Supporting Information for

Photo-responsive liquid crystalline polymer from renewable furfural derivatives of dimethyl 2,5-furandicarboxylate via catalytic carbonylative esterification

Tian Wang,† Jinlian Zhu,† Kaiwei Zhang, Jing Wang, Yonggui Liao,* Guochuan Yin*, and Xiaolin Xie

Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Engineering Research Center for Biomaterials and Medical Protective Materials, Hubei Key Laboratory of Materials Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

Contents

Table S1 The influence of ligand loadings on the catalytic efficiency in DMFD synthesis

Entry	Ligand	Conv.(%)	Yield (%)	
			DMFD	methyl-furoate
1	0	21	11	9
2	5%	85	80	5
3	10%	93	89	3
4	15%	98	95	2
5	20%	98	96	2

Conditions: methyl 5-bromofuroate (0.2 mmol), 5% $PdCl_2$ loading (10 μmol), Sphos, Et_3N (0.6 mmol), CH_3OH (2 mL), 70 °C, 24 h, CO balloon.

Table S2 The influence of temperature on the catalytic efficiency in DMFD synthesis

Entry	*T* (℃)	Conv.(%)	Yield (%)	
			DMFD	methyl-furoate
1	30	16	5	10
2	40	20	12	6
3	50	45	41	3
4	60	92	90	2
5	70	98	95	2

Conditions: methyl 5-bromofuroate (0.2 mmol), $PdCl_2$ (10 μmol), Sphos (30 μmol), TEA (0.6 mmol), CH_3OH (2 mL), 24 h, *T*, CO balloon.

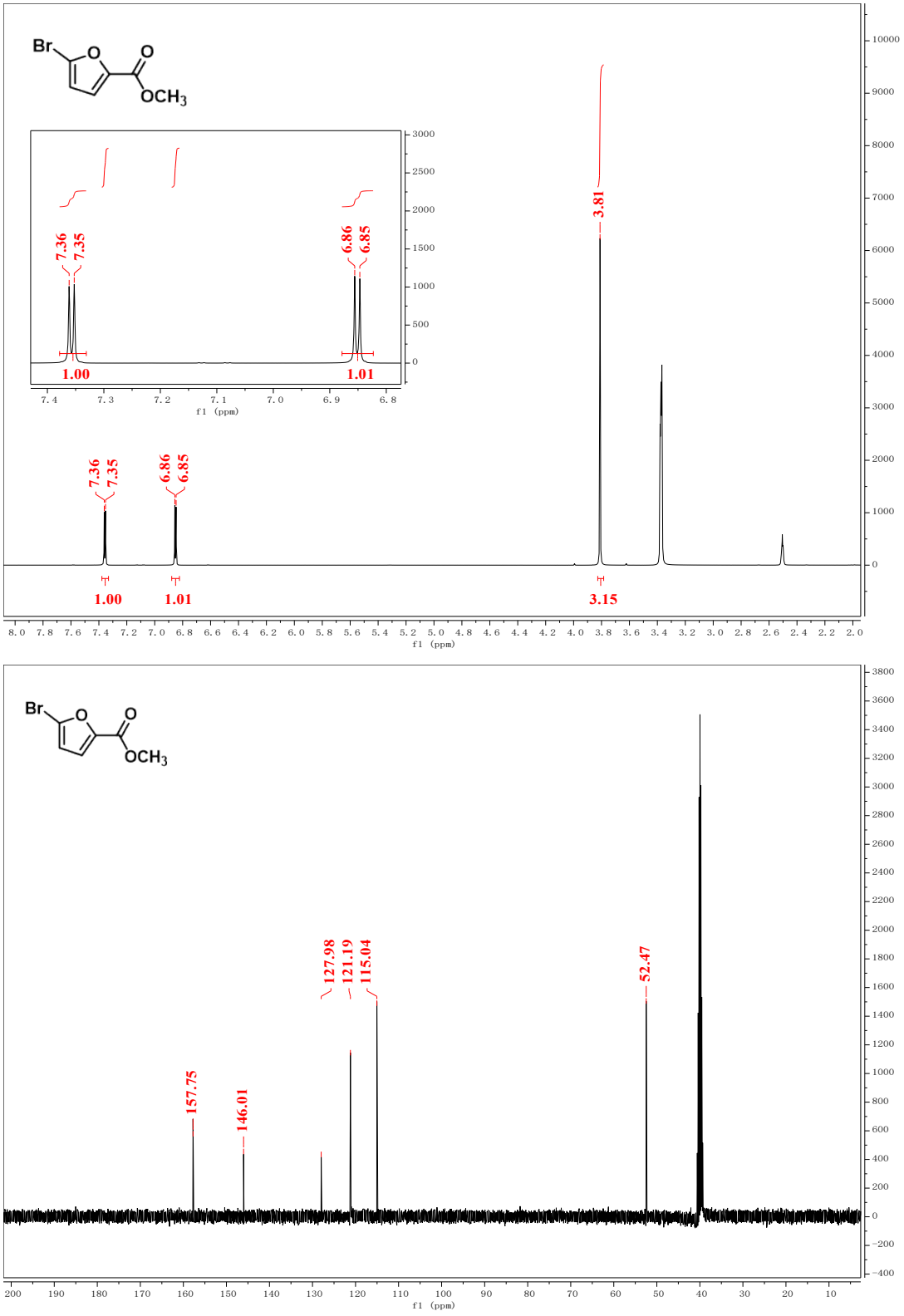

Fig. S1 ^{1}H and ^{13}C NMR spectra of methyl 5-bromofuroate

^{1}H NMR (400 MHz, DMSO-d_6), δ 7.36 (d, J = 3.6 Hz, 1H), 6.85 (d, J = 3.6 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6), δ 157.75, 146.01, 127.98, 121.19, 115.04, 52.47.

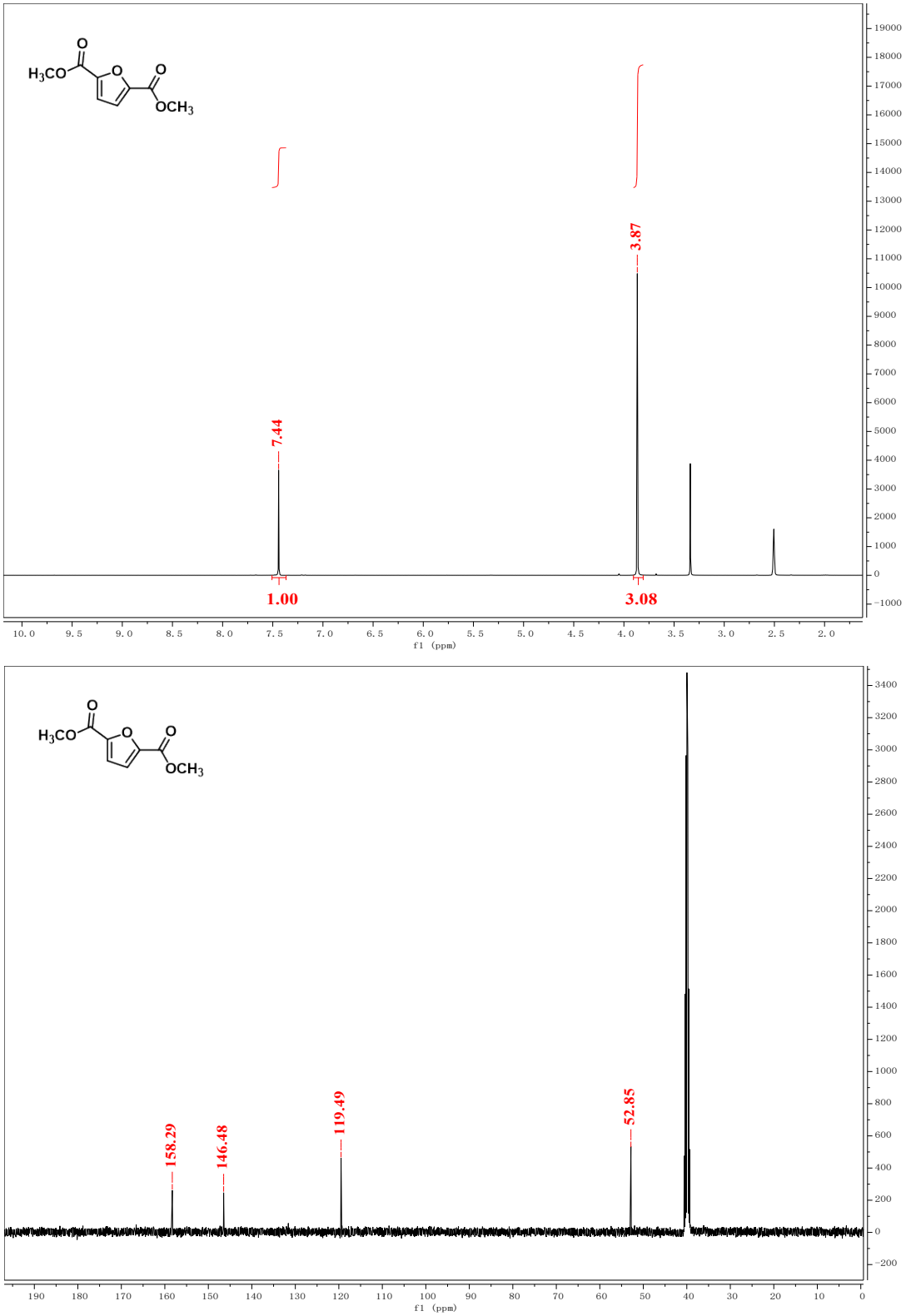

Fig. S2 ^{1}H and ^{13}C NMR spectra of DMFD

^{1}H NMR (400 MHz, DMSO-d_6), δ 7.44 (s, 1H), 3.87 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6), δ 158.29, 146.48, 119.49, 52.85.

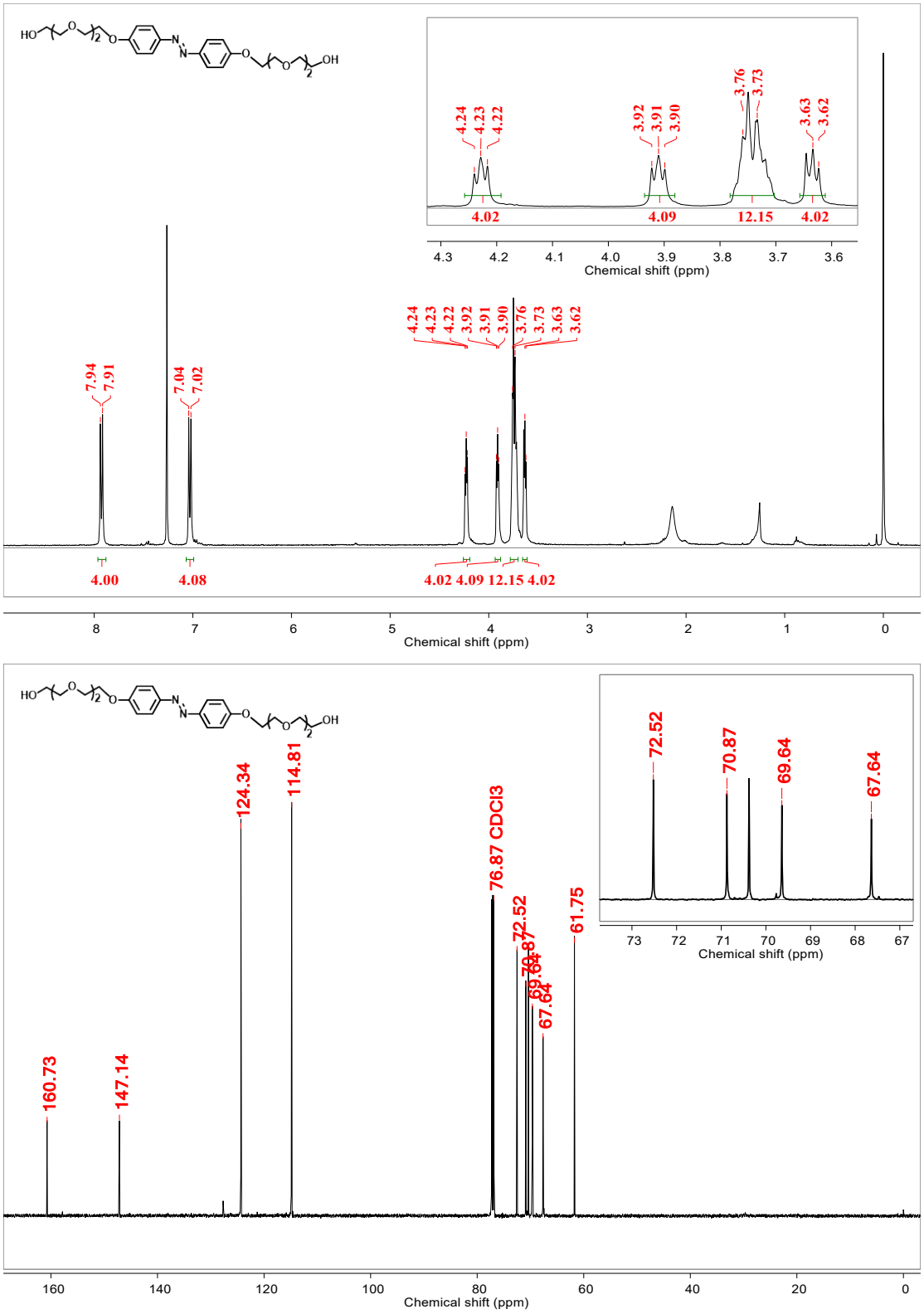

Fig. S3 ^{1}H and ^{13}C NMR spectra of Azo-C_{12}

^{1}H NMR (400 MHz, $CDCl_3$), δ 7.94−7.91 (d, J = 8.9 Hz, 4H, Ar−N), 7.04−7.02 (d, J = 12.1 Hz, 4H, Ar−O), 4.24−4.22 (t, 4H, Ar−O−CH_2), 3.92−3.90 (t, 4H, −CH_2O), 3.77−3.62 (m, 16H, CH_2CH_2−O−CH_2CH_2).

^{13}C NMR (101 MHz, $CDCl_3$), δ 160.7, 147.2, 124.3, 114.8, 76.8, 72.5, 70.9, 69.6, 67.6, 61.8.

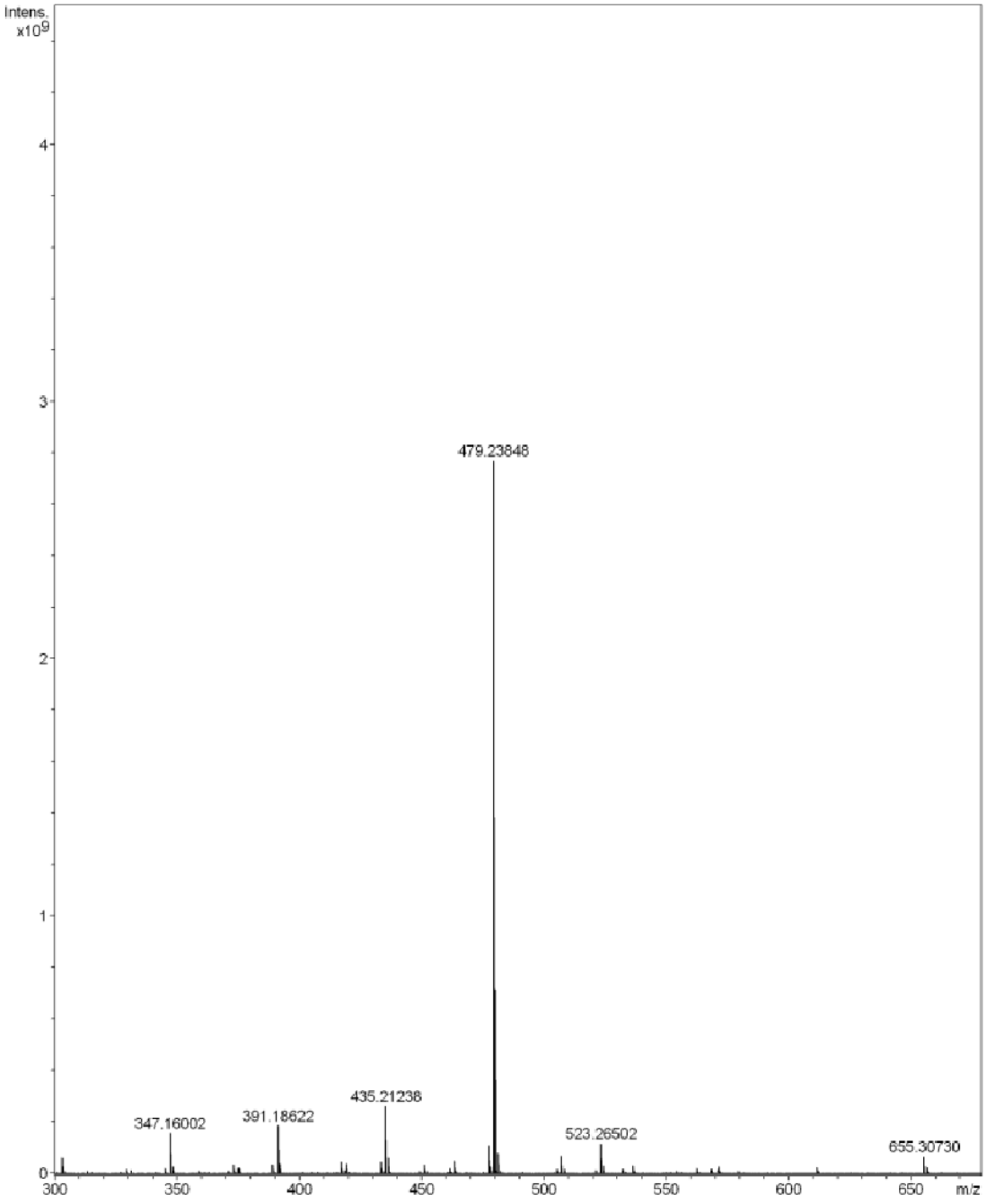

Fig. S4 ESI-MS spectrum of Azo-C_{12}

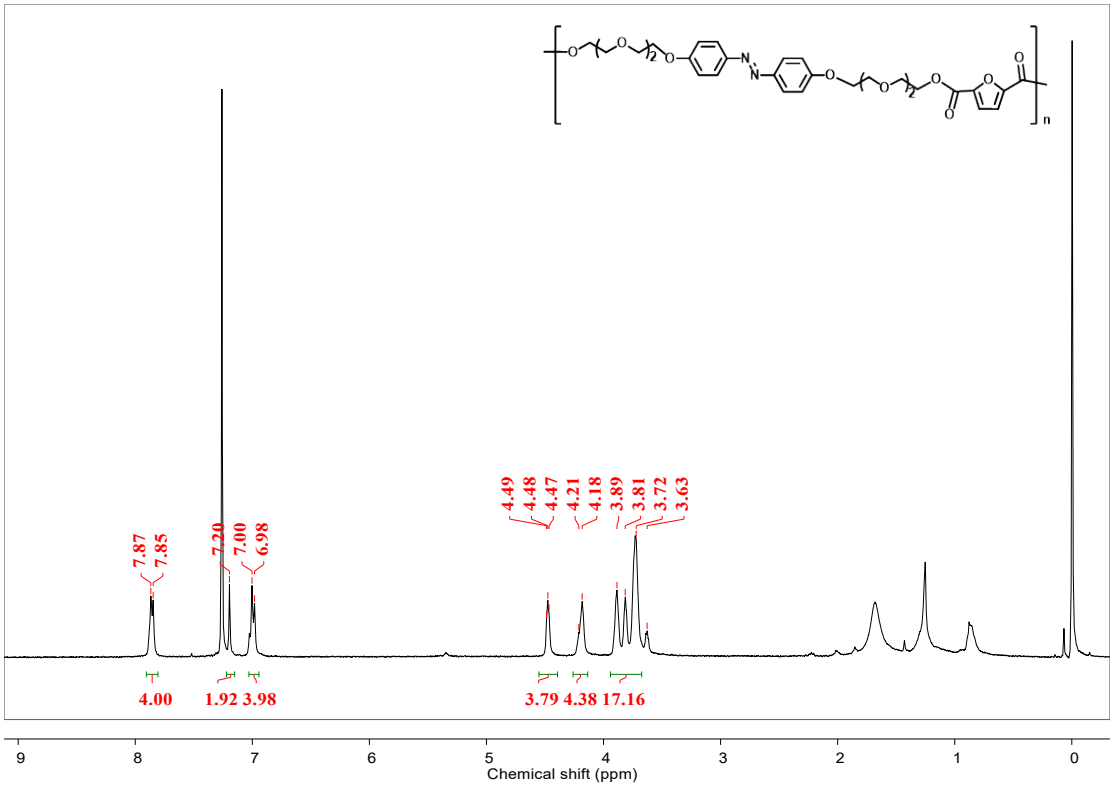

Fig. S5 ^{1}H NMR spectrum of PAzo-DMFD

^{1}H NMR (400MHz $CDCl_3$): δ 7.87−7.85 (m, 4H, Ar−N), 7.20 (s, 2H, furan ring), 7.03−6.98 (t, 4H, Ar−O), 4.49−4.47 (m, 4H, Ar−O−CH_2), 4.21−4.18 (m, 4H, −CH_2O), 3.89−3.63 (m, 16H, −CH_2CH_2−O−CH_2CH_2−).

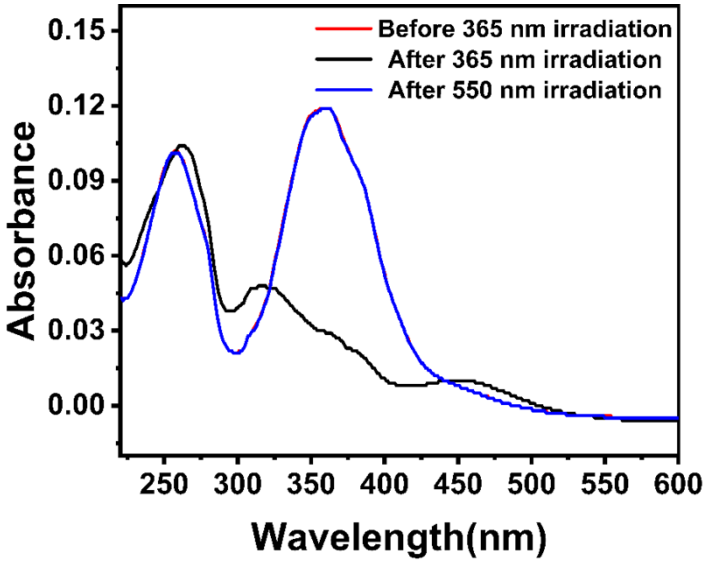

Fig. S6 UV-vis spectra of PAzo-DMFD film before and after UV light (365 nm, 25 mW·cm^{-2}, 10 min) and then visible light (550 nm, 10 mW·cm^{-2}, 10 min) irradiations.

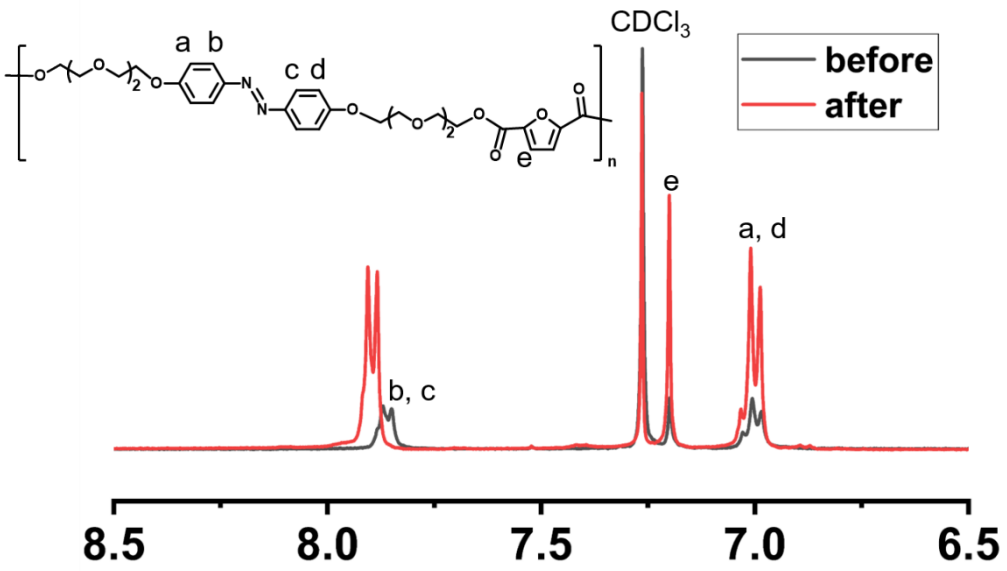

Fig. S7 ^{1}H-NMR spectra of PAzo-DMFD in $CDCl_3$ before (black) and after (red) 365 nm UV irradiation.

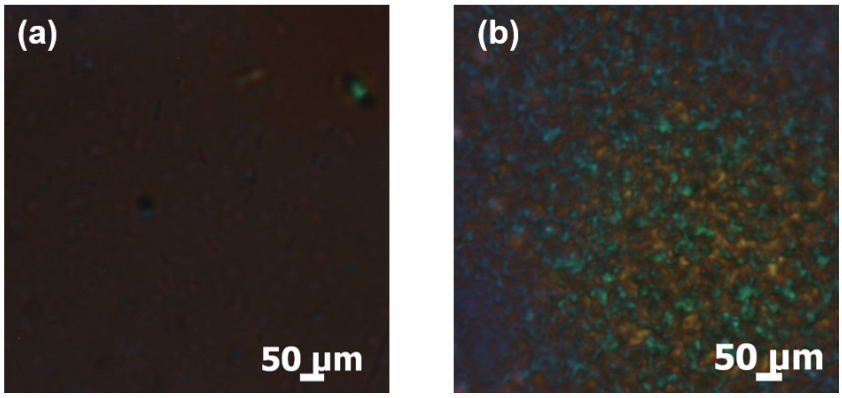

Fig. S8 POM images of a very thin sample of PAzo-DMFD (a) upon UV light irradiation (25 $mW \cdot cm^{-2}$, 60 min) at 50 °C, (b) upon heating to 120 °C and then cooling to 50 °C after UV irradiation.