Supporting Information

Enhancing Long-Term Morphological Stability in BHJ Organic Solar Cells through Thermocleavable Sidechains under Continuous Thermal Stress

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List of supporting figures

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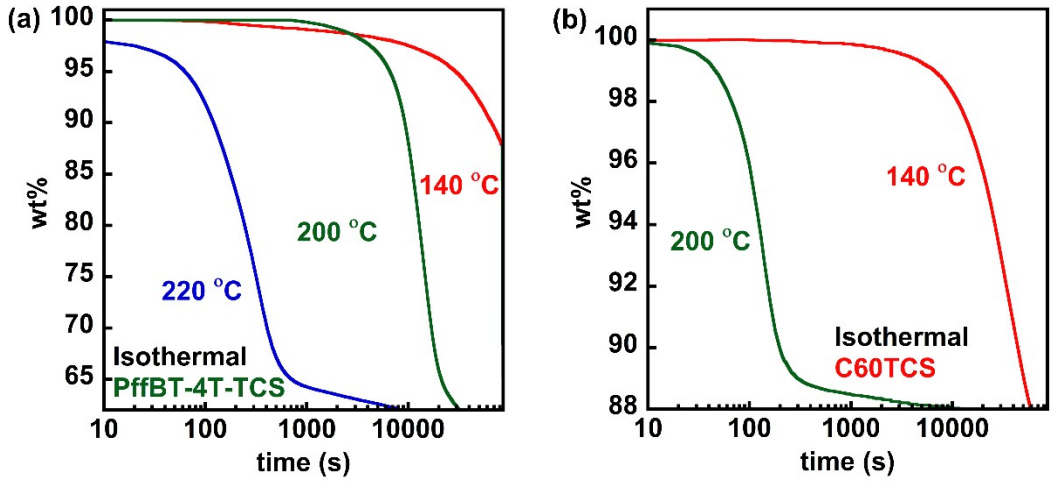

Figure S1. Isothermal TGA of thermal cleavable materials: (a) PffBT-4T-TCS and (b) C60TCS at different annealing temperature of 140 ^{0}C, 200 ^{0}C, and 220 ^{0}C.

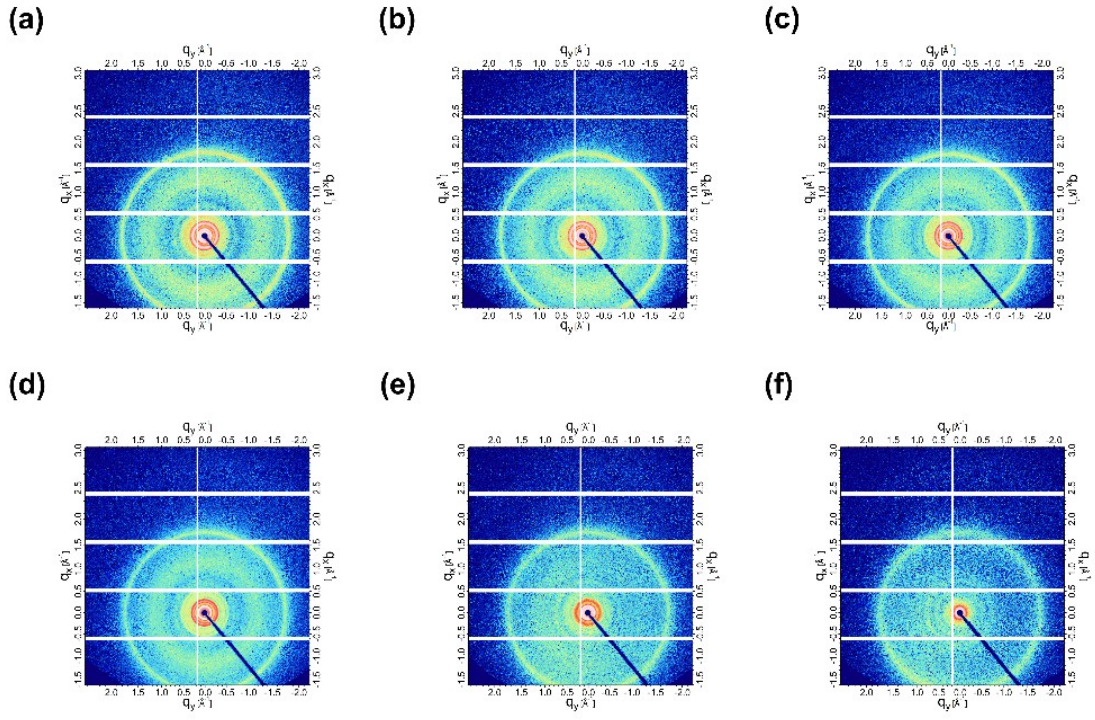

Figure S2. *in situ* heating WAXS 2D scattering images for PffBT-4T-TCS at various temperatures. (a) 25 °C; (b) 100 °C; (c) 150 °C; (d) 200 °C; (e) 250 °C; (f) 300 °C.

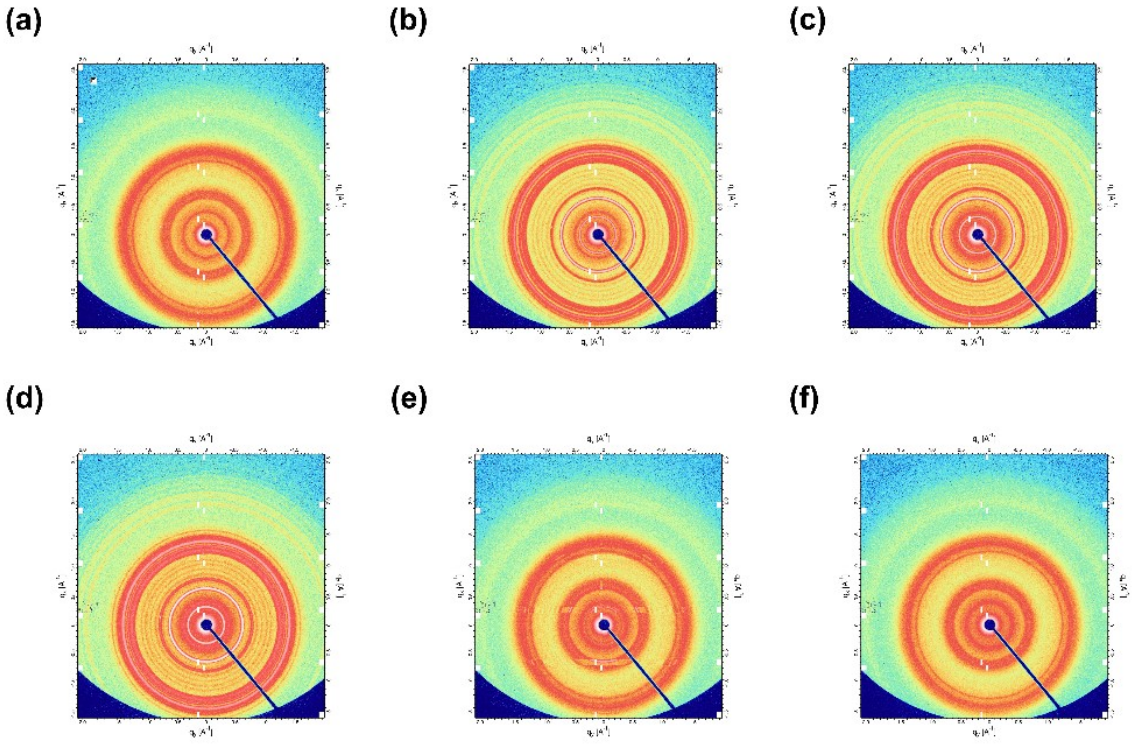

Figure S3. *in situ* heating WAXS 2D scattering images for C60TCS at various temperatures. (a) 25 °C; (b) 50 °C; (c) 100 °C; (d) 150 °C; (e) 200 °C; (f) 225 °C.

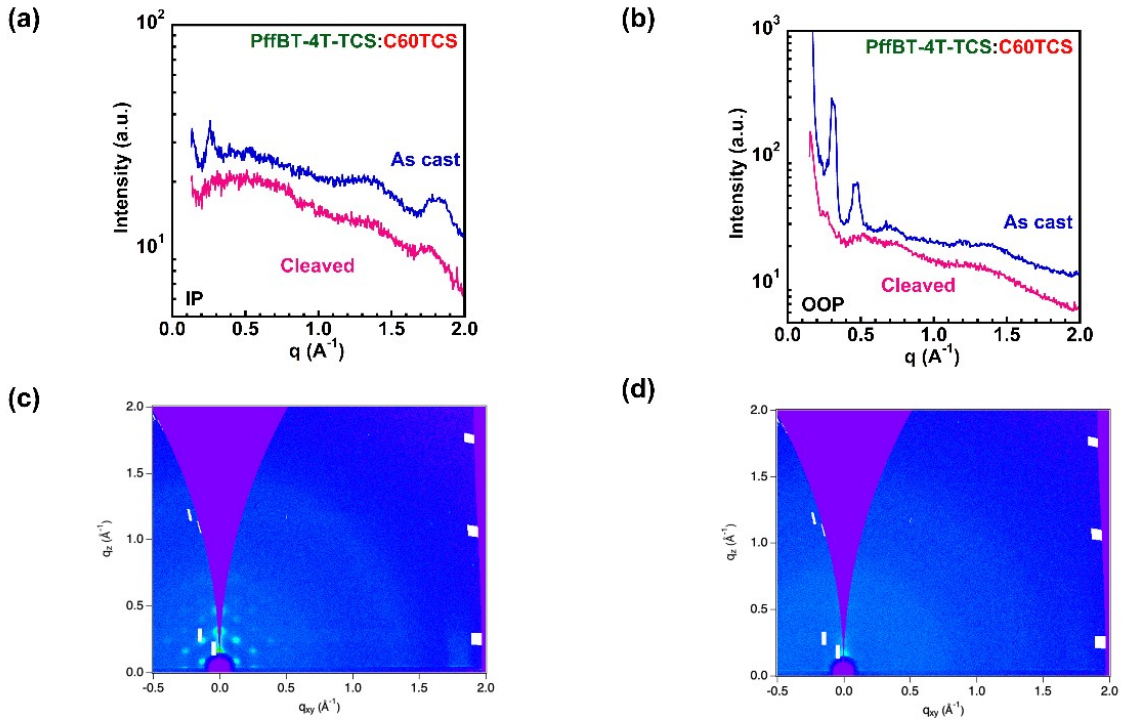

Figure S4. *ex situ* GIWAXS characterization of the PffBT-4T-TCS: C60TCS (1:1.2 wt%) blend film before and after thermal cleavage. (a) 1D in-plane scattering profiles for as cast and cleaved blend; (b) 1D out-of-plane scattering profiles for as-cast and cleaved blend; (c) 2D GIWAXS pattern for the as cast blend; (d) 2D GIWAXS pattern for cleaved blend. A notable decrease in the alkyl chain packing peak at q = 0.3 $Å^{-1}$ was observed after thermal annealing at 220 °C for 30 minutes, indicating the successful removal of alkyl side chains.

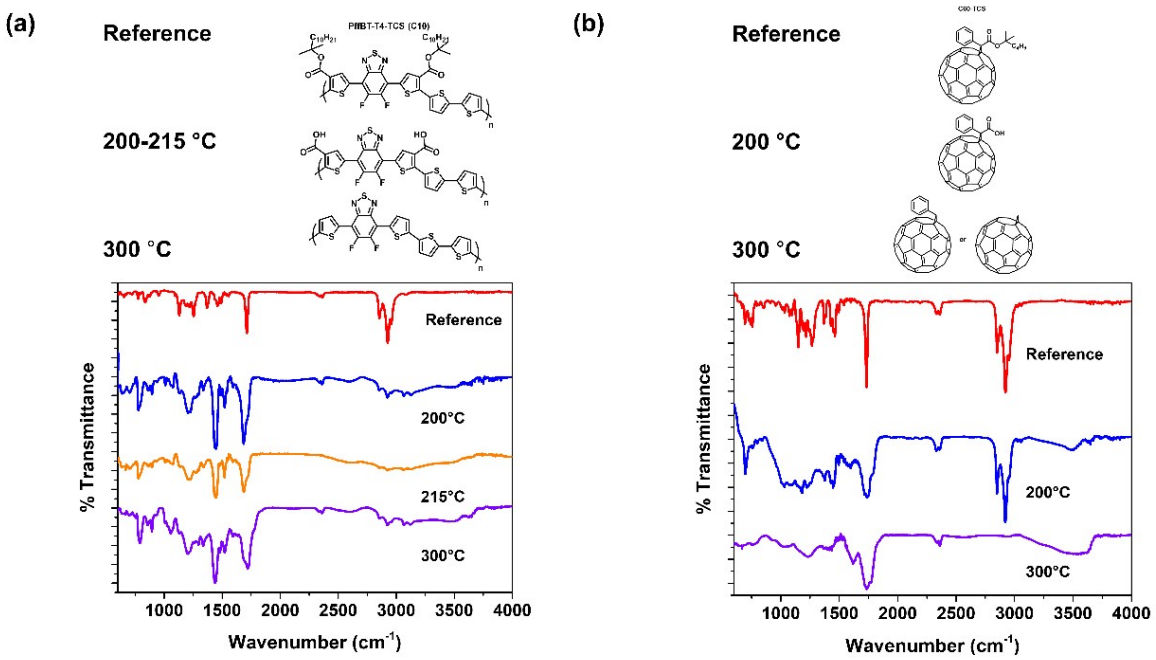

Figure S5. Bulk FTIR spectra showing the absorption peaks of the thermocleavable donor and acceptor before and after thermal cleavage. (a) PffBT-4T-TCS and (b) C60TCS.

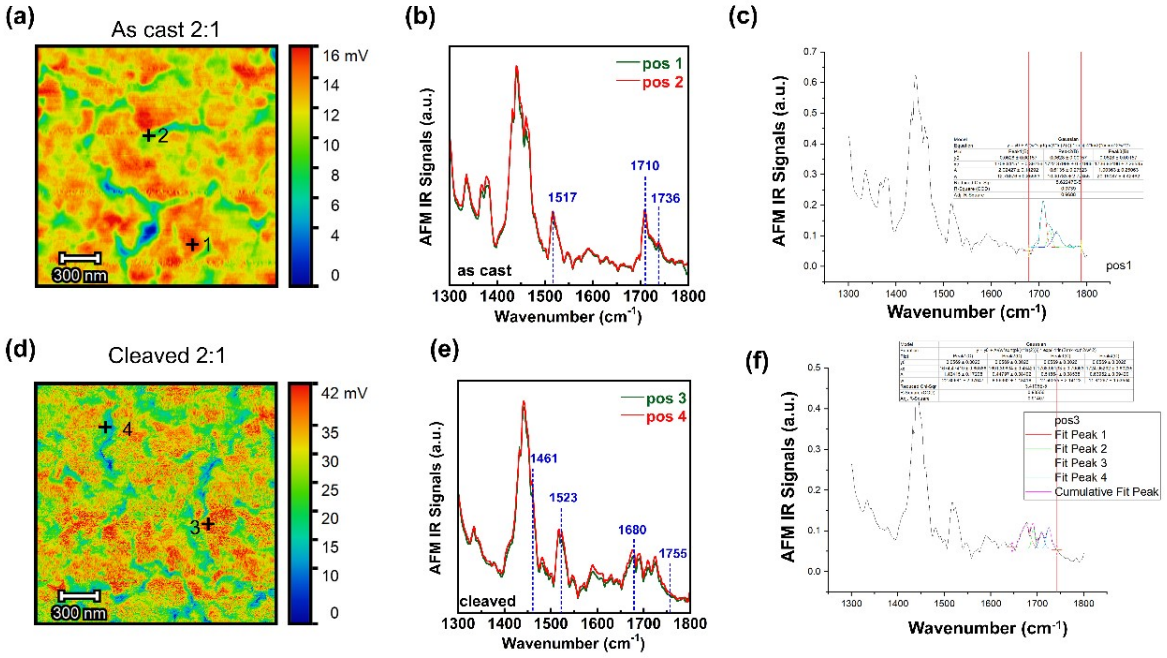

Figure S6. IR spectral analysis of thermocleavable donor/acceptor blend at a 2:1 ratio. (a) AFM-IR image of the as-cast film; (b) IR spectra of as-cast film; (c) peak fitting for as cast film to obtain signal ratio of donor and acceptor; (d) AFM-IR of the cleaved film; (e) IR spectra of the cleaved film; (f) fitting peak for cleaved film to obtain signal ratio between donor and acceptor.

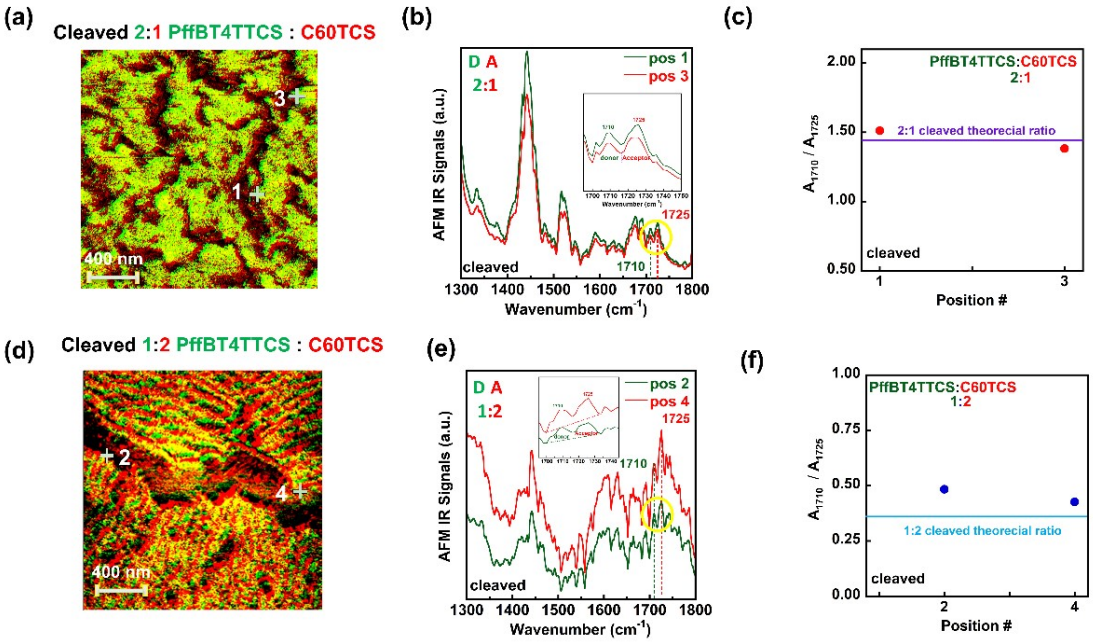

Figure S7. Calibration curve development using thermocleavable donor/acceptor blend at varying concentrations. (a) AFM-IR image of cleaved 2:1 blend; (b) IR spectra analysis of cleaved 2:1 blend; (c) peak ratio analysis at different positions for 2:1 blend; (d) AFM-IR image of cleaved 1:2 blend; (e) IR spectra analysis of cleaved 1:2 blend; (f) peak ratio analysis at different positions for 1:2 blend.

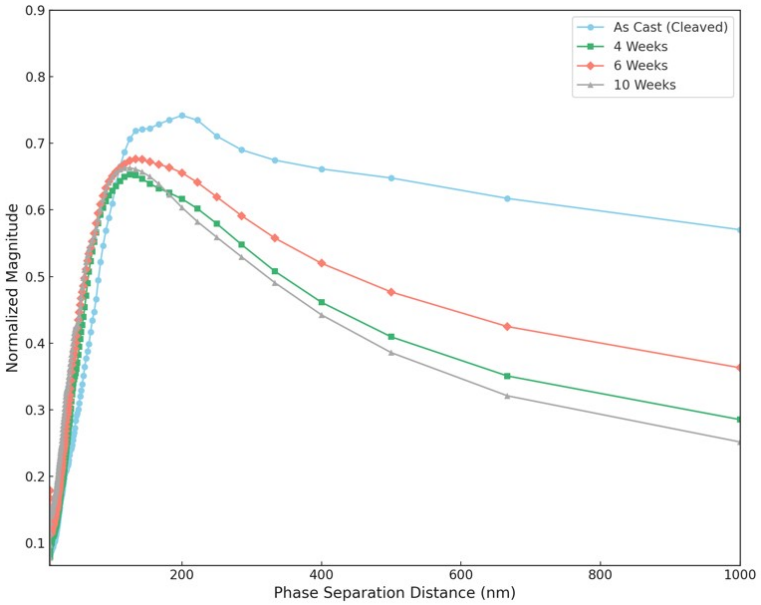

Figure S8. 2D Fourier transform analysis of thermally annealed samples with different time as listed in figure 4. The Y axis represents the distribution histogram of domain spacing in the phase -separated sample.

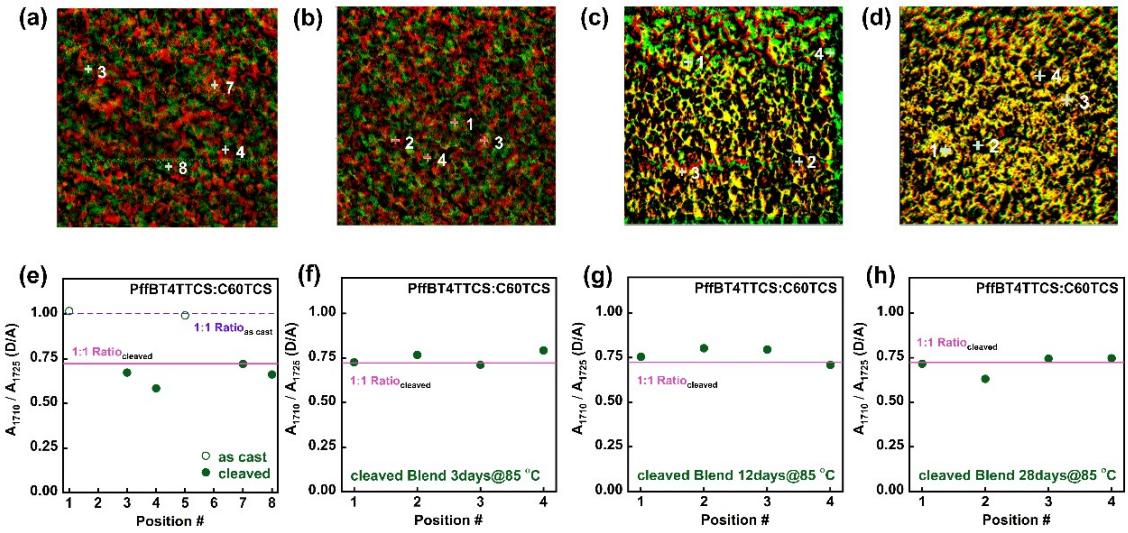

Figure S9. Morphological stability assessment of the cleaved donor:acceptor blend. (a) Overlay image of freshly cleaved blends; (b) overlay image after annealing at 85 °C for 3 days; (c) after 12 days; d) after 28 days; (e-h) corresponding local chemical compositions for each condition, where dashed line indicates the theoretical donor:acceptor 1:1 ratio during sample formulation.

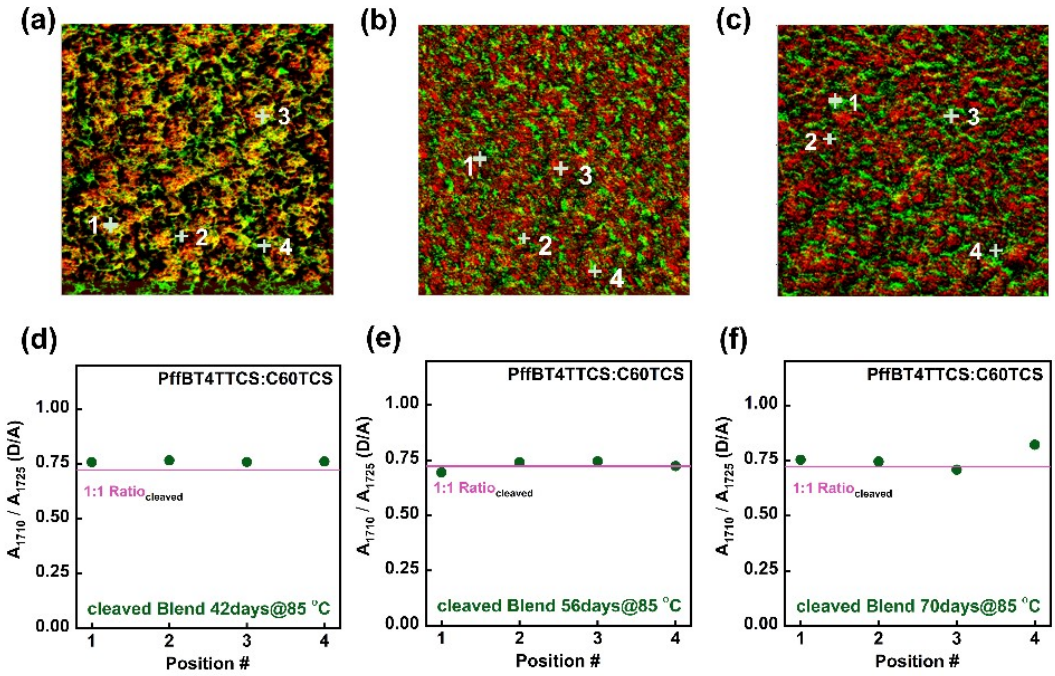

Figure S10. Long-term morphological stability test of cleaved donor:acceptor blend. (a) Overlay image after annealing at 85 °C for 42 days; (b) for 56 days ; (c) for 70 days; (d-f) corresponding local chemical compositions for each condition, where dashed line indicates the theoretical donor:acceptor 1:1 ratio during sample formulation.

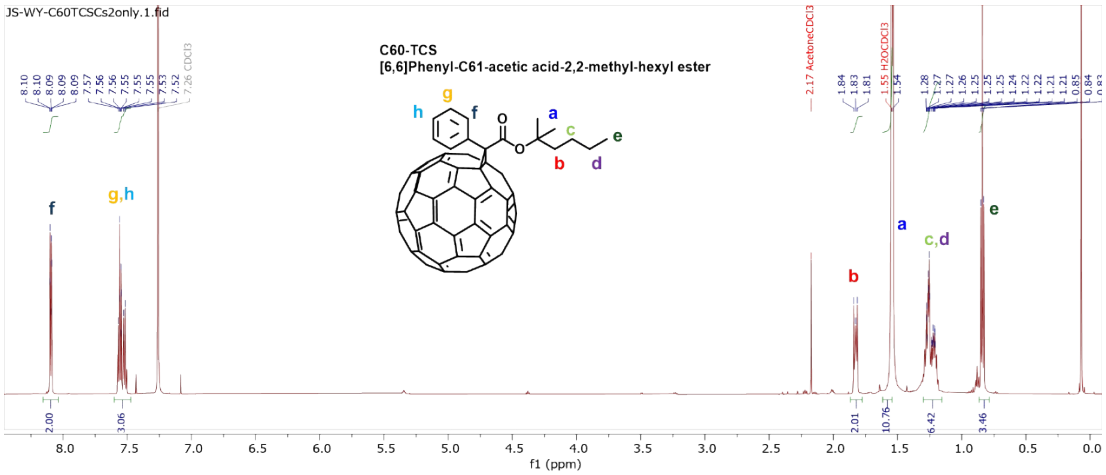

Figure S11. ^{1}H-NMR spectra of C60-TCS in $CDCl_3$

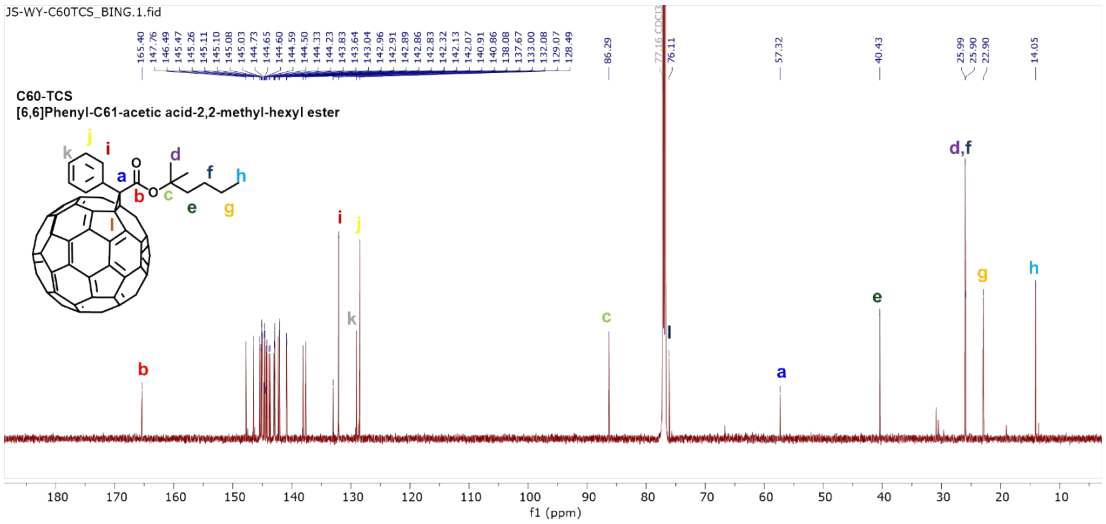

Figure S12. ^{13}C-NMR spectra of C60-TCS in $CDCl_3$

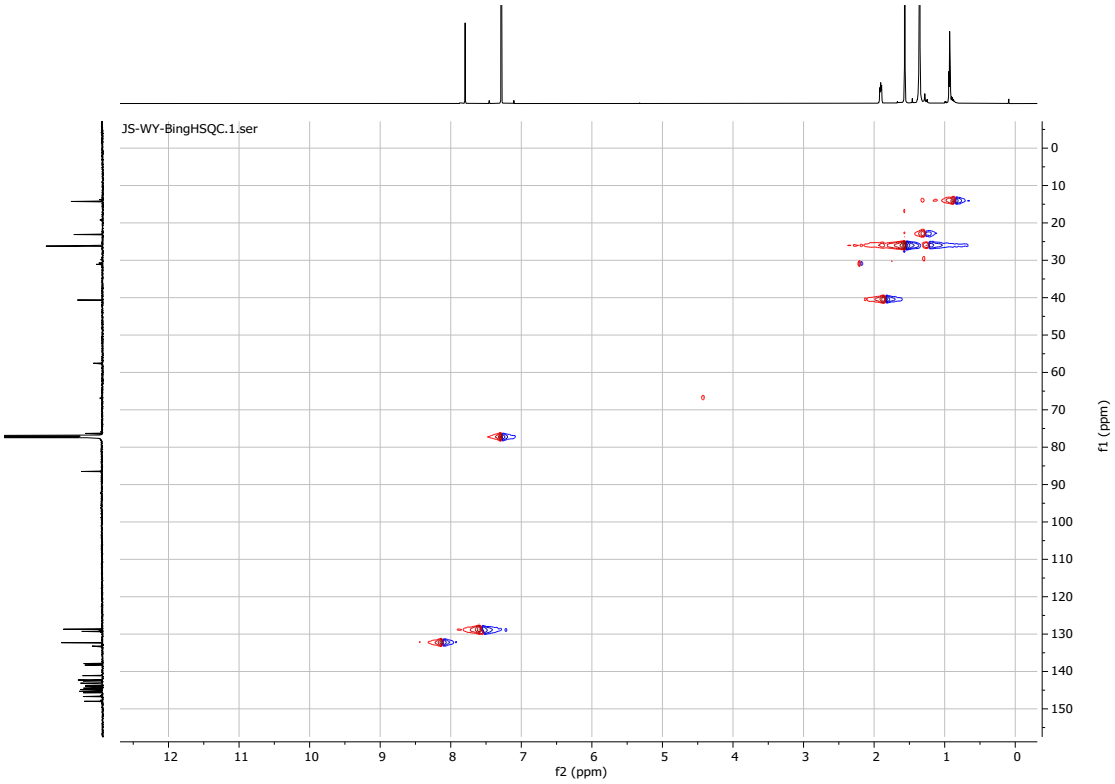

Figure S13. HSQC 2D NMR of C60-TCS in $CDCl_3$