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Supporting information for: Stabilizing Cations in the Backbones of Conjugated Polymers

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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.

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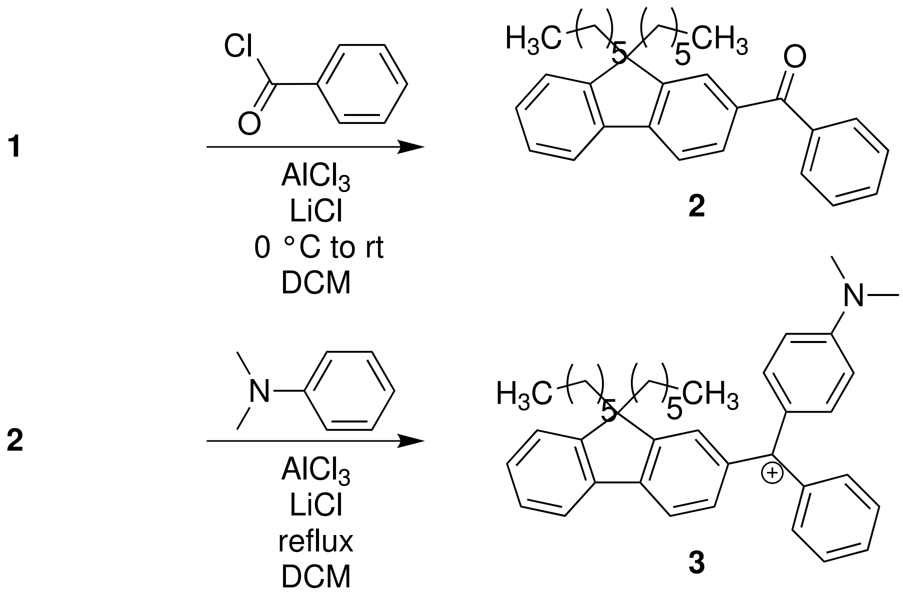

Scheme 1:

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

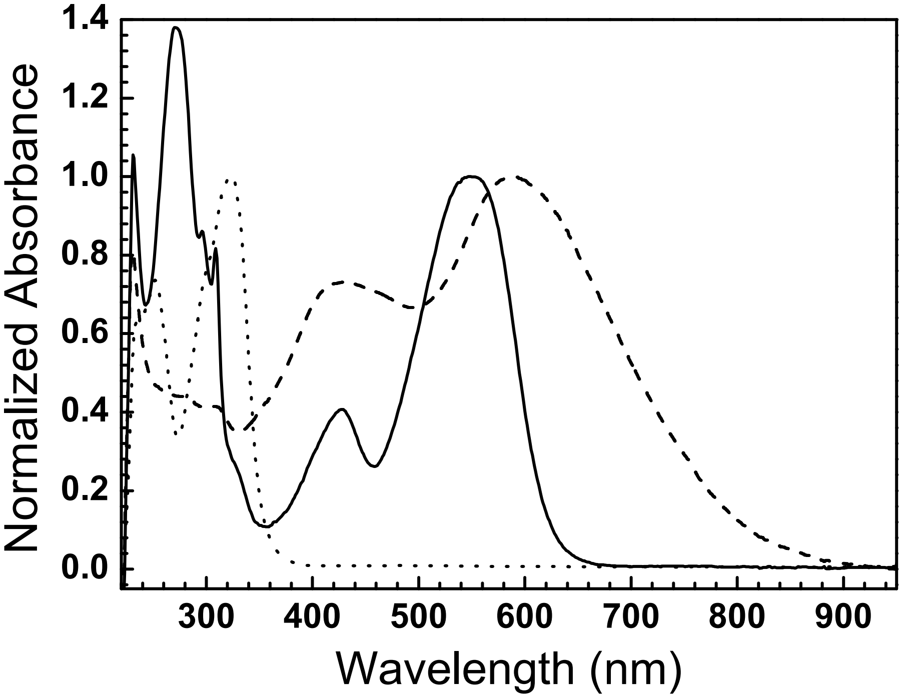

Figure S1: UV-Vis absorption spectra of the mono-ketone (dotted line), mono-cation (solid line), and **PFC** (dashed line) measured in CH_2Cl_2. While the absorption spectra of the mono-cation and **PFC** are qualitatively similar in shape, the maximum absorption of the low-energy band in the mono-cation 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 chromaphores.

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 absoprtion 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-

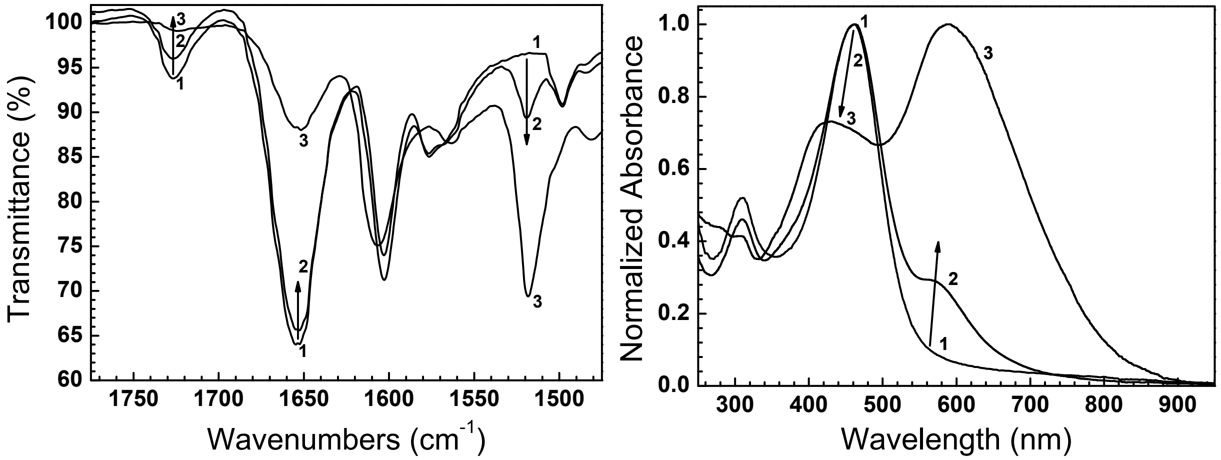

Figure S2: Blow-up of FT-IR spectra (left) and absorption spectra (right) of **PFC** at different stages of conversion during the polymer analogous reaction, demonstrating the gradual decrease of the peaks at 1654 cm^{-1} and 1725 cm^{-1} and the development of a new peak at 1519 cm^{-1}. These IR spectral 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.

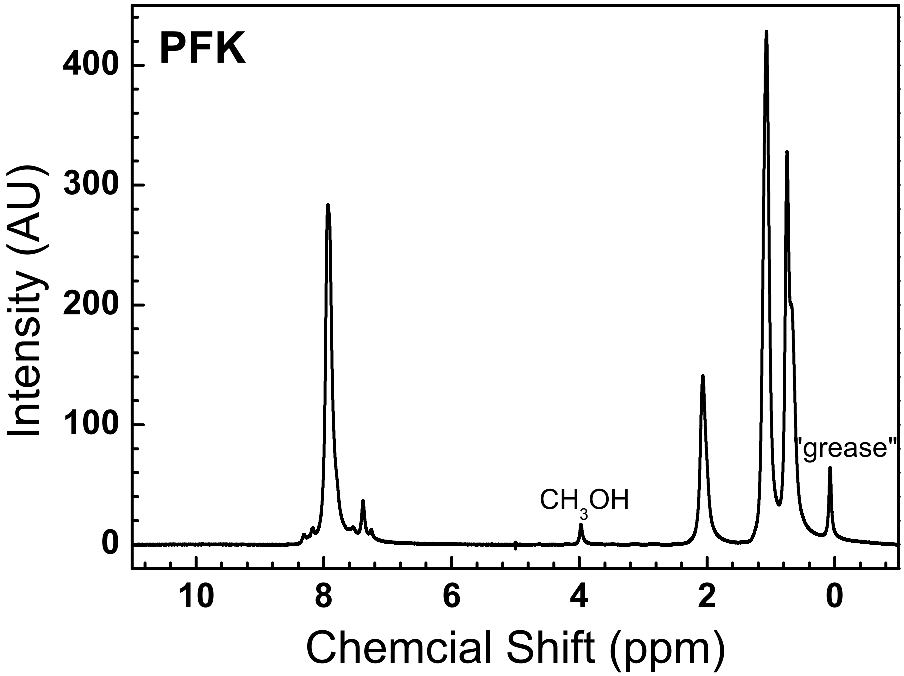

Figure S3: ^{1}H-NMR spectrum of **PFK** clearly showing the peak broadening typical for polymers. The aromatic region integrates to 10 protons and the aliphatic region to 26 protons which matches the proposed structure. The small peaks at 0 ppm and 4 ppm originate from silicone grease and residual solvent.

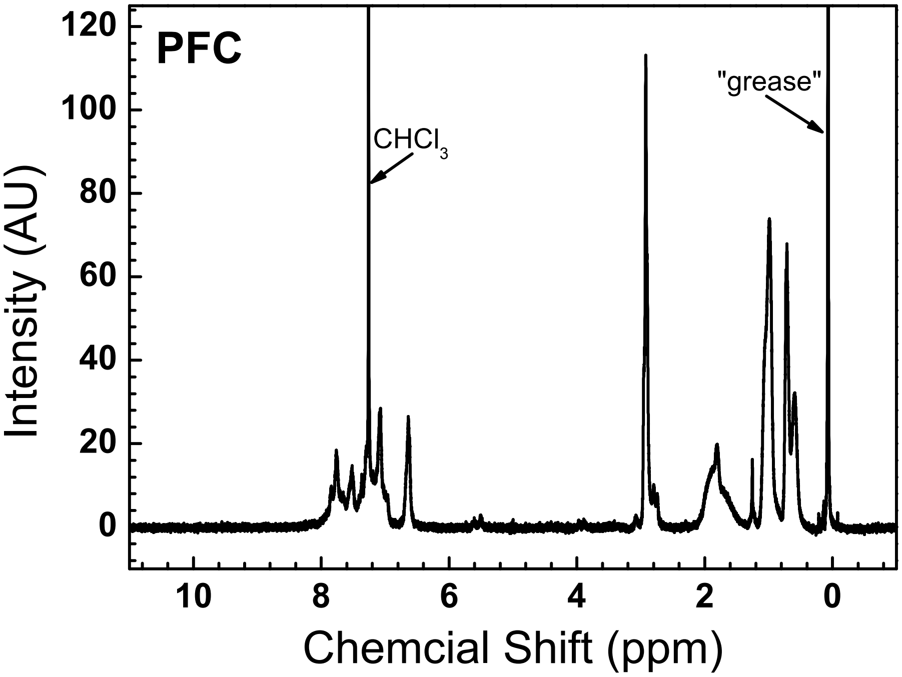

Figure S4: While **PFK** could be easily characterized by ^{1}H-NMR, we encountered difficulties obtaining clean spectra of **PFC** due to problems with locking and shimming, possibly due to the combination of the ionic and polymeric nature of CPIs driving aggregation in organic solvents (**PFC** is 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 $\frac{dn}{dc}$ 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.

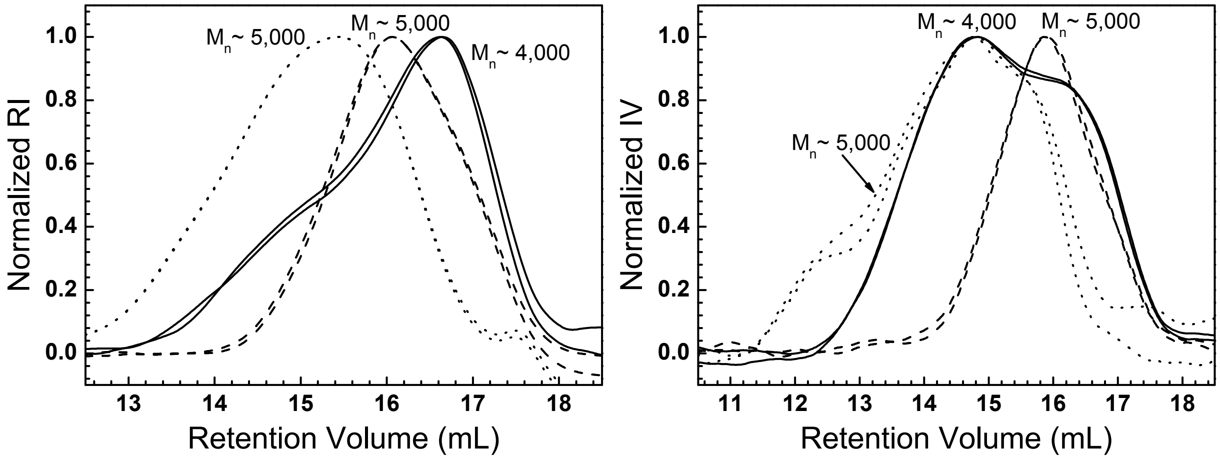

Figure S5: Refractive index (left) and intrinsic viscosity (right) GPC traces of three batches of **PFK**, batch 1 (dotted line, THF), batch 2 (dashed line, $CHCl_3$), and batch 3 (solid line, $CHCl_3$) (each injected twice), clearly demonstrating the batch-to-batch variations in molecular weight and 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 $\frac{dn}{dc}$ values are slightly dependent of molecular weight, when comparing structurally identical polymers the $\frac{dn}{dc}$ should remain constant within experimental error. However, when analyzing the GPC results obtained from **PFK** batch 4 we observed a relatively low calculated $\frac{dn}{dc}$ value of 0.068 while in the other batches $\frac{dn}{dc}$ ranged from 0.163 to 0.188. Although it is unclear to us why the $\frac{dn}{dc}$ 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 $\frac{dn}{dc}$ value nicely demonstrates the large impact it has on the calculated molecular weights; with $\frac{dn}{dc} = 0.068$ 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 $\frac{dn}{dc}$ 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.

	Universal			TriSEC		
	M_n	M_w	M_p	M_n	M_w	M_p
PFK 1 (CH_2Cl_2)[a]	5,500	16,300	6,000	–	–	–
PFK 2 (CH_2Cl_2)[a]	5,700	11,100	9,000	16,400	28,600	25,800
PFK 3 (CH_2Cl_2)[b]	4,200	9,900	3,300	19,100	47,300	15,400
PFK 4 (1,3,5-trichlorobenzene)[c]	5,200[d]	27,700[d]	31,700[d]	108,500[d]	278,500[d]	365,000[d]

[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 $P_n \sim 10$.

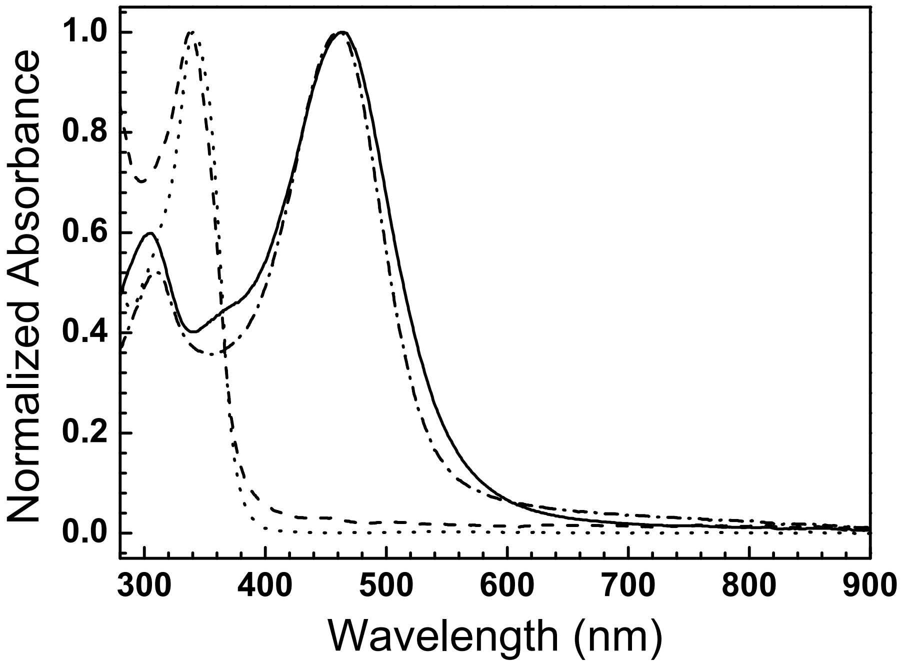

Figure S6: Absorption spectra of two batches of **PFK** in neutral and acidic conditions when polymerized in DCM (acidic; dash-dotted line, neutral; dotted line) or 1,3,5-trichlorobenzene (acidic; solid line, neutral; dashed line). The lack of a significant red shift of the absorption band-edge in acidic 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.

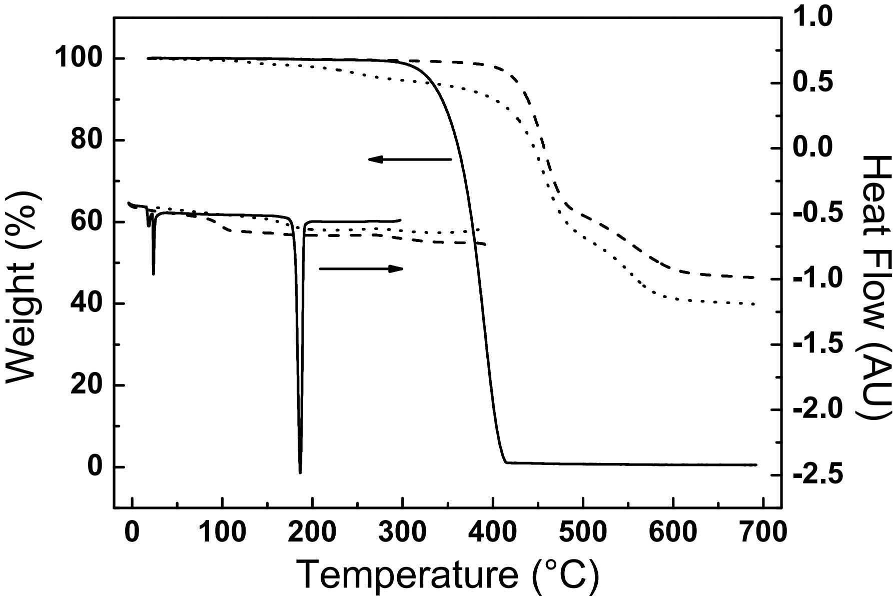

Figure S7: TGA and DSC traces of **PFK** (dashed lines), **PFC-OMe** (dotted lines), and **PFC** as the BF_4^- salt, demonstrating the large differences in the physical properties between **PFK** and **PFC** while the differences between **PFK** and **PFC-OMe** are smaller. All polymers have a sharp decomposition temperature (*i.e.*, 10% weight-loss) above 340 °C but **PFC-OMe** also has a stepwise decomposition witch 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.

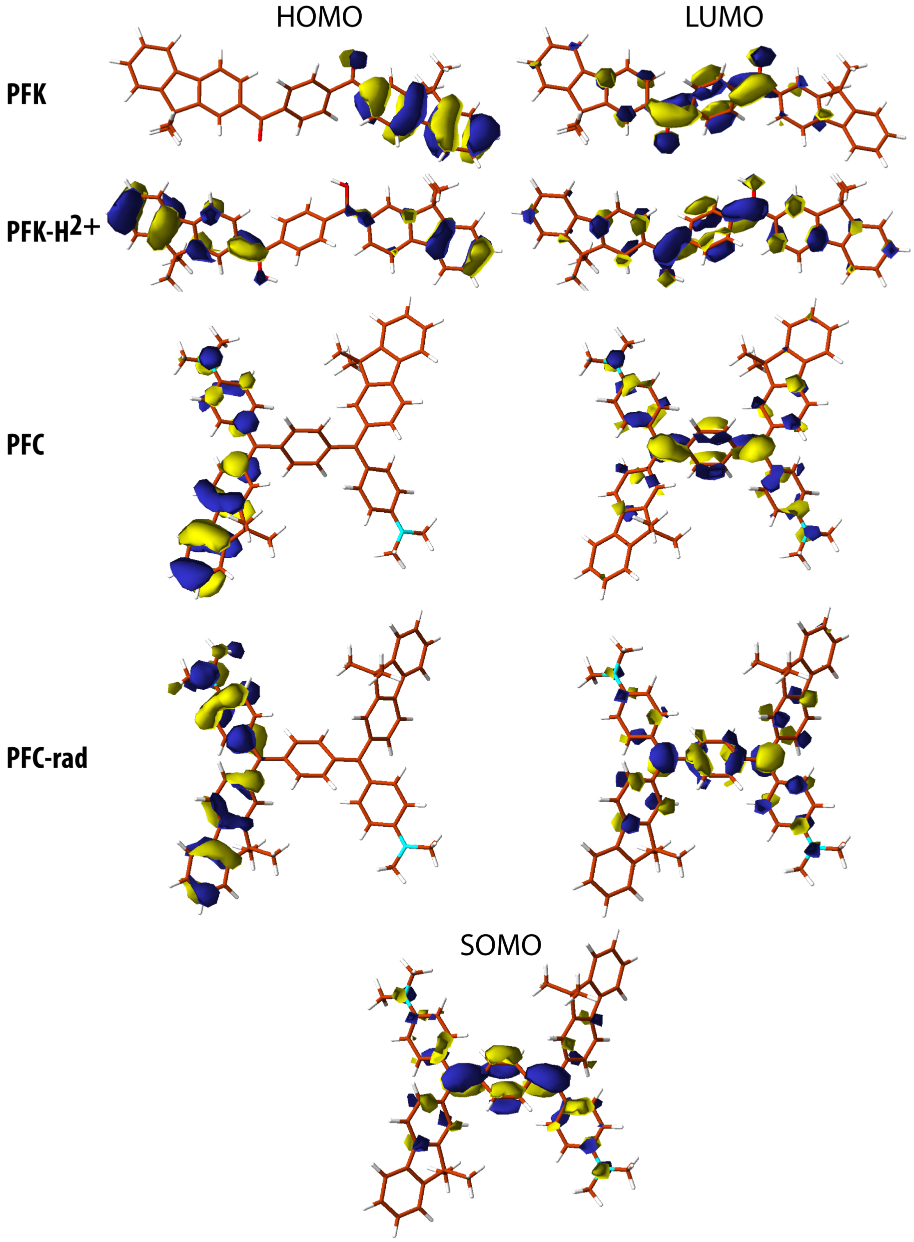

Figure S8: Calculated HOMO, LUMO, and SOMO energy levels for **PFK PFK-H+ PFC** and **PFC-Rad**.

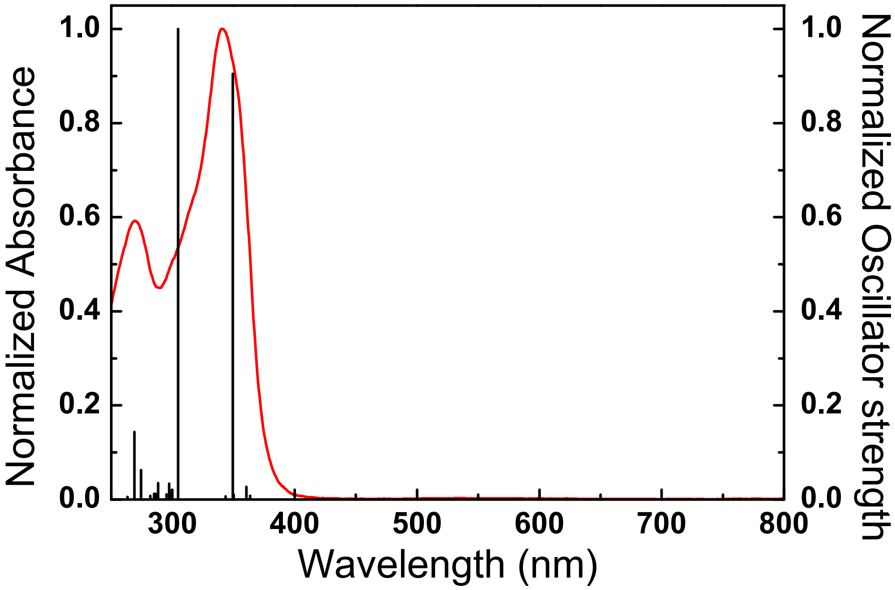

Figure S9: DFT calculated absorption bands (black) and experimental absorption data (red) for **PFK**.

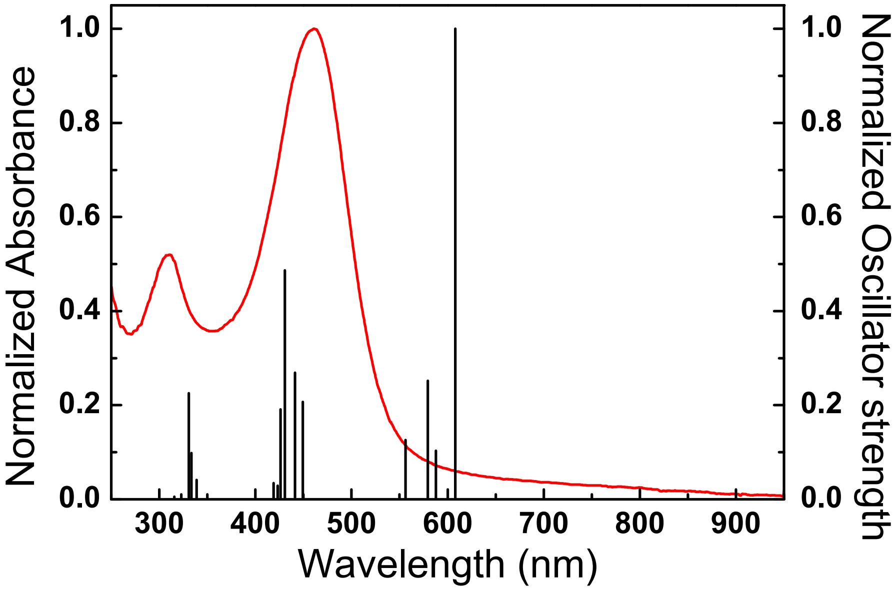

Figure S10: DFT calculated absorption bands (black) and experimental absorption data (red) for **PFK-H+**.

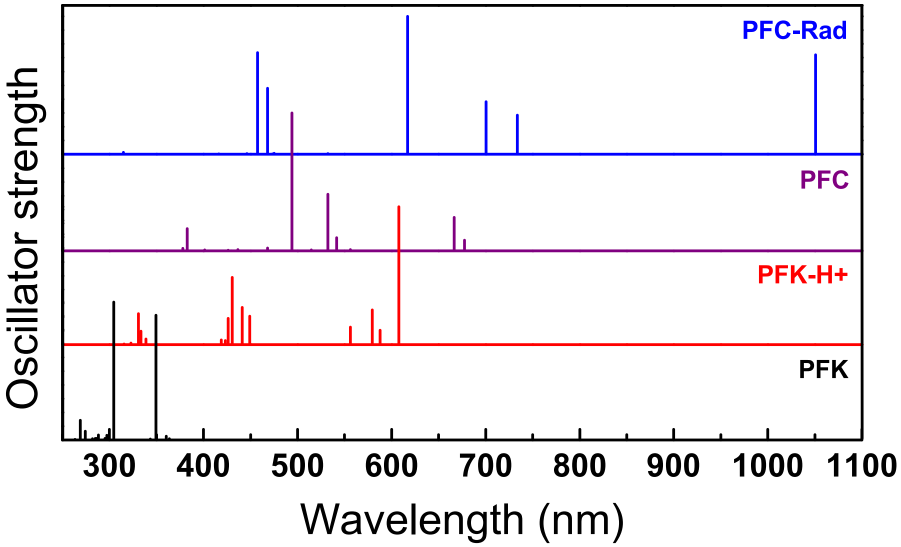

Figure S11: DFT calculated absorption spectra for **PFK PFK-H+ PFC** and **PFC-Rad** showing a clear, systematic decrease in band gap that is in agreement with experimental values and a very large drop in **PFC-Rad** resulting from the inclusion of unpaired spins. Quantitatively, the band gap of **PFK-H+** 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 $AlCl_3$) were added to 20 mL dry CH_2Cl_2 in a dried three-necked round-bottom flask. The solution was cooled to 0 °C and via a solid addition arm $AlCl_3$ (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 H_2O before extracting with 150 mL of CH_2Cl_2. The organic layer was next washed with saturated $NaHCO_3$ 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, CD_3Cl) 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). ^{13}C NMR (101 MHz, CD_3Cl) 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 $AlCl_3$ (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_2Cl_2. The organic layer was next washed with 1N HCl and next dried over Na_2SO_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 $C40H48N^+$: 542.378. Found: 542.378.

Polymers

Poly[(9,9-dihexylflourene)-*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 slowely adding 3 mL of CH_3OH resulting in a color change from red to yellow. Next, a short-path vacuum distillation set-up was attached and the CH_3OH 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_3OH (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_3OH, CH_3COCH_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, $CDCl_3$) δ 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.