measurements were carried out an on Perkin Elmer LS 55 spectrometer. The excitation wavelength corresponds to the maximum absorption band. Time-resolved fluorescence data were acquired with an Edinburgh FLS 980 photoluminescence spectrometer with 1 cm quartz cells. A 375 nm pulsed diode laser (EPL-375, maximum average power: 5 mW, pulse width: 73.2 ps) was used as a light source. Decay data analysis was performed by the deconvolution procedure with multiexponential decay models. The quality of the fit was estimated by the parameter  $\chi^2$  (0.90  $\leq \chi^2 \leq 1.10$ )

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and the symmetrical distribution of the residuals about the zero axis. All measurements were performed at ambient temperature. The absolute determination of fluorescence quantum yield ( $\Phi_{PL}$ ) was performed using a commercial FLS 980 spectrophotometer with a 150 mm integrating sphere (IS) detector equipped with an internal cuvette holder inside the IS at 371 nm excitation wavelength.<sup>5,6</sup> All measurements were carried out with fresh solutions to avoid additional uncertainties. The  $\Phi_{PL}$  was obtained following three steps: 1) the determination of the excitation light peak ( $I_a(\lambda_{ex})$ ) and the emitted light ( $I_a(\lambda_{em})$ ) of the polymeric sample solution in DCM and a blank DCM-filled cuvette ( $I_b(\lambda_{ex})$ ;  $I_b(\lambda_{em})$ ) under identical measurements conditions (excitation, wavelength, temperature, cell position), each within a single scan; 2) evaluation data including choice of the excitation and emission wavelength region for spectral emission, correction and signal integration; 3) calculation of  $\Phi_{PL}$  using the standard equation of the software instrument.<sup>7</sup> Cyclic voltammograms (CV) were carried out in a three-electrode cell in which Pt (1 mm diameter) was used as a working electrode, a Pt-wire as counter-electrode and Ag wire as pseudo-reference electrode. 0.1 M TBACIO<sub>4</sub> solution in anhydrous ACN was used as the supporting electrolyte. The set-up was introduced into a glove box and controlled by AUTOLAB PGSTAT 101 (Ecochemie) by using NOVA software. The pseudo-reference was calibrated with a 10<sup>-3</sup> M of Fc solution in ACN. The polymer samples were drop-casted onto the working electrode from a concentrated DCM solution and studied in the interval -2.5 and +1.5 V vs Ag wire for which the apparent redox potential (half-sum of oxidation and reduction potential) was  $E^{\circ}_{app.}(F_c/F_c^+) = +0.434 \text{ V}$ vs. Ag wire. Cathodic and anodic scans were performed independently. The morphological aspects of the polymeric films were highlighted by atomic force microscopy (AFM) using NTEGRA Spectra (NT-MDT, Russia) instrument with a commercially available NSC10 (NT-MDT, Russia) silicon nitride cantilevers. 10 µL of sample were drop casted on freshly cleaved mica and dried at ambient temperature. Squares of 10 and 3 µm side were scanned in the semicontact mode in air. The resulted topographical AFM images were analyzed using the software Nova v.1.26.0.1443 for Solver. The surface pressure-area isotherms were performed on a KSV Nima Langmuir trough (KSV Nima LB MEDIUM purchased from Quantum Design SARL, Les Ulis, France). BAM images were taken using the apparatus developed by Meunier et al.8

#### 1.4. Procedures

For the Langmuir monolayer study, clearly DCM solutions of **PF**, **PF**-**TMS**-**β**-**CD** and **PF**-**TMS**-**γ** - **CD** compounds (~ 1 mg·mL<sup>-1</sup>) were prepared by slightly sonication and heating at ~ 30° C for 5 min and then cooled to ambient temperature. The water subphase for the monolayer study was purified by a Millipore Simplicity, Billerica, MA purification system and exhibited a resistance of 18.2 MΩ·cm and a surface tension of 72.6 mN·m<sup>-1</sup>. The injected volume of **PF**, **PF**-**TMS**-**β**-**CD** and **PF**-**TMS**-**γ**-**CD** solutions was ~ 100 µL. After spreading the sample onto the Milli-Q ultrapure water subphase, the solvent was evaporated for 10 min and the Langmuir layers were then compressed at a speed of 5 mm·min<sup>-1</sup>. The isotherms were the average of three measurements. All the experiments were conducted in a clean room with constant humidity and temperature of 50 ± 1% and 20 ± 1°C, respectively.

## 2. Characterization data of the compounds

#### 2.1. Matrix assisted laser desorption ionization mass spectrometry analysis

To confirm the total modification of the TMS-CDs, MALDI MS analysis was carried out on each of the modified CDs compounds (Figures S1 and S2).





The MS peaks cluster starting with the monoisotopical peak at m/z = 2670.4 was assigned to the  $\beta$ -CD modified with 21 trimethyl silyl grups (theoretical m/z = 2670.189 for  $[C_{105}H_{238}O_{35}Si_{21}+Na]^+$ ). The resemblance between the experimental and theoretical isotopic distribution profiles validates the assignment (Fig. S1 (left) *vs* Fig. S1 (right)). Also, the TMS<sub>24</sub>·γ-CD MALDI MS spectrum confirms the modification of γ-CD with 24 trimethyl silyl grups. Thus, the monoisotopical peak with m/z = 3048.1 from the MS spectrum corresponds to a chemical formula  $[C_{120}H_{272}O_{40}Si_{24}+Na]^+$  (theoretical m/z = 3048.360). The theoretical isotopical profile matches the experimental one, as there may be observed in Fig. S2 (left) and Fig. S2 (right), thus confirming the structural assignment.



**Figure S2**. MALDI MS spectrum of TMS24·γ-CD isotopical profile: experimental (left) and theoretical (right).

# 2.2. The complexation ability

The complexation ability ( $K_s$ ) of TMS· $\beta$ -CD or TMS· $\gamma$ -CD with DBF was proved by UV-vis titrations in DCM. To measure the  $K_s$ , 50  $\mu$ M of DBF was dissolved in DCM and the change in the absorption spectra was recorded with the addition of TMS· $\beta$ -CD or TMS· $\gamma$ -CD, keeping the concentration of DBF constant. The  $K_s$  was determined by measuring the absolute optical density variation (OD) at 320 nm of DBF with increasing the concentration of TMS· $\beta$ -CD or TMS· $\gamma$ -CD macrocycles. It should be mentioned that TMS· $\beta$ -CD or TMS· $\gamma$ -CD in DCM had no UV absorption peak. According to a 1:1 host-guest complexation stoichiometry,  $K_s$  of DBF·TMS· $\beta$ -CD inclusion complex could be approximately around 500 (±80) M<sup>-1</sup> (Figure S3). The estimated  $K_s$  for DBF·TMS· $\gamma$ -CD of 268 (±30) M<sup>-1</sup> denoted reduced ability of the TMS· $\beta$ -CD (not shown). The greater  $K_s$  value of TMS· $\beta$ -CD confirms the greater stability of the complex in the cross-coupling reaction as a result of better coverage ratio of the **PF-TMS·\beta-CD** polyrotaxane.



**Figure S3.** Changes in the absorption spectra of the monomer DBF upon addition of increasing amounts of TMS· $\beta$ -CD in DCM. The fitted binding constant curve (according to a

1:1 host-guest complexation stoichiometry) is shown in the inset.

# 2.3. IR spectrum of the polyrotaxane PF·TMS·β-CD

The chemical structures of compounds were further supported by IR and NMR spectroscopies. The IR spectrum of **PF·TMS·β-CD** shows all the characteristic bands of **PF** backbones and additional bands corresponding to the macrocyclic TMS·β-CD compound located in 805-1262 cm<sup>-1</sup> region (Figure S4).



Figure S4. IR spectrum of the polyrotaxane copolymer PF·TMS·β-CD.

The vibration bands of the stretching modes of **PF** backbones reveal distinct vibration peaks located at 2963 and 2853 cm<sup>-1</sup> region (aromatic  $\beta$  C–H and  $\Phi$  C–H stretching). As a result of the DBF encapsulation with TMS· $\beta$ -CD, in the spectrum of **PF·TMS·\beta-CD** polyrotaxane the stretching modes are shifted towards lower frequency compared with those of the reference **PF**.<sup>4</sup> Note, that both IR spectra of **PF·TMS·\beta-CD** and **PF·TMS·\gamma-CD** show all the characteristic bands of the **PF** backbones and additional bands attributed to TMS· $\beta$ -CD and TMS· $\gamma$ -CD macrocyclic compounds.

#### 2.4. <sup>1</sup>H NMR spectra of PF·TMS·β-CD and PF·TMS·γ-CD polyrotaxanes

The <sup>1</sup>H NMR spectrum of **PF·TMS·β-CD** polyrotaxane recorded in  $CD_2Cl_2$  is presented in Figure S5. The <sup>1</sup>H NMR spectrum shows peaks corresponding to the aromatic protons of PFs chains at 7.92-7.35 ppm; H1-H6 protons characteristic to glucopyranose units of TMS·β-CD at 4.10 - 3.59-ppm; peaks characteristics for the protons from the 9 position of DBF units at 4.10 ppm; protons of CH<sub>2</sub> from dioctyl units of DOF at 2.10 ppm; aliphatic protons from the dioctyl units of DOF at 1.24-0.78 ppm; protons from Si-CH<sub>3</sub> units of TMS·β-CD at 0.12 ppm. The presence of these characteristic peaks confirms the chemical structure of the polyrotaxane **PF·TMS·β-CD**. The average number of TMS·β-CD macrocycles per monomer DBF repeat unit was found to be 27 % coverage.



**Figure S5**. <sup>1</sup>H NMR spectrum of **PF·TMS·β-CD**.

As expected, the <sup>1</sup>H NMR spectrum of **PF·TMS·** $\gamma$ **-CD** polyrotaxane also exhibited all protons resonance peaks of the **PF** copolymer as well TMS· $\gamma$ -CD (Figure S6). The <sup>1</sup>H NMR spectrum shows peaks corresponding to the protons of the polymeric PFs backbones between 7.99 -7.38 ppm, CH<sub>2</sub> from DBF at 4.10 ppm, H1-H6 from the glucopyranose units of TMS· $\gamma$ -CD at 4.02 - 3.58 ppm, aliphatic protons from the dioctyl units of DOF at 1.24 - 0.79 ppm and protons from Si-CH3 units at 0.14 ppm. By using the ratio of the integrated area of the H<sup>1</sup> from TMS· $\gamma$ -CD (4.02 ppm, I<sub>H-1</sub>) and the methylene proton from DBF (4.15 ppm) as I<sub>H-1</sub>/8)/(I/2) the coverage molar ratio was found to be 14 % coverage ratio (Figure S6).



**Figure S6**. <sup>1</sup>H NMR spectrum of **PF·TMS·γ-CD**.

## 2.5. Thermal properties

The thermal properties of the synthesized compounds were evaluated by TGA and DSC analyses. **PF** sample exhibited two degradation steps with the onset of decomposition at about 412 °C, whereas the **PF·TMS·β-CD** three decomposition steps of degradation process, starting at 321 °C (Figure S7). It should be noted, that **PF·TMS·γ-CD** also exhibited three decomposition steps but starting at 343 °C. Therefore, both polyrotaxane copolymers were stable up to 300 °C. Unfortunately, the presence of macrocycles decreased the thermal stability of **PF** backbones. DSC analysis indicated that the reference **PF** exhibits a glass transition temperature ( $T_g$ ) of about 88 °C. In comparison, **PF·TMS·β-CD** and **PF·TMS·γ-CD** 

exhibited  $T_g$  at 109 and 96 °C, respectively (Figure S8). From this point of view the high  $T_g$  value for the polyrotaxane **PF·TMS·β-CD** can be associated with a higher coverage that increased the rigidity of the PFs backbones.



Figure S7. TGA curves of PF (blue) and PF·TMS·β-CD (red).



Figure S8. Second heating DSC curves of PF·TMS·γ-CD (red) and PF·TMS·β-CD (blue).

#### 2.6. UV-vis absorption spectra of PF and PF·TMS·β-CD

Further insight is provided by UV-vis absorption spectra of **PF** and **PF-TMS-** $\beta$ -**CD** in 10<sup>-3</sup> mg·mL<sup>-1</sup> solutions in DCM (Figure S9). The absorption spectrum of the polyrotaxane **PF-TMS-** $\beta$ **CD** (371 nm) was blue shifted in comparison to **PF** (375 nm), thereby suggesting a slightly lower aggregates or excimers formations. This observation is also in accordance with the electrochemical data reported in the main manuscript.



Figure S9. UV-vis absorption spectra of PF (left) and PF·TMS·β-CD (right) in DCM.

#### 2.7. Normalized emission spectrum of PF·TMS·γ-CD

The normalized fluorescence emission spectrum of **PF·TMS**· $\gamma$ -**CD** in DCM revealed that the hypsochromic shifts are less pronounced of ~ 2 nm, relative to those of **PF** and **PF·TMS**· $\gamma$ -**CD** (Figure S10).



Figure S10. Normalized emission spectrum of PF·TMS·γ-CD.

The behavior observed in Figure S10 suggests that the high coverage ratio of **PF·TMS·β-CD** could be more effective in the reduction of intermolecular interactions and/or a variation of the polarity when the DBF core is encapsulated inside of the TMS·β-CD` cavity.<sup>9-11</sup>

### 2.8. Studies on persilylated CD hydrolysis within rotaxanes in aqueous medium

Additional studies concerning the hydrolysis of TMS-CDs that could affect the structure and physical properties of the investigated **PF·TMS·β-CD** and **PF·TMS·γ-CD** polyrotaxanes were also performed. Taking into consideration the compression isotherm results, it can be concluded that only a partial hydrolysis occured when TMS-CDs are on the water surface

(Figure S11). The compression isotherms recorded in time of the layers showed that the isotherms are reproducible and stackable regardless of the waiting time prior to compression. The features of the isotherms are similar and not different in time denoting that the partial hydrolysis of TMS· $\beta$ -CD and TMS· $\gamma$ -CD is instantaneous on the water surface and does not affect the structure and physical properties of PF.



**Figure S11.** Compression isotherms of **PF·TMS·β-CD** and **PF·TMS·γ-CD** monolayers after 5 minute and 1 hour.

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