Synthesis and Characterization of the Mono-Cation

To prove that the closed-shell cations are delocalized in the backbone of the polymer and do not represent a chain of isolated chromophores, we synthesized a small molecule mono-cation (one repeat of PFC, sans one cation due to synthetic constraints) according to Scheme 1. Qualitatively, the mono-ketone 2 has very different physical (and optoelectronic) properties than PFK and, furthermore, 2 is unstable towards acids and decomposes on a silica column. After neutralizing the silica gel (5% triethylamine in heptane solution) the product could be isolated from unreacted starting compounds in good yield. We synthesized the mono-cation 3 in a one-pot synthesis applying the same procedure to make 2 but then immediately converted the ketone to a closed-shell cation.
Unfortunately, we were unable to resolve a clear $^1$H-NMR spectrum of the mono-cation. Therefore, to remove un-charged impurities, we washed the crude product with heptanes by vigorous shaking, after which the compound was collected by centrifugation. To isolate the mono-cation we then fractionated it on a silica plug. However, the material streaks heavily on the column and, at least partly, turns color from deep purple to colorless to later reappear again as a purple band. Nevertheless, we were able to isolate a fraction that only contained one bright purple spot with $R_f = 0.58$ on TLC but also showed a faint spot above ($R_f = 0.76$). By $^1$H-NMR we could still not resolve the spectrum because of locking and shimming difficulties, but, we no longer see obvious signs of residual mono-ketone or unreacted starting materials. With high-resolution mass spectroscopy we found the exact mass belonging to the structure of the mono-cation as the major peak along side three smaller peaks.

By comparing the absorption spectra of the mono-cation and PFC in Figure S1 we can clearly see that they are qualitatively very similar but that the maximum of the low-energy band of the mono-cation is hypsochromic compared to PFC. Furthermore, PFC has a typical broad absorption tail that is common for conjugated polymers that is not present in the small molecule mono-cation. The shorter wavelength low-energy band and the absence of an absorption tail in the mono-cation
Figure S1: UV-Vis absorption spectra of the mono-ketone (dotted line), mono-cation (solid line), and PFC (dashed line) measured in CH$_2$Cl$_2$. While the absorption spectra of the mono-cation and PFC are qualitatively similar in shape, the maximum absorption of the low-energy band in the mono-cation is hypsochromic (38 nm) with respect to the absorption maximum of PFC. Furthermore, PFC has a long absorption tail that is not present in the mono-cation. The difference in the maximum absorption of the low-energy bands and the absence of an absorption tail in the mono-cation, implies that the closed-shell cations are delocalized in the backbone of the polymer of PFC and are not isolated chromophores.
compared to PFC implies that the closed-shell cations are delocalized in PFC along the polymer backbone.

**Post-Polymerization Modification**

We followed the post-polymerization modification by correlating FT-IR spectra with absorption spectra of PFC at several stages of conversion during the polymer analogous reaction. A blow-up of the relevant part of the FT-IR spectra and the UV-Vis absorption spectra are shown in Figure S2. We observe that at different degrees of conversion the peak at 1654 cm$^{-1}$ decreases in intensity by 67% and the peak at 1725 cm$^{-1}$ diminishes by 83%, which we ascribe to a decrease in the number of carbonyl groups. Furthermore, a new peak appears at 1519 cm$^{-1}$, which we ascribe to the inclusion of N,N-dimethylaniline into the backbone. These spectral changes correlate to the absorption spectra of protonated PFC at the same degrees of conversion. At very low levels of conversion the predominant absorption originates from cations that are generated by protonation of the residual ketones, however, a small peak can already be seen at ~570 nm originating from cations that are stabalized by N,N-dimethylaniline. The optical band gap of acidified PFC is the result of maximizing the average conjugation length by protonation of the small amount of residual ketones (converting cross-conjugated carbonyls to conjugated methines, which we ascribe to the peak at ~430 nm) increasing the delocalization of the permanent carbocations.

**Molecular Weight Assessment by GPC**

Although it is generally acknowledged that GPC overestimates molecular weights of conjugated polymers by a factor of two to four, there is more complexity to the story which is often overlooked. It has become common practice to report only $M_n$, $M_w$, and PDI values excluding any experimental detail on the calibration method or how samples were prepared. Considering the quadratic dependence of the light scattering signal to $\frac{dn}{dc}$, accurate preparation of samples is very important. If the $\frac{dn}{dc}$ used to calculate molecular weight is 5% lower than the actual value, the molecular weight will be overestimated by 10%. In a typical GPC set-up $\frac{dn}{dc}$ is measured using a concentration detec-
Figure S2: Blow-up of FT-IR spectra (left) and absorption spectra (right) of PFC at different stages of conversion during the polymer analogous reaction, demonstrating the gradual decrease of the peaks at 1654 cm\(^{-1}\) and 1725 cm\(^{-1}\) and the development of a new peak at 1519 cm\(^{-1}\). These IR spectral changes correlate to the changes in absorption spectra in acidic DCM in which the peak at 460 nm, originating from cations of protonated residual ketones, decreases in intensity and shifts to a lower wavelength while a new peak appears at ~570 nm and red shifts to ~590 nm.

Figure S3: \(^1\)H-NMR spectrum of PFK clearly showing the peak broadening typical for polymers. The aromatic region integrates to 10 protons and the aliphatic region to 26 protons which matches the proposed structure. The small peaks at 0 ppm and 4 ppm originate from silicone grease and residual solvent.
Figure S4: While PFK could be easily characterized by $^1$H-NMR, we encountered difficulties obtaining clean spectra of PFC due to problems with locking and shimming, possibly due to the combination of the ionic and polymeric nature of CPIs driving aggregation in organic solvents (PFC is sparingly soluble in CDCl$_3$), limiting the usefulness of the spectrum.

...tor (e.g., refractive index), however, for reliable results a very precise sample concentration must be known. Any deviation in the real concentration due material that is not completely dissolved results in a significant error. Furthermore, since $dn/dc$ values are unknown for most conjugated polymers, verification against published values is nearly impossible. The TriSEC calibration method is highly dependent on the light scattering detector and should, therefore, be used with caution when measuring molecular weights of conjugated polymers. It is also worth pointing out that the light scattering detector is incapable of detecting bimodality in the sample. The Universal Calibration method relies on the viscosity detector for which the sensitivity to low molecular weight (as compared to thermoplastics) materials exceeds that of the light scattering detector; therefore, conjugated polymers are better measured using Universal Calibration. In Table S1 the large differences between Universal Calibration and TriSEC are summarized. We believe that the molecular weights calculated using TriSEC are overestimated—not systematically, varying from lab to lab and batch to batch—and, therefore, we chose to use the Universal Calibration method instead,
despite the fact that it reports the lowest values of $M_n$ and $M_w$ of any of the detection methods.

Figure S5: Refractive index (left) and intrinsic viscosity (right) GPC traces of three batches of PFK, batch 1 (dotted line, THF), batch 2 (dashed line, CHCl$_3$), and batch 3 (solid line, CHCl$_3$) (each injected twice), clearly demonstrating the batch-to-batch variations in molecular weight and PDI. Overall the calculated $M_n$ is around 5,000 g/mol and a PDI around 3.0, corresponding to number of repeats, $P_n$, of $\sim 8 - 25$. The relatively broad molecular weight distribution is caused by the low selective nature of the Friedel-Crafts polycondensation. PFK from batch 3 was used for further characterization and for the polymer analogous reaction as discussed in the main text.

Typically, molecular weight distributions are relatively monodisperse and have a normal distribution where $M_n$ and $M_w$ are close to the peak molecular weight ($M_p$). However, the chemistry used to prepare conjugated polymers is quite different than the traditional anionic, radical, etc. polymerizations and tends to give less monodisperse products and non-normal distributions (see Figure S5). Thus, we also compared (the main) $M_p$ of all batches. At low reaction temperatures the highest value of $M_p$ we found was 9,000 g/mol, however, PFK from batch 3 has a small shoulder with a $M_p$ of 19,300 g/mol. After switching to a higher boiling solvent the $M_p$ went up significantly, however, the resulting polymer has a bimodal molecular weight distribution (with the first peak close to $M_n$). Although $dn/dc$ values are slightly dependent of molecular weight, when comparing structurally identical polymers the $dn/dc$ should remain constant within experimental error. However, when analyzing the GPC results obtained from PFK batch 4 we observed a relatively low calculated $dn/dc$ value of 0.068 while in the other batches $dn/dc$ ranged from 0.163 to 0.188. Although it is unclear to us why the $dn/dc$ value was so low, we do not suspect an error during the sample
preparation stage since no material was left on the filter. This apparent error in the $dn/dc$ value nicely demonstrates the large impact it has on the calculated molecular weights; with $dn/dc = 0.068$ we obtained $M_n = 295,300$ and $M_w = 853,800$ with the TriSEC method. Of course we cannot rule out that there was a significant error in the concentration, however, the Universal Calibration method gave a more realistic result. Even these, in our opinion, are still largely overestimated. To address this discrepancy we manually set $dn/dc$ to 0.188. These recalculated results are given in Table S1.

Table S1: Summary of the GPC data obtained from three batches of PFK demonstrating the effect of the reaction conditions such as reaction time, temperature, and Lewis acid loading on the molecular weight distribution as calculated using either the Universal Calibration or TriSEC method. All units are in g/mol.

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<th></th>
<th>Universal</th>
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<th>TriSEC</th>
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<td></td>
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<td>$M_n$</td>
<td>$M_w$</td>
<td>$M_p$</td>
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<tr>
<td>PFK 1 (CH$_2$Cl$_2$)$^a$</td>
<td>5,500</td>
<td>16,300</td>
<td>6,000</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>PFK 2 (CH$_2$Cl$_2$)$^a$</td>
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<td>9,000</td>
<td>16,400</td>
<td>28,600</td>
<td>25,800</td>
<td></td>
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<tr>
<td>PFK 3 (CH$_2$Cl$_2$)$^b$</td>
<td>4,200</td>
<td>9,900</td>
<td>3,300</td>
<td>19,100</td>
<td>47,300</td>
<td>15,400</td>
<td></td>
</tr>
<tr>
<td>PFK 4 (1,3,5-trichlorobenzene)$^c$</td>
<td>5,200$^d$</td>
<td>27,700$^d$</td>
<td>31,700$^d$</td>
<td>108,500$^d$</td>
<td>278,500$^d$</td>
<td>365,000$^d$</td>
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$^a$Polymerization performed at 40 °C, with 10 eq. of AlCl$_3$ for 24h
$^b$Polymerization performed at 40 °C, with 3 eq. of AlCl$_3$ for 72h
$^c$Polymerization performed at 80 °C, with 3 eq. of AlCl$_3$ for 24h
$^d$Calculated using a $dn/dc$ value of 0.188 to match the experimental $dn/dc$ values of PFK 1-3

The polymerization in 1,3,5-trichlorobenzene clearly needs further optimization to improve yields and decrease PDI but it demonstrates that the Friedel-Crafts reaction can yield high molecular weight polymers at elevated reaction temperatures. More importantly, the optoelectronic properties of PFK from batch 4 are almost identical to those of PFK from batch 3, as shown in Figure S6, suggesting that the effective conjugation length saturates after P$_n$ $\sim$ 10.
Figure S6: Absorption spectra of two batches of PFK in neutral and acidic conditions when polymerized in DCM (acidic; dash-dotted line, neutral; dotted line) or 1,3,5-trichlorobenzene (acidic; solid line, neutral; dashed line). The lack of a significant red shift of the absorption band-edge in acidic DCM signifies that, despite the nine-fold increase in molecular weight when PFK is synthesized in a higher boiling solvent such as 1,3,5-trichlorobenzene, the optical properties are already saturated after ~10 repeats.
Figure S7: TGA and DSC traces of PFK (dashed lines), PFC-OMe (dotted lines), and PFC as the BF$_4^-$ salt, demonstrating the large differences in the physical properties between PFK and PFC while the differences between PFK and PFC-OMe are smaller. All polymers have a sharp decomposition temperature (i.e., 10% weight-loss) above 340 °C but PFC-OMe also has a step-wise decomposition which might indicate the loss of methoxy groups since it is not visible in either PFK or PFC (10% weight-loss at 439 °C and 402 °C, respectively). Both PFK and PFC-OMe have a glass transition temperature of 97 °C and 175 °C, respectively, but PFC has a very sharp melting peak at 186 °C. PFK and PFC-OMe both show a small exotherm at ~270 °C but this feature is too small to be ascribed to a thermal transition.
Figure S8: Calculated HOMO, LUMO, and SOMO energy levels for PFK, PFK-H+, PFC, and PFC-rad.
Figure S9: DFT calculated absorption bands (black) and experimental absorption data (red) for PFK.

Figure S10: DFT calculated absorption bands (black) and experimental absorption data (red) for PFK-H+.
Figure S11: DFT calculated absorption spectra for PFK PFK-H+ PFC and PFC-Rad showing a clear, systematic decrease in band gap that is in agreement with experimental values and a very large drop in PFC-Rad resulting from the inclusion of unpaired spins. Quantitatively, the band gap of PFK-H+ is under-estimated, probably because the calculations were performed on the fully protonated structure.
**Experimental**

**Unimers**

*(9,9-dihexyl-9H-fluoren-2-yl)(phenyl)methanone (2)* To a dried three-necked round-bottom flask 1 (566 mg; 1.692 mmol), benzoyl chloride (237.82 mg; 1.692 mmol), and LiCl (10 wt% of AlCl₃) were added to 20 mL dry CH₂Cl₂ in a dried three-necked round-bottom flask. The solution was cooled to 0 °C and via a solid addition arm AlCl₃ (225.58 mg; 1.692 mmol) was slowly added resulting in a bright yellow color that slowly shifts to green after a couple of minutes. The reaction mixture was allowed to warm up to rt and stirring was continued for 24h. The now deep green reaction mixture was quenched by pouring it out over ice H₂O before extracting with 150 mL of CH₂Cl₂. The organic layer was next washed with saturated NaHCO₃ and brine after which the organic layer was concentrated on a rotary evaporator. The crude produce was then applied on a silica plug after neutralizing the silica gel with 5% triethylamine in heptane. Unreacted 1 and benzoyl chloride was removed by flushing the plug with heptane. By switching the eluent to ethyl acetate 2 was obtained as a colorless oil (615 mg, 83%). ¹H NMR (400 MHz, CD₃Cl) δ 7.85 – 7.74 (m, 6H), 7.61 (t, J = 7.3, 1H), 7.50 (t, J = 7.6, 2H), 7.38 (s, 3H), 2.04 – 1.92 (m, 4H), 1.17 – 0.98 (m, 12H), 0.76 (t, J = 7.1, 6H), 0.67 – 0.57 (m, 4H). ¹³C NMR (101 MHz, CD₃Cl) δ 196.90, 151.92, 150.66, 145.54, 139.81, 138.33, 135.91, 132.13, 130.01, 129.92, 128.33, 128.19, 127.00, 124.57, 123.04, 120.64, 119.24, 77.32, 77.00, 76.68, 55.27, 40.15, 31.47, 29.61, 23.76, 22.54, 13.98. FT-IR (ATR) 3064, 2955, 2925, 2852, 1655, 1605, 1571, 1467, 1445, 1417, 1377, 1344, 1316, 1270, 1220, 1175, 1143, 1098, 1074, 1027, 1004, 953, 905, 840, 778, 740, 722, 696, 634 cm⁻¹. HRMS calculated for C₃₂H₃₉O: 439.299. Found: 439.2.

*(9,9-dihexyl-9H-fluoren-2-yl)(4-(dimethylamino)phenyl)(phenyl)methylium (3)* The same procedure was applied for 2 but, instead of first isolating the product, the reaction was continued in a one-pot reaction. Dimethyl aniline (314.6 mg; 2.597 mmol) and AlCl₃ (225.58 mg; 1.692 mmol) were added and the mixture was refluxed for 24h resulting in a color shift from deep red to purple. Cooled down to rt the now deep purple reaction mixture was quenched by pouring
it out over ice before extracting with 150 mL of CH$_2$Cl$_2$. The organic layer was next washed with 1N HCl and next dried over Na$_2$SO$_4$ after which the organic layer was concentrated. The crude produce was then dispersed in 200 mL of heptane by vigorous shaking and allowed to phase separate over night after which it was collected by centrifugation at 4000 RPM for 20 minutes. The produce was fractionated on a silica plug by slowly increasing the polarity of the eluent (ethyl acetate in heptane) until the desired spot on TLC was collected affording 3 as a purple tacky solid (9 mg; 1%). FT-IR (ATR) 2959, 2928, 2858, 1706, 1598, 1520, 1445, 1405, 1345, 1257, 1214, 1108, 1071, 1017, 898, 798, 750, 700, 665, 548 cm$^{-1}$. HRMS calculated for C$_{40}$H$_{48}$N$: 542.378. Found: 542.378.

**Polymers**

**Poly[(9,9-dihexylfluorene)-alt-(1,4-phenylene)dimethanone] (PFK).** 1 (1.995 g; 5.96 mmol), terephthaloyl chloride (1.211 g; 5.96 mmol), and 1,3,5-trichlorobenzene (~30 g) were added to a dried three-necked round-bottom flask. AlCl$_3$ (2.385 g; 17.88 mmol) and LiCl (10 wt% of AlCl$_3$) were added to a solid addition arm and carefully attached to one of the necks of the flask. The entire set-up was evacuated of air by several cycles of high vacuum and back-filling with dry N$_2$. The flask was then slowly heated to 80 °C resulting in a slight green monomer solution after which the Lewis acids were added under stirring resulting in an immediate color change to deep red. The reaction mixture was kept at 80 °C for 24h under nitrogen atmosphere. The reaction mixture was allowed to cool down to ~50 °C before quenching the reaction by slowly adding 3 mL of CH$_3$OH resulting in a color change from red to yellow. Next, a short-path vacuum distillation set-up was attached and the CH$_3$OH and 1,3,5-trichlorobenzene was removed at 20 Torr, ~120 °C, and no cooling water. The set-up was regularly unclogged of crystallized 1,3,5-trichlorobenzene using a heat-gun. The remaining produce was then dissolved in a minimal amount of hot THF and any insolubles were removed by filtration before precipitating into a large excess of ice-cold CH$_3$OH (500 mL). The precipitate was then concentrated by centrifugation at 4000 RPM for 20 min. and filtered over a soxhlet timble. The produce was purified further via continuous soxhlet extraction.
with hexanes, CH$_3$OH, CH$_3$COCH$_3$, and CHCl$_3$ to afford **PFK** from the CHCl$_3$ fraction, after removal of the solvent by rotary evaporation, as an orange powder (160 mg; 6%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.37 – 7.27 (m, 10H), 2.28 – 1.74 (m, 4H), 1.36 – 0.81 (m, 12H), 0.86 – 0.39 (m, 10H). FT-IR (ATR) 3337, 3054, 2955, 2927, 2850, 1729, 1654, 1602, 1569, 1498, 1455, 1401, 1343, 1299, 1256, 1177, 1095, 1068, 1016, 968, 904, 861, 798, 742, 720 cm$^{-1}$. GPC (THF) $M_n$ 5,200 g/mol, $M_w$ 27,700 g/mol, PDI = 5.3.