

## Supporting Information for

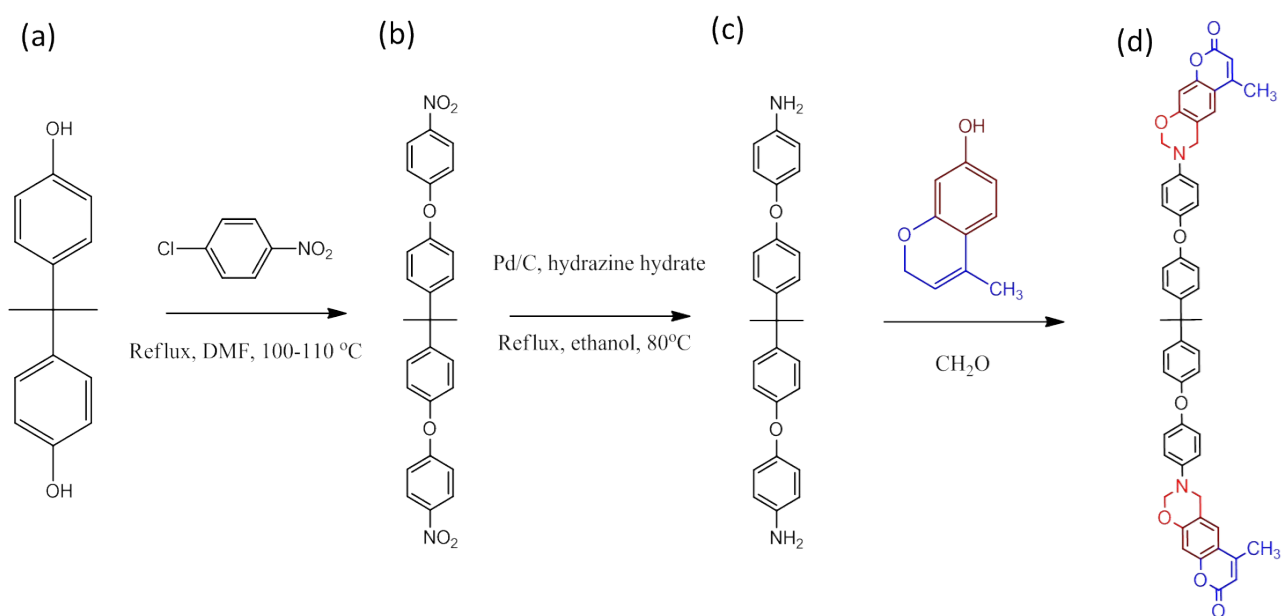
### Multivalent Photo-Crosslinkable Coumarin-Containing Polybenzoxazines Exhibiting Enhanced Thermal and Hydrophobic Surface Properties

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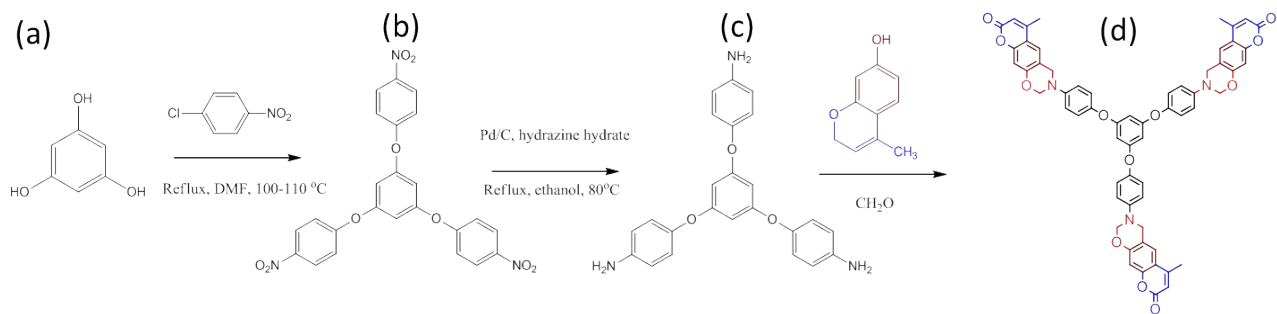
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**Scheme S1:** Chemical Structures of (a) Bisphenol A, (b) Bisphenol A-NO<sub>2</sub>, (c) Bisphenol A-NH<sub>2</sub>, and (d) Di-Coumarin BZ.



**Scheme S2:** Chemical Structures of (a) Phloroglucinol, (b) 1,3,5-Tris(4-nitrophenoxy)benzene, (c) 1,3,5-Tris(4-aminophenoxy)benzene, and (d) Tri-Coumarin BZ.

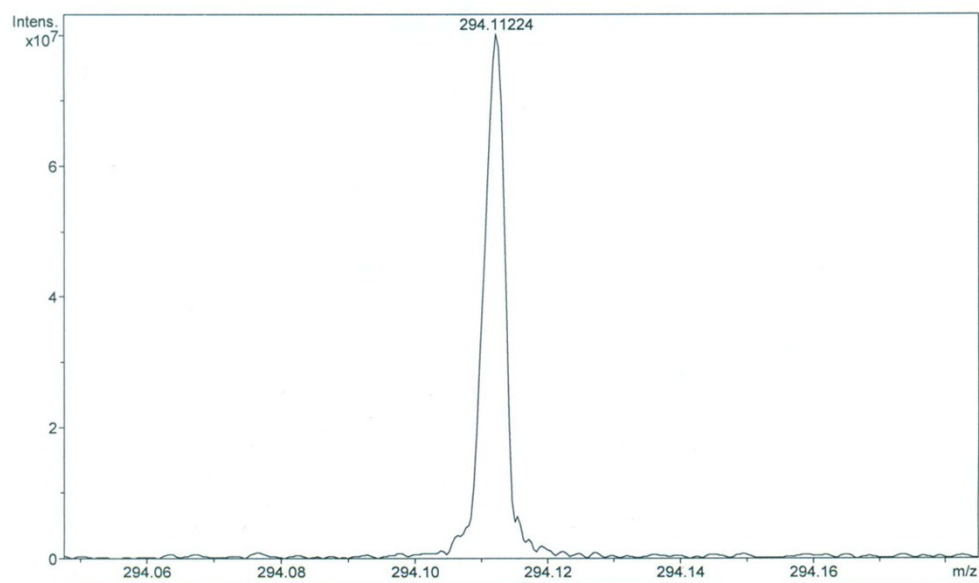
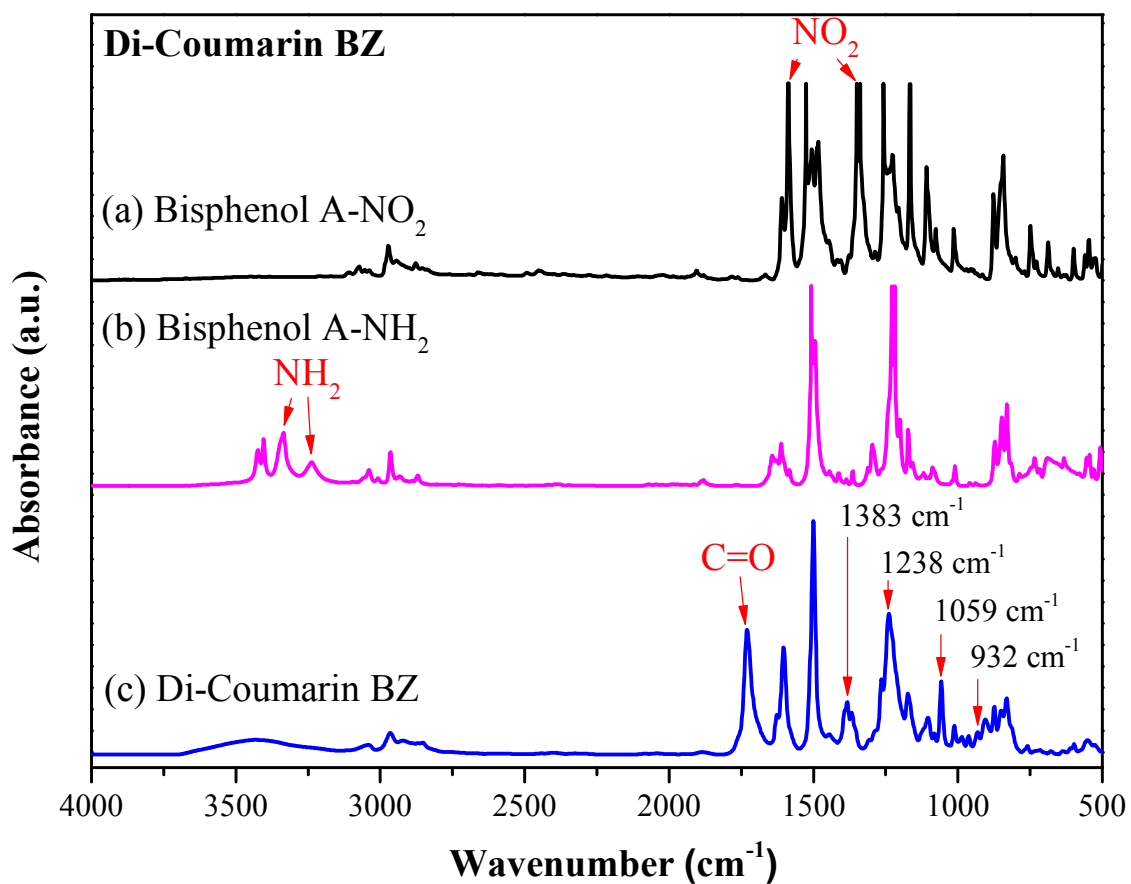


Figure S1: High resolution FT-MS of Mono-Coumarin BZ.



**Figure S2:** FTIR spectra of (a) Bisphenol A-NO<sub>2</sub>, (b) Bisphenol A-NH<sub>2</sub>, and (c) Di-Coumarin BZ.

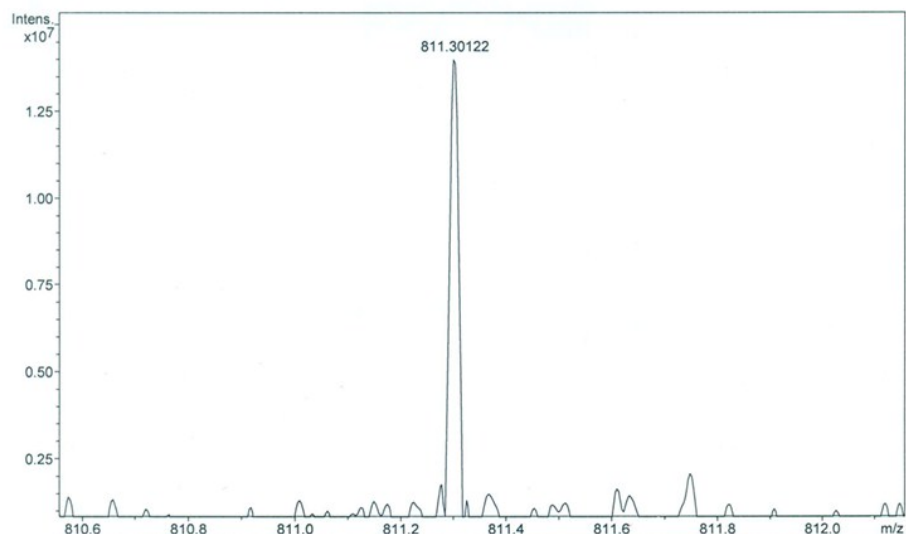
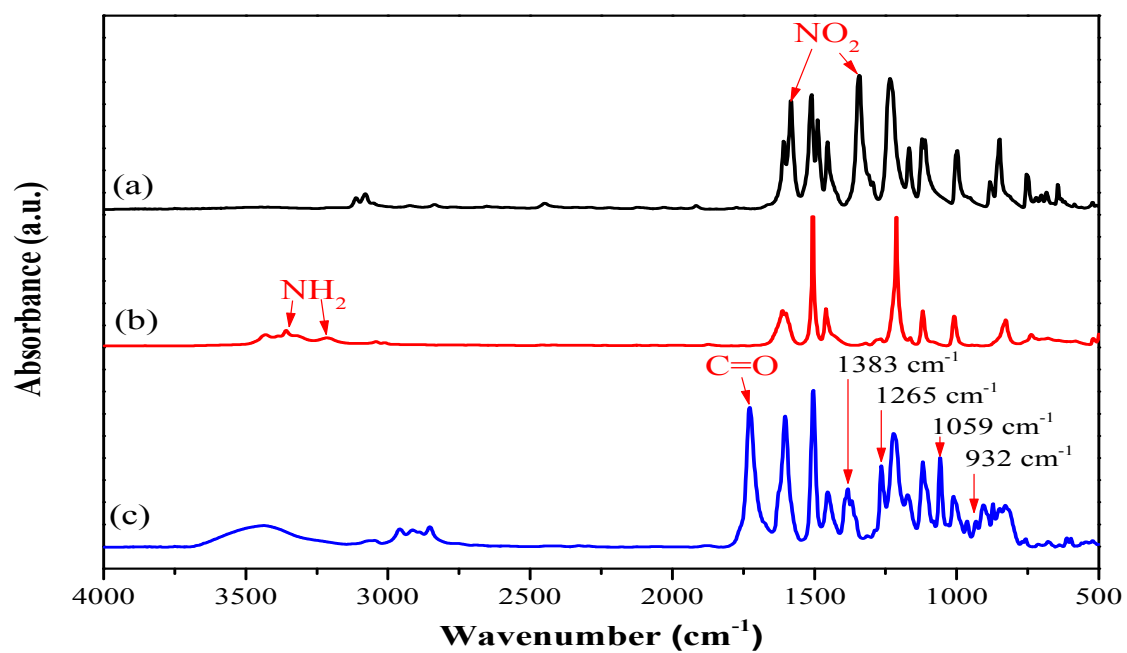


Figure S3: High resolution FT-MS of Di-Coumarin BZ.



**Figure S4:** FTIR spectra of (a) 1,3,5-Tris(4-nitrophenoxy)benzene, (b) 1,3,5-Tris(4-aminophenoxy)benzene, and (d) Tri-Coumarin BZ.

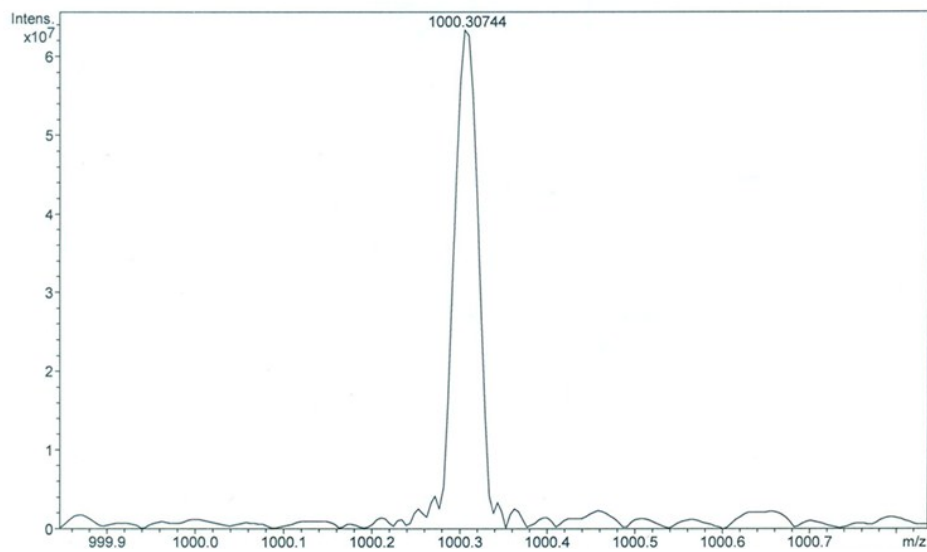
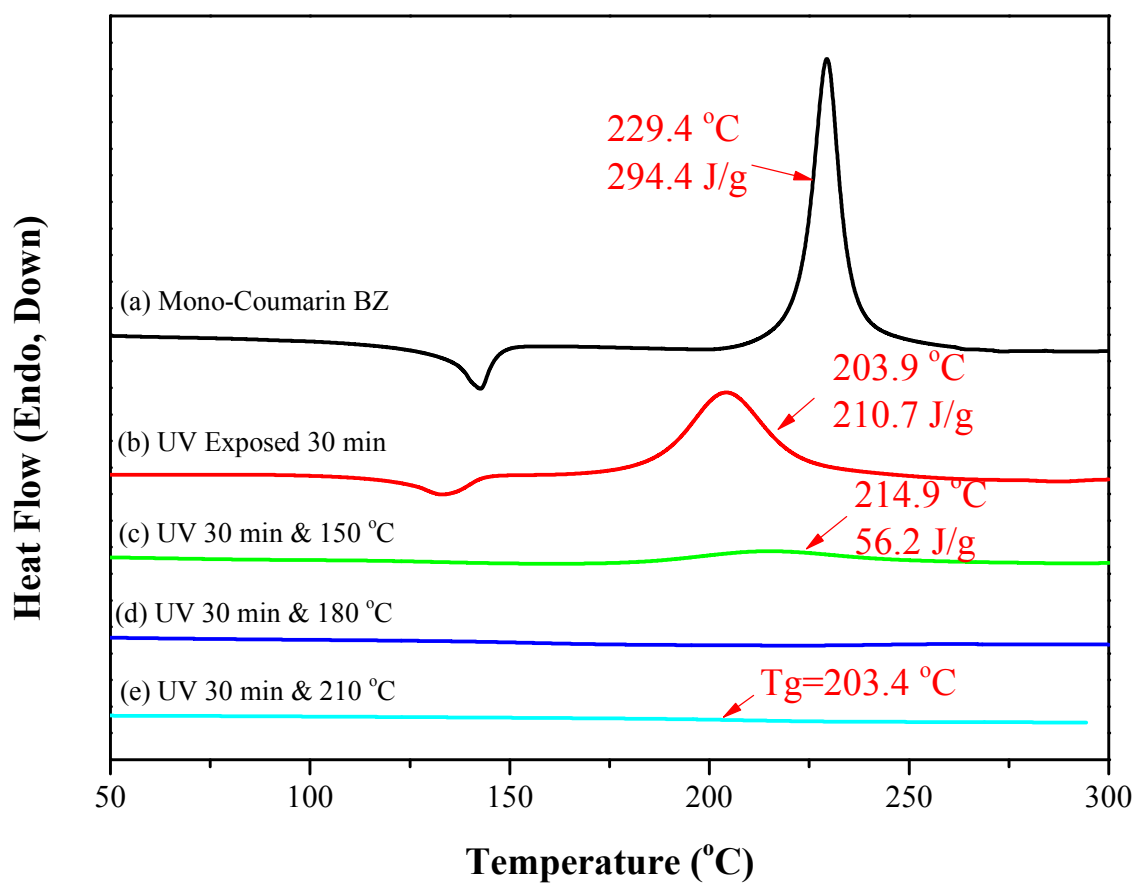
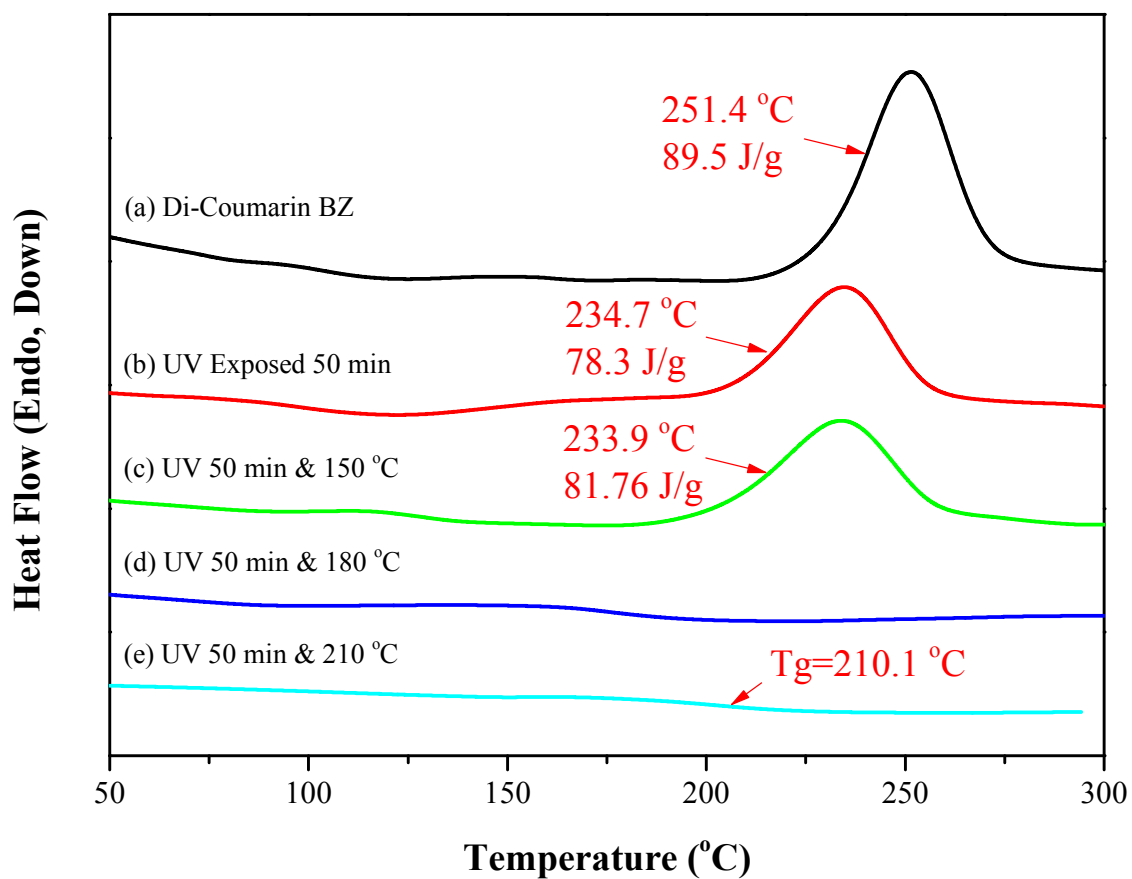


Figure S5: High resolution FT-MS of Tri-Coumarin BZ.

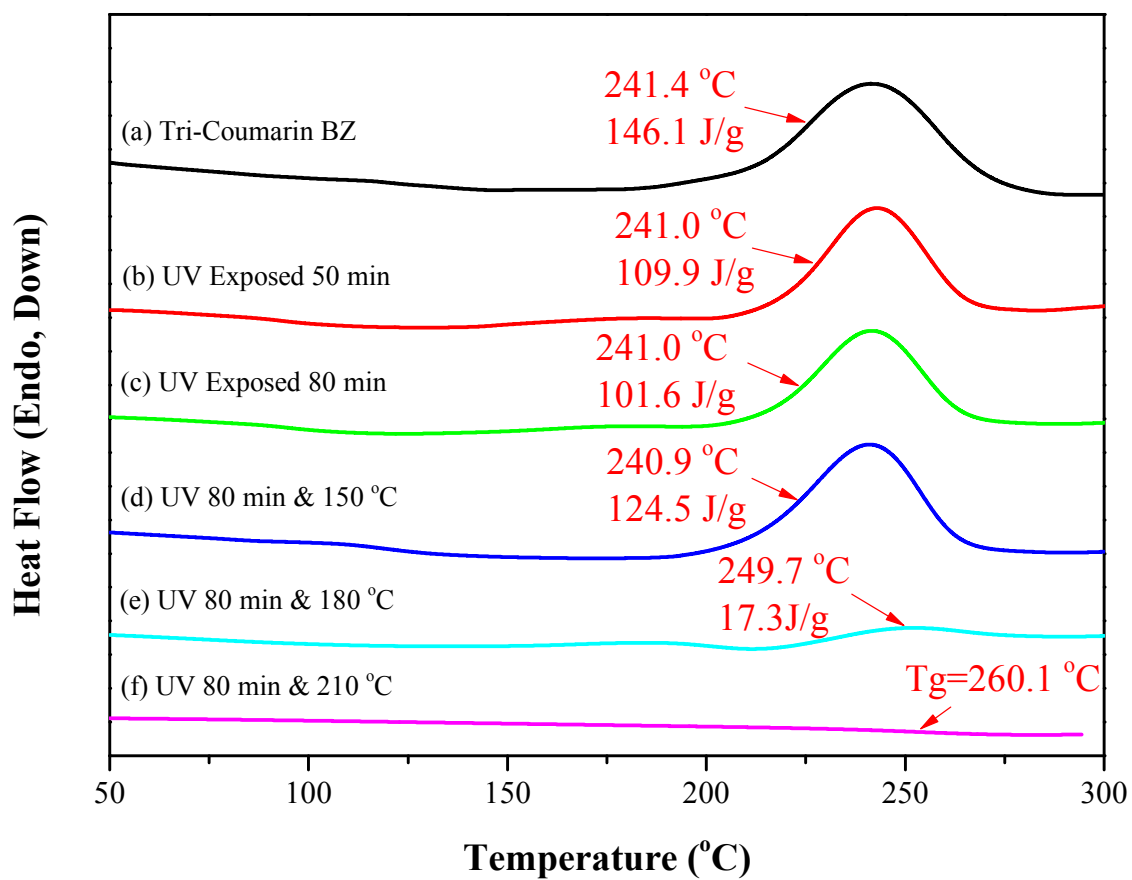


**Figure S6:** DSC thermograms of Mono-Coumarin BZ: (a) uncured, (b) after photodimerization for 30 min, and (c–e) after thermal curing at (c) 150, (d) 180, and (e) 210 °C.

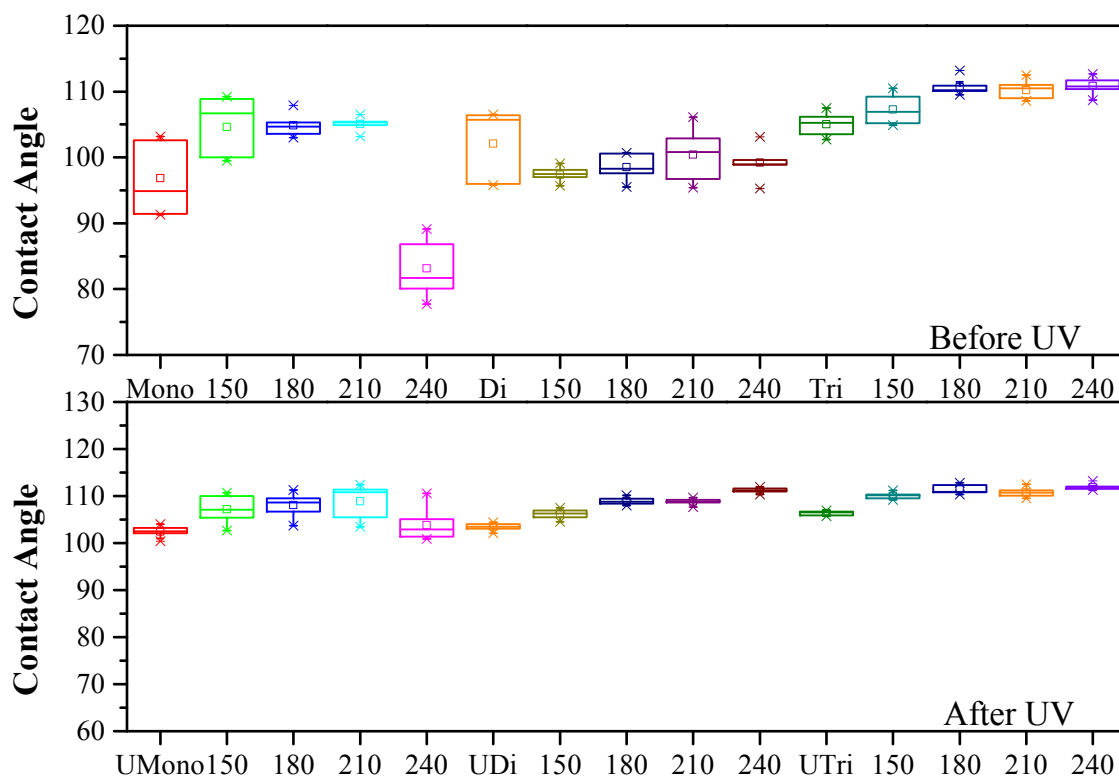




**Figure S7:** DSC thermograms of Di-Coumarin BZ: (a) uncured, (b) after photodimerization for 50 min, and (c–e) after thermal curing at (c) 150, (d) 180, and (e) 210 °C.



**Figure S8:** DSC thermograms of Tri-Coumarin BZ: (a) uncured, (b) after photodimerization for 80 min, and (c–e) after thermal curing at (c) 150, (d) 180, and (e) 210 °C.



**Figure S9:** WCAs of poly(Mono-Coumarin BZ), poly(Di-Coumarin BZ), and poly(Tri-Coumarin BZ) before and after UV irradiation at 365 nm, recorded at different thermal curing polymerization.