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Controlling Morphology and Molecular Packing of Alkane Substituted Phthalocyanine Blend Bulk Heterojunction Solar Cells†

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Device. The solutions used to prepare the active layers were made at constant relative ratios of dye to solvent (w/w). The relative mole ratios of the dyes and C_{60} in the active layers ranged from 1:1 to 1:2.7 for the individual dye devices and 1.5:1 to 2:1 for the blended systems (Pc:Pyr C_{60}).

SYNTHESIS

A variety of Pc for solar cell applications have been reported. [1-26]

N-methyl-2-(4'-pyridyl)-3,4-fulleropyrrolidine was prepared as described in the literature. [27]

Pc-4-C12. To a stirring solution of 15 mL of freshly distilled THF under Ar was added $ZnPcF_{16}$ (50 mg, 0.0576 mmol), dodecanethiol (1.69 mL, 8.2 mmol) and potassium carbonate (50 mg) and the solution was stirred at room temperature for 24 hours. Reaction was mixture was poured into separatory funnel and washed with water, extracted into dichloromethane, and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula $C_{80}H_{100}F_{12}N_8S_4Zn$, MALDI-MS calculated 1595.32, found: 1594.94 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 708 nm.

Pc-4-C5. To a stirring solution of 15 mL of freshly distilled THF under Ar was added $ZnPcF_{16}$ (50 mg, 8.2 mmol), pentanethiol (1.01 mL, 8.2 mmol) and potassium carbonate (50 mg). The resulting solution was stirred at 50 C for 2 hours and reaction progress monitored by UV-visible spectroscopy to determine the degree of substitution. The crude reaction mixture was washed with water, extracted into dichloromethane, and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula $C_{52}H_{44}F_{12}N_8S_4Zn$, MALDI-MS calculated mass 1202.58, found: 1202.09 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 708 nm.

Pc-4-C8. $ZnPcF_{16}$ (75 mg, 8.6 mmol) was stirred in 15 mL of freshly distilled THF under Ar for 10 minutes. 2-ethylhexanethiol (1.06 mL, 6.2 mmol) and potassium carbonate (150 mg) were added and the solution was stirred at 50 C for 24 hours and monitored by UV-visible spectroscopy to determine the degree of substitution. The crude product was washed with water, extracted into dichloromethane and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula, $C_{64}H_{68}F_{12}N_8S_4Zn$, MALDI-MS calculated 1370.89, found:1370.61 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 711 nm.

Pc-8-C12. To 15 mL of freshly distilled THF under Ar for 10 was added $ZnPcF_{16}$ (50 mg, 0.0576 mmol), dodecanethiol (1.69 mL, 8.2 mmol) and potassium carbonate (50 mg). The solution was stirred at reflux for 8 hours and monitored by UV-visible spectroscopy to determine the degree of substitution. The crude reaction mixture was then was washed with water, extracted into dichloromethane and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula, $C_{128}H_{200}F_8N_8S_8Zn$, MALDI-MS calculated 2324.89, found: 2325.89 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 736 nm.

Pc-8-C5. To 15 mL of freshly distilled THF under Ar was added $ZnPcF_{16}$ (50 mg, 8.2 mmol), pentanethiol (1.01 mL, 8.2 mmol) and potassium carbonate (50 mg). The solution was stirred at reflux for 3 hours and monitored by UV-visible spectroscopy to determine the degree of substitution. The crude reaction mixture was washed with water, extracted into dichloromethane and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula, $C_{72}H_{88}F_8N_8S_8Zn$, MALDI-MS calculated 1539.4, found: 1538.71 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 733 nm.

Pc-8-C8. To 15 mL of freshly distilled DMF under Ar was added $ZnPcF_{16}$ (75 mg, 8.6 mmol), 2-ethylhexanethiol (1.06 mL, 6.2 mmol) and potassium carbonate (150 mg). The solution was stirred at reflux for 2 hours and monitored by UV-visible spectroscopy to determine the degree of substitution. The crude reaction mixture was then washed with water, extracted into dichloromethane and dried over Na_2SO_4. The solvent was removed under vacuum. Silica gel chromatography (4x15 cm) with hexane followed by hexane/ethyl acetate 1:2 (v/v) yielded an emerald green solid. Formula, $C_{104}H_{153}F_7N_8S_9Zn$ MALDI-MS calculated 2002.33, found: 2002.33 as the major component. UV-Vis. λ_{max} in CH_2Cl_2: 727 nm.

AFM

Samples were prepared by the same method used to prepare solar cells and x-ray samples. After spin coating the blend of dyes for the active layer, a razor blade was used to cut a line through the active layer and the underlying PEDOT:PSS layer, which is ca. 55 nm. Contact mode AFM was then used to determine the total thickness. Active layer thicknesses reported herein were calculated by subtracting the PEDOT:PSS thickness from the total AFM measured heights. Solutions used for all devices tested in this manuscript were prepared by weight percentage. To guarantee that the optical density differences observed arise from differences in molecular packing we diluted the lower molecular weight solutions and spin coated a series of samples from equimolar solutions all made to the concentration of the original Pc-4-C12 solution of 7.5 M. These samples demonstrated the reported trend. These cells are referred to as "Pc-X-CY dilute". Solutions used for all devices tested in this manuscript were prepared by weight percentage. To guarantee that the optical density differences observed arise from differences in molecular packing we diluted the lower molecular weight solutions and spin coated a series of samples from equimolar solutions all made to the concentration of the original Pc-4-C12 solution of 7.5 M. These samples demonstrated the reported trend. These cells are referred to as "Pc-X-CY dilute".

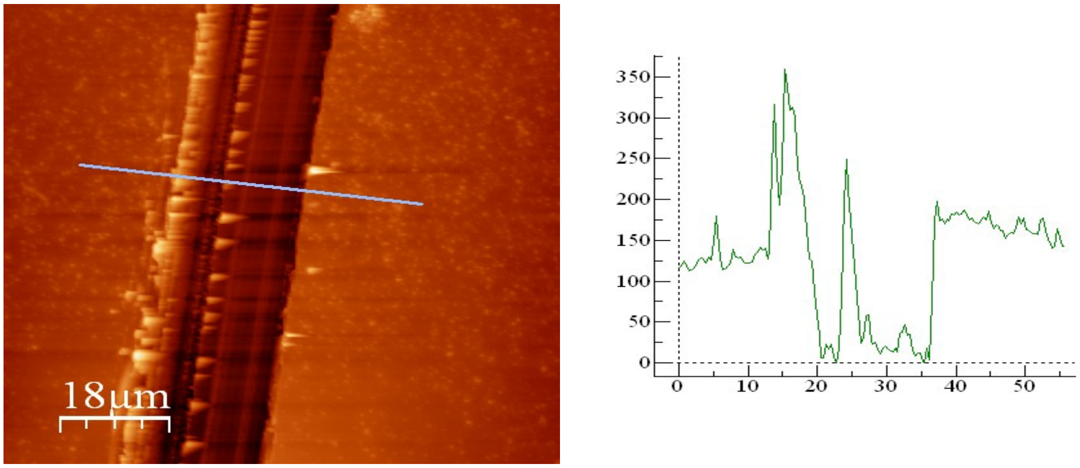

Figure SI-1. The 125 nm height measured by AFM of films of **Pc-4-C5** on PEDOT:PSS indicate an active layer thickness of ca.70 nm.

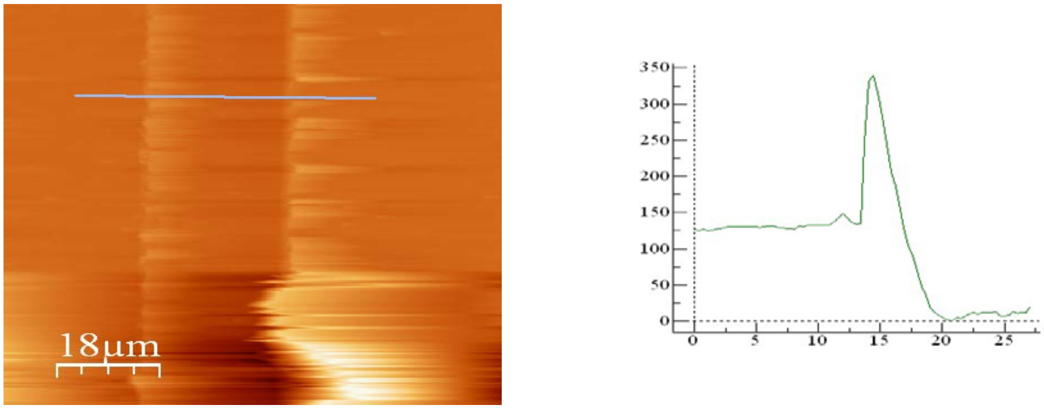

Figure SI-2. The 125 nm height measured by AFM of films of **Pc-4-C8** on PEDOT:PSS indicate an active layer thickness of ca.70 nm.

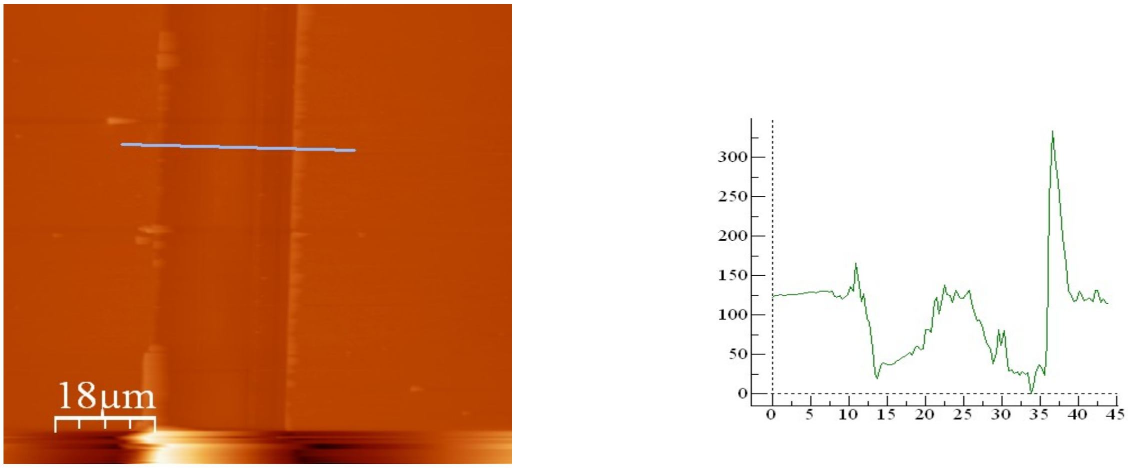

Figure SI-3. The 125 nm height measured by AFM of films of **Pc-4-C12** on PEDOT:PSS indicate an active layer thickness of ca.70 nm.

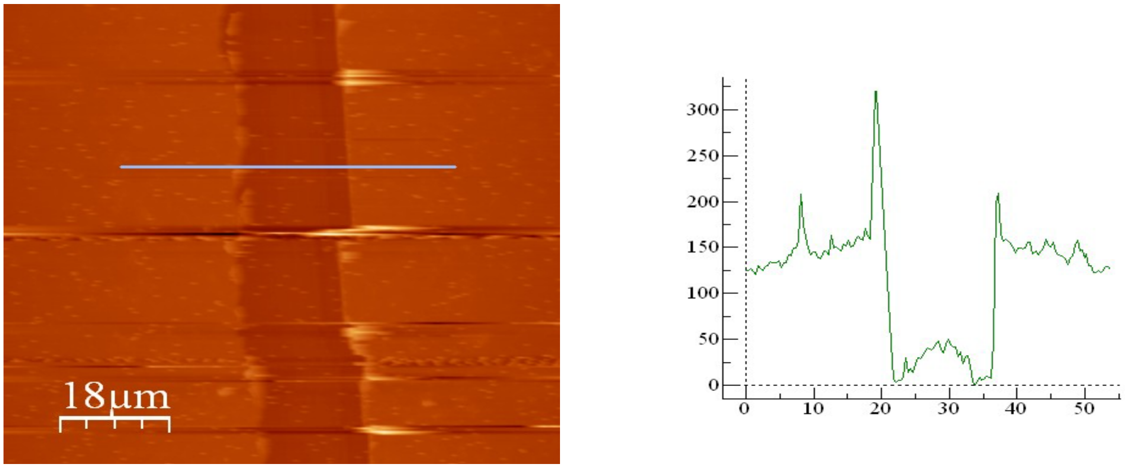

Figure SI-4. The 125 nm height measured by AFM of films of Pc-4-C5 on PEDOT:PSS indicate an active layer thickness of ca.70 nm. This sample was prepared from a dilute solution. Note that the film thicknesses are the same.

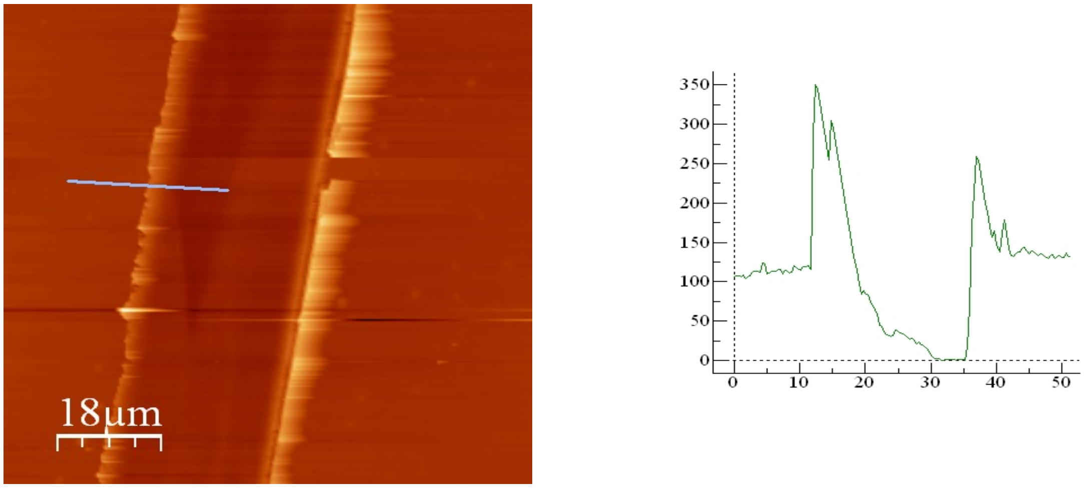

Figure SI-5. The 125 nm height measured by AFM of films of Pc-4-C8 on PEDOT:PSS indicate an active layer thickness of ca.70 nm. Prepared from a dilute solution.

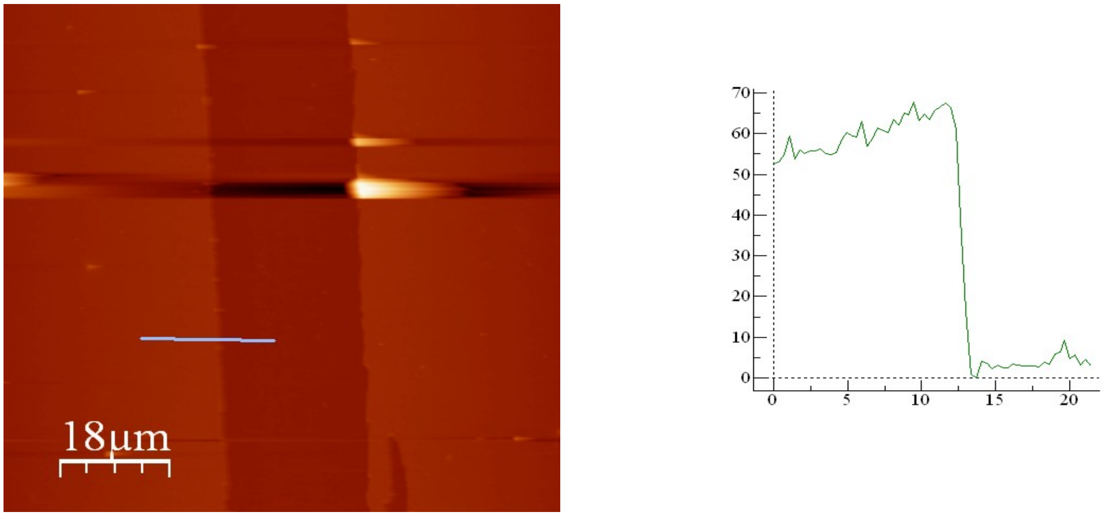

Figure SI-6. AFM indicating the thickness of the PEDOT:PSS film is 55nm.

MALDI spectra

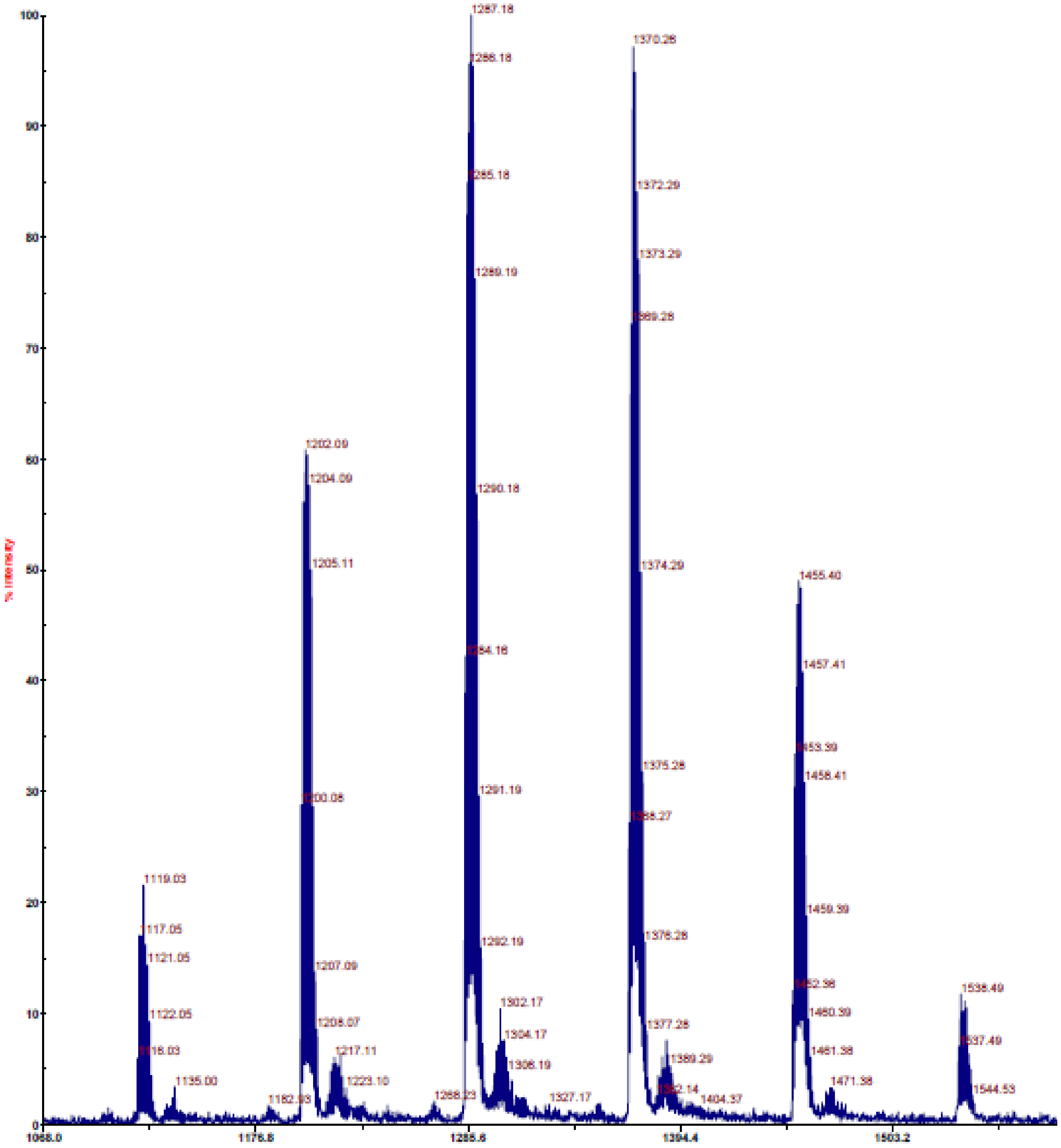

Figure SI-7. MALDI-MS of the **Pc-4-C5** used.

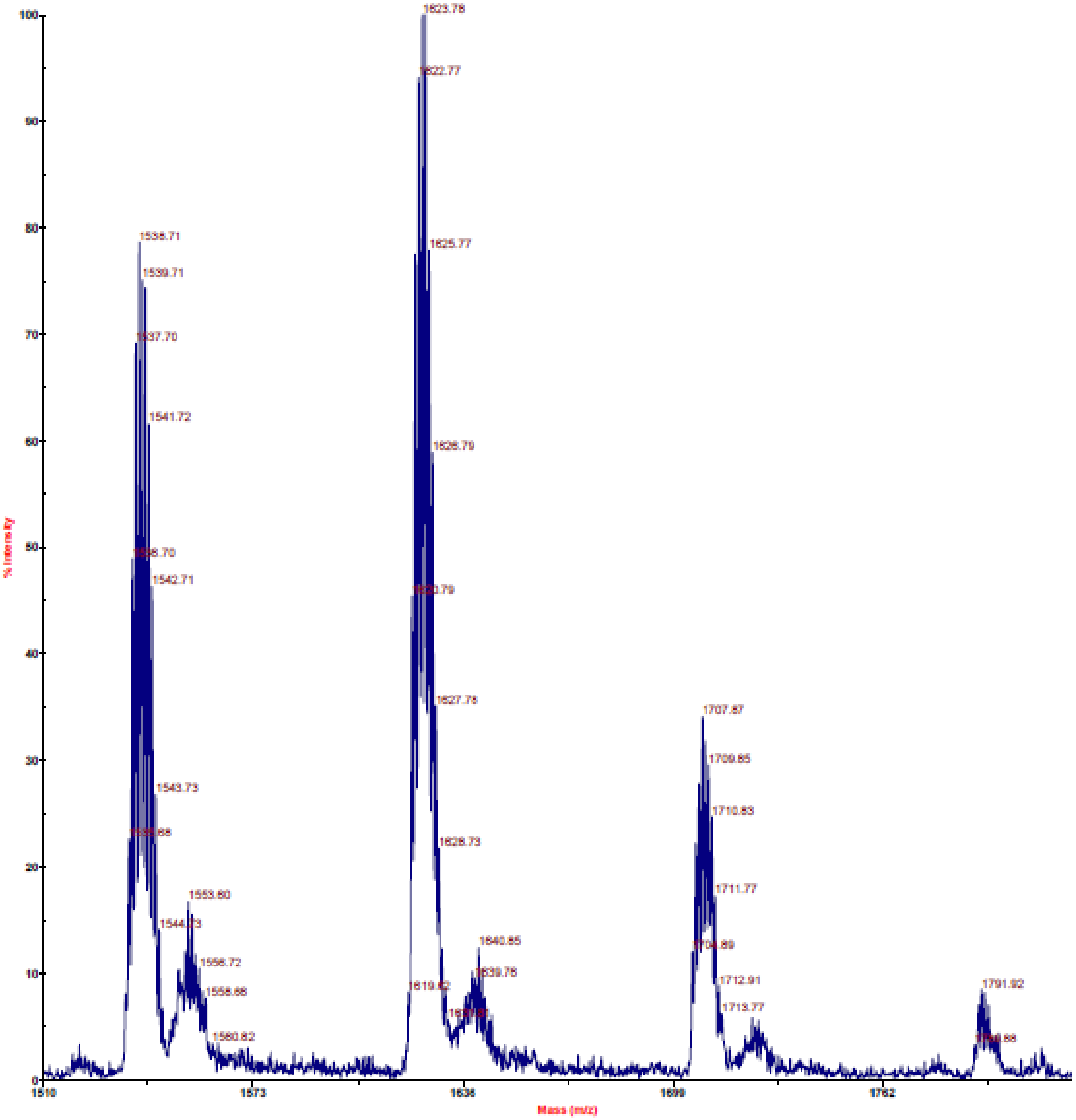

Figure SI-8. MALDI-MS of the **Pc-8-C5** used.

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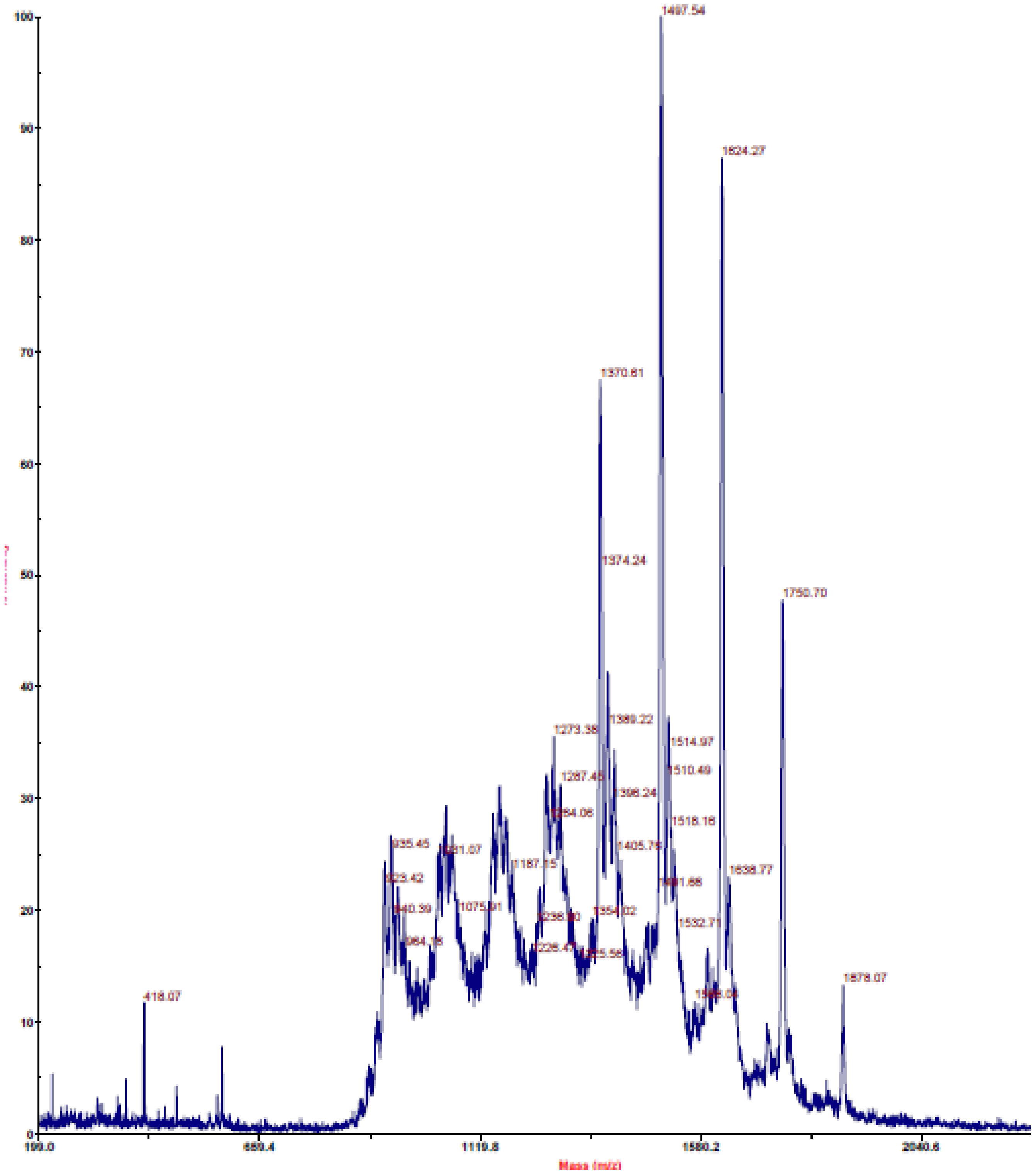


Figure SI-9. MALDI-MS of the **Pc-4-C8** used.

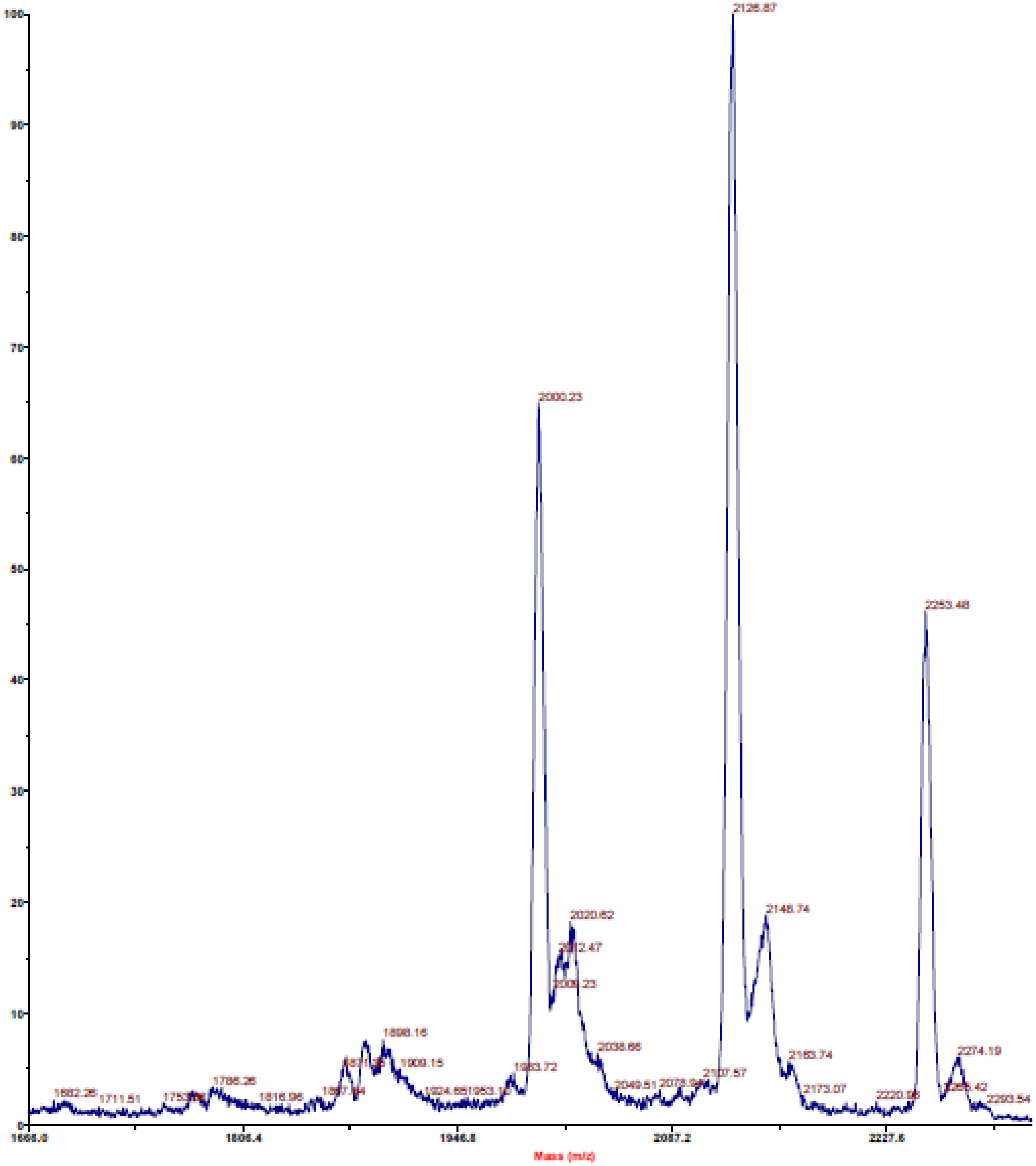


Figure SI-10. MALDI-MS of the **Pc-8-C8** used.

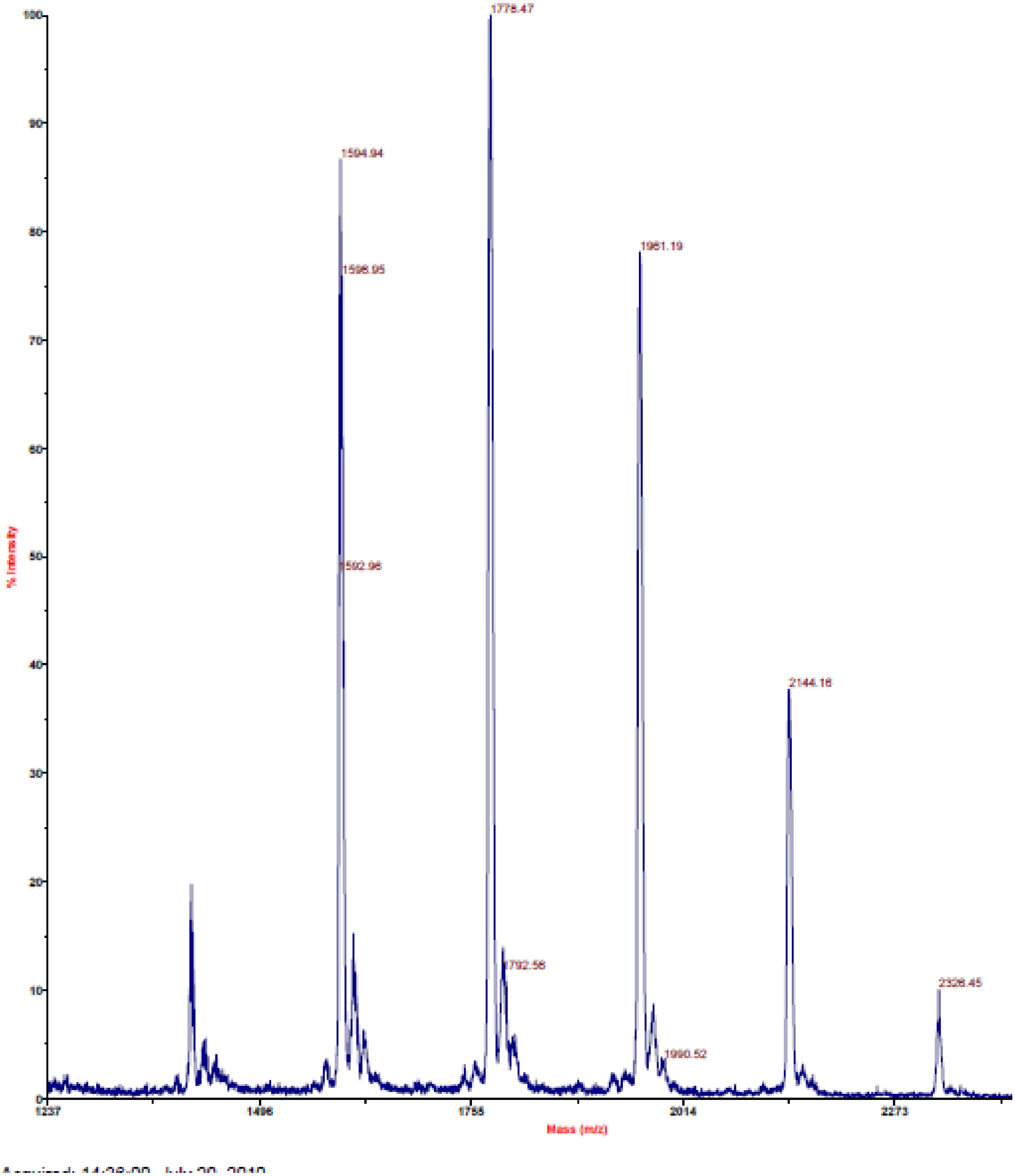


Figure SI-11. MALDI-MS of the **Pc-4-C12** used.

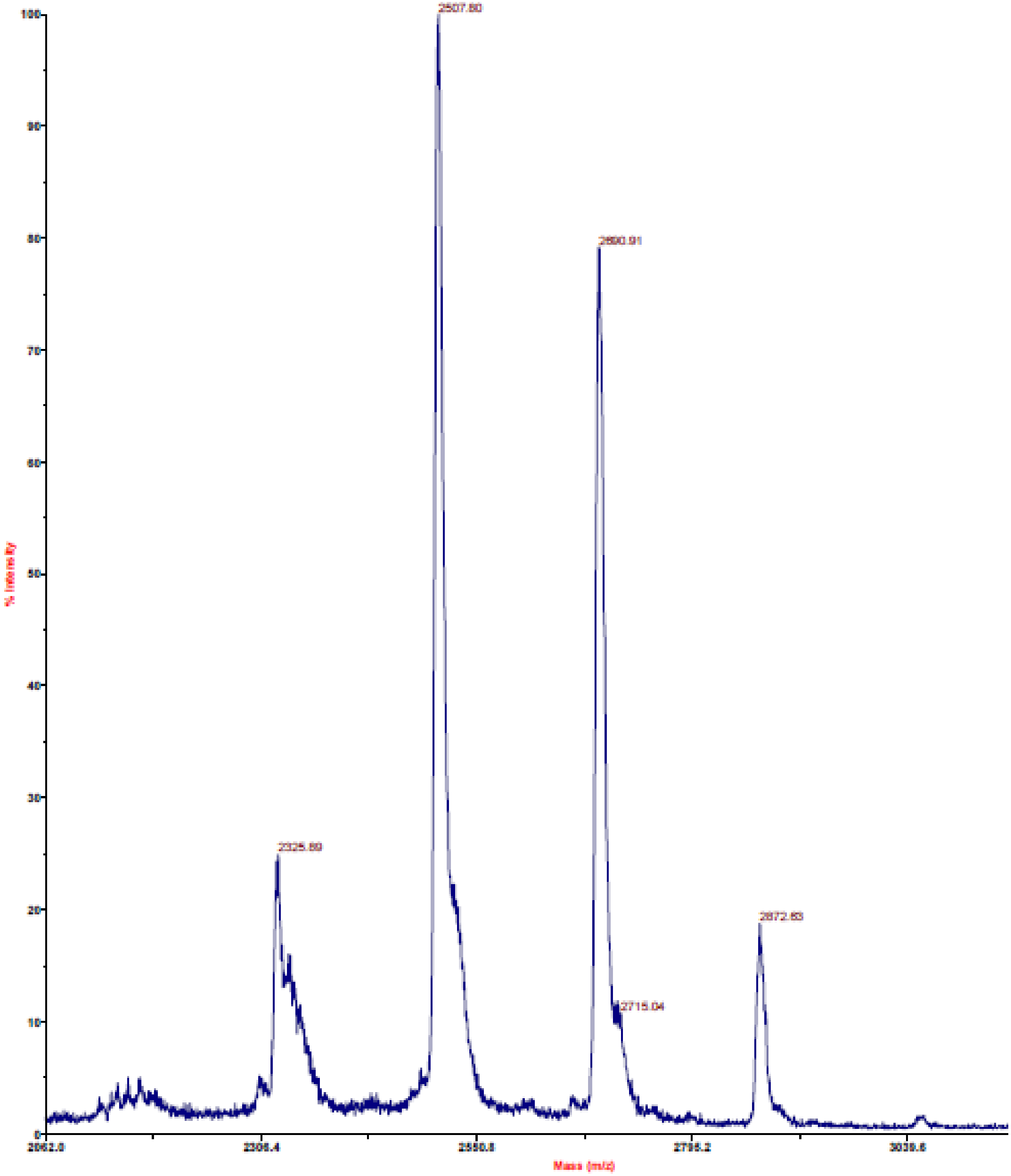


Figure SI-12. MALDI-MS of the **Pc-8-C12** used.

UV-visible spectra

Data reported from dyes in solution were tested in dichloromethane at a concentration of 17 µM.

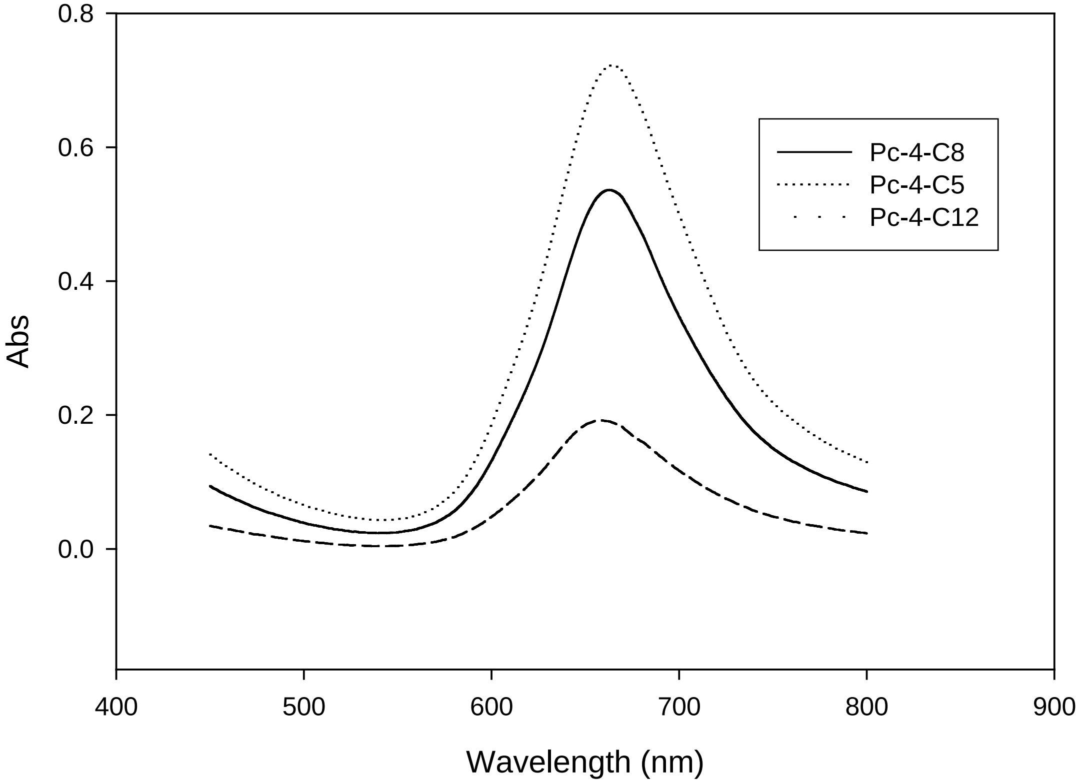
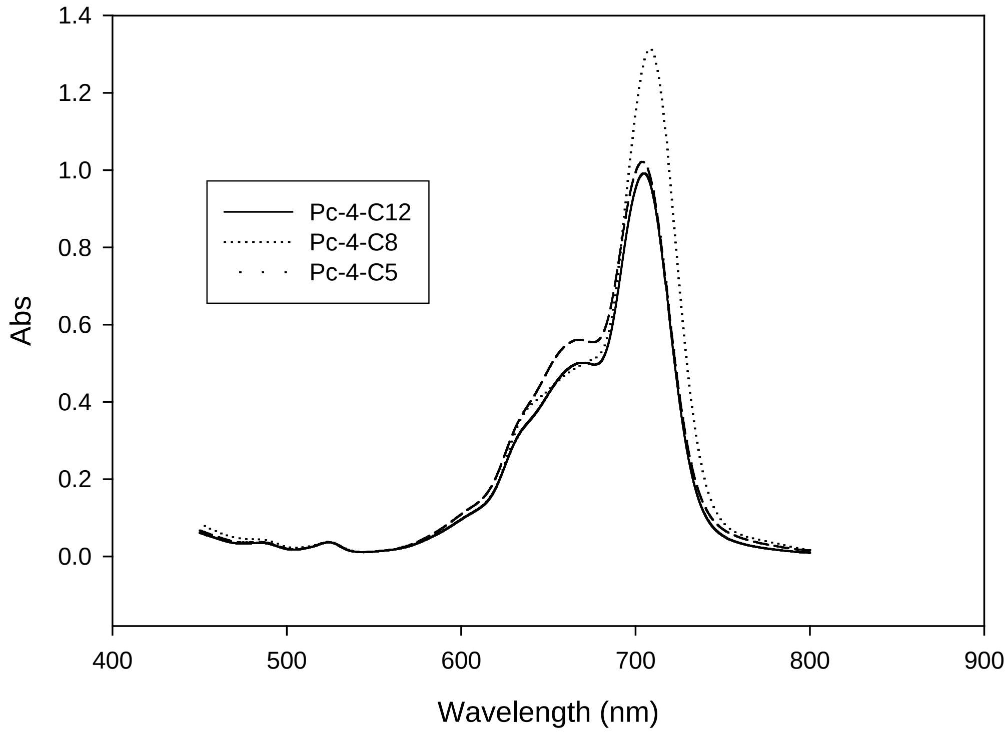


Figure SI-13. UV-visible spectra of the low energy Q band for the ZnPc tetra-substituted with three different alkanes shows that the absorbance increases as the chain decreases for the same thickness of the films.



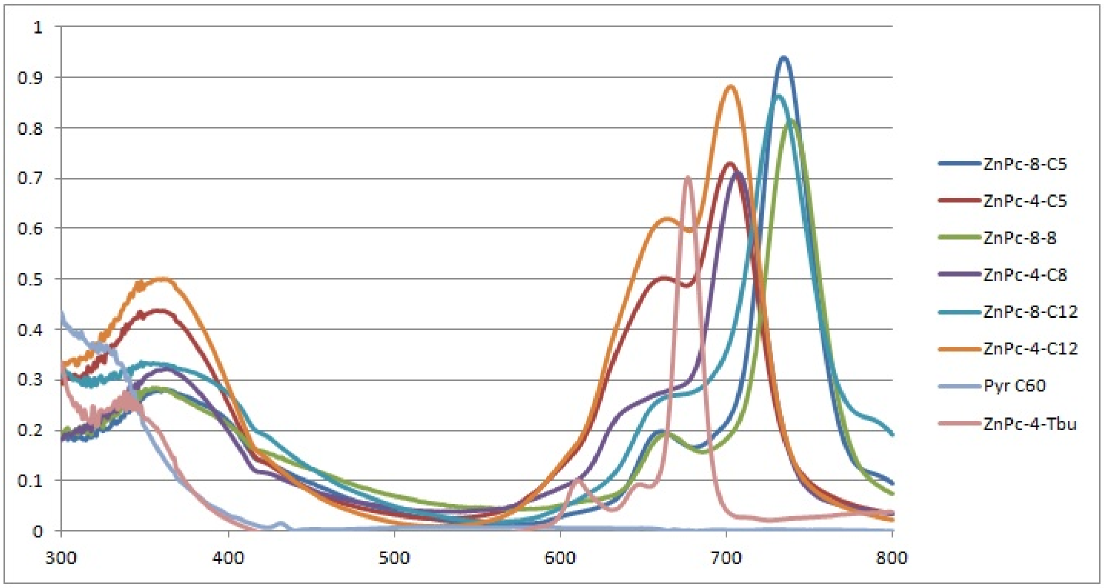


Figure SI-14. Top: UV-visible spectra of the low energy Q band for the ZnPc tetra-substituted with three different alkanes shows that the absorbance in solution are similar. Bottom: UV-visible spectra of all of the ZnPc used; note the red-shift and broadening of the low energy Q band with increasing substitution,

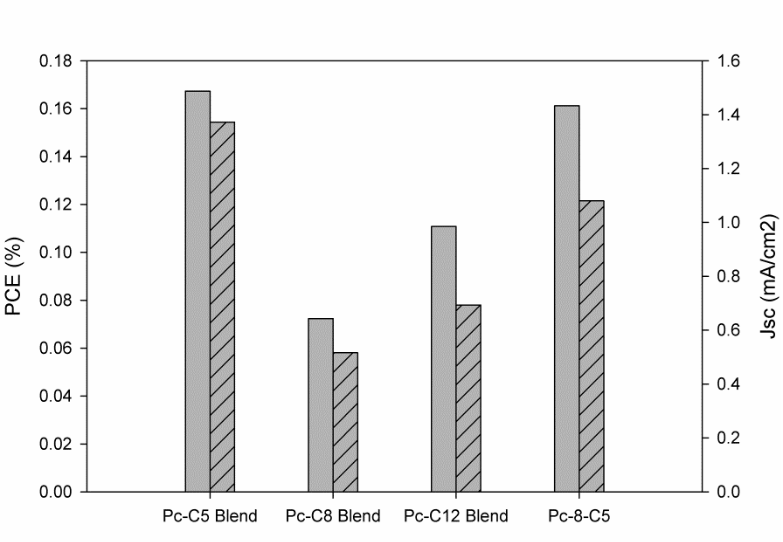


Figure SI-15. Comparison of the key PV parameters for the different blended cells.

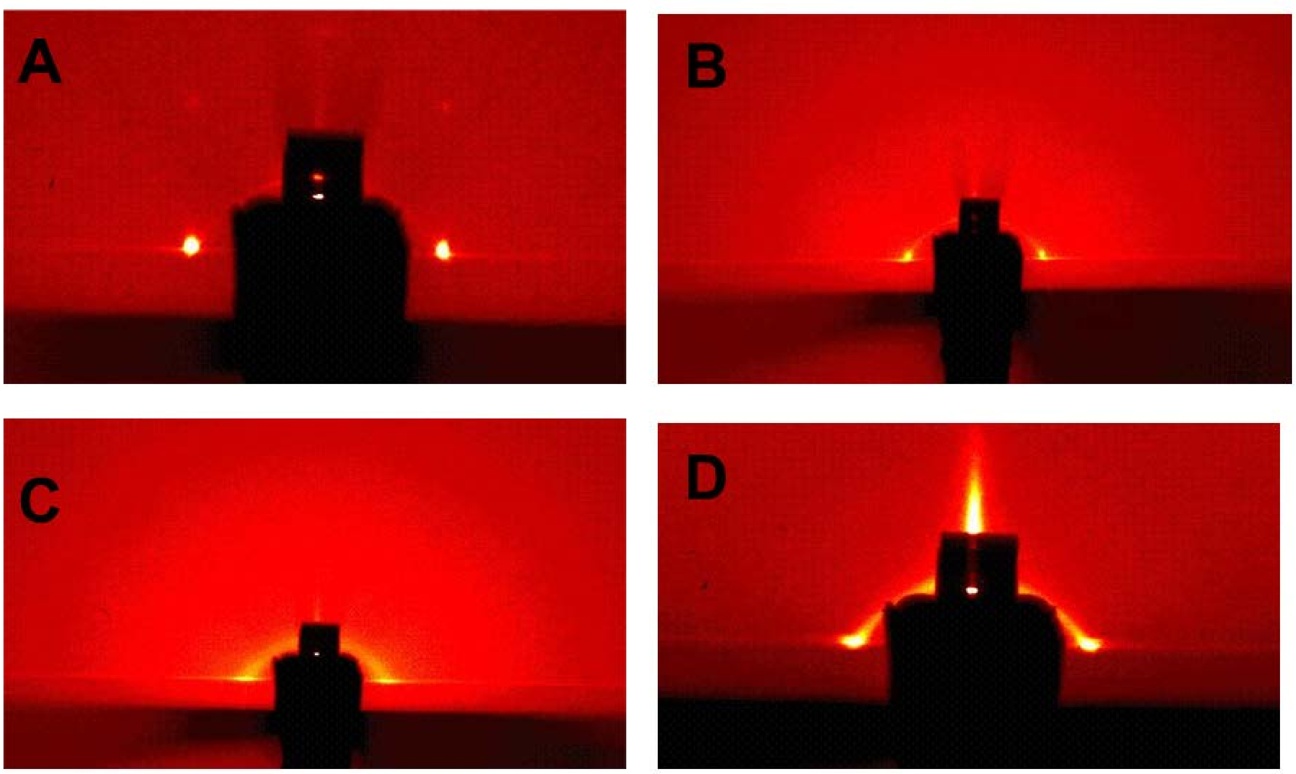


Figure SI-14. GISAXS false color images taken at 10.2 KeV of ZnPc acivey layers on PEDOF:PSS on ITO. The patterns suggest short range hexagonal packing order on the ~35 Å scale. The addition of ZnPc-4-TBu diminishes the organization of the active layer. The lack of distinct separate, diffraction patterns suggests that there are no discrete domains of individual dyes and instead there exists a blend. The ratio alkane subbed ZnPc: ZnPc-4-TBu was (A) 100:7.8, (B) 100:10.8, (C)100:19.29, and (D)is a blend of the three ZnPc with PyC$_{60}$.

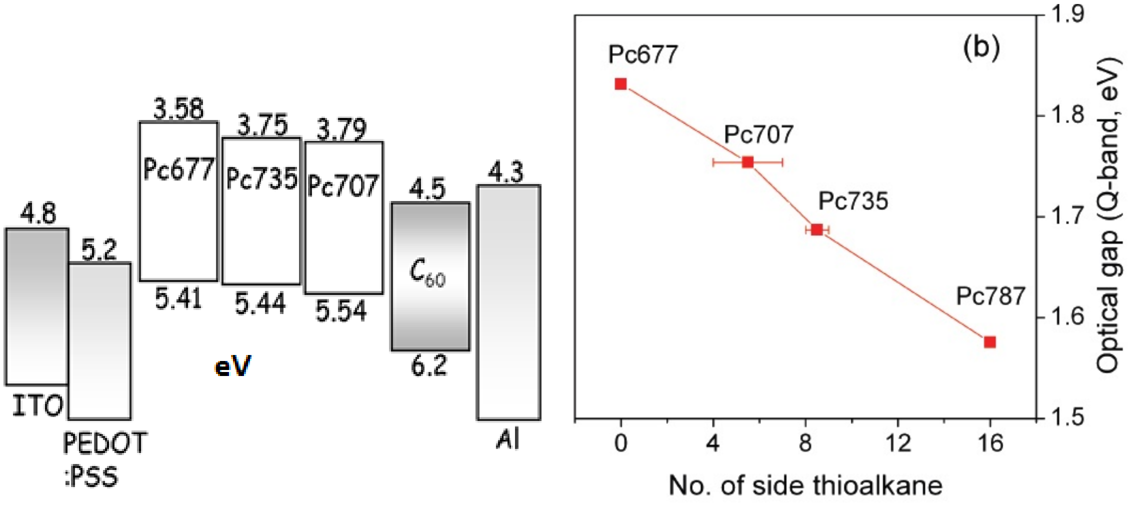


Figure SI-15. Left: relative energy levels of the device components (all values in eV).. Pc677=ZnPc-4-TBu; Pc707=ZnPc-4-C12; Pc735=ZnPc-8-C12. Right: the number of F- and S-C12 substituents dictates the HOMO-LUMO gap. Figures taken from Varotto et al.[18]

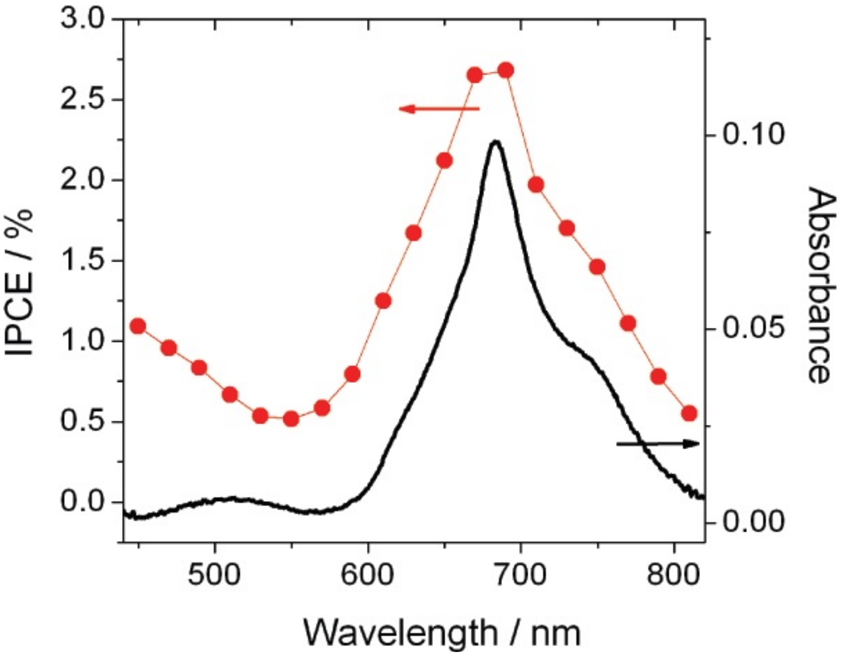


Figure SI-16. Comparison of the IPCE and the absorbance of a ZnPc-C12 Blend cell. Figure taken from Varotto et al.[18]

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