Electronic Supplementary Information

GREEN SYNTHESIS OF THERMO/PHOTOCHROMIC DOPED CELLULOSE POLYMER: A BIOCOMPATIBLE FILM FOR POTENTIAL APPLICATION IN COLD CHAIN VISUAL TRACKING.

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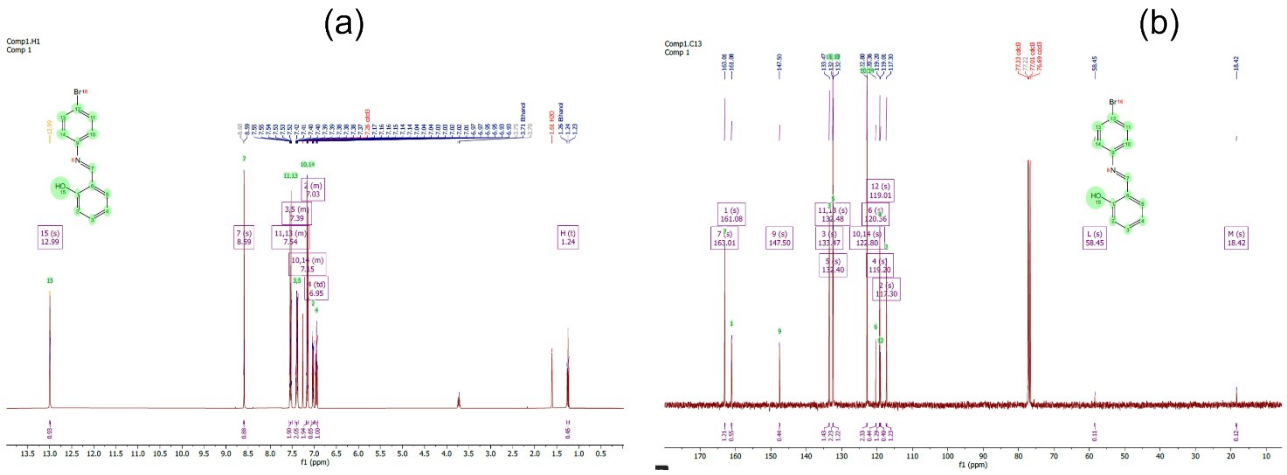

Figure S1. (a) ^{1}HNMR (400 MHz) and (b) ^{13}CNMR (100 MHz) of compound **1** in $CDCl_3$. ^{1}H NMR (400 MHz, $cdcl_3$) δ 12.98 (s, 1H, H15), 8.57 (s, 1H, H7), 7.57 – 7.47 (m, 2H, H11,H13), 7.42 – 7.32 (m, 2H, H3,H5), 7.18 – 7.09 (m, 2H, H10,H14), 7.04 – 6.98 (m, H, H2), 6.93 (td, *J* = 7.5, 1.0 Hz, H, H4), 1,61 (water), 1.23 (t, *J* = 7.0 Hz, Ethanol).

^{13}C NMR (101 MHz, $cdcl_3$) δ 162.99 (s, C7), 161.07 (s, C1), 147.48 (s, C9), 133.45 (s, C3), 132.46 (s, C11, C13), 132.38 (s, C5), 122.79 (s, C10,C14), 120.34 (s, C6), 119.19 (s, C12), 118.99 (s, C4), 117.29 (sC2), 18.42 (s).

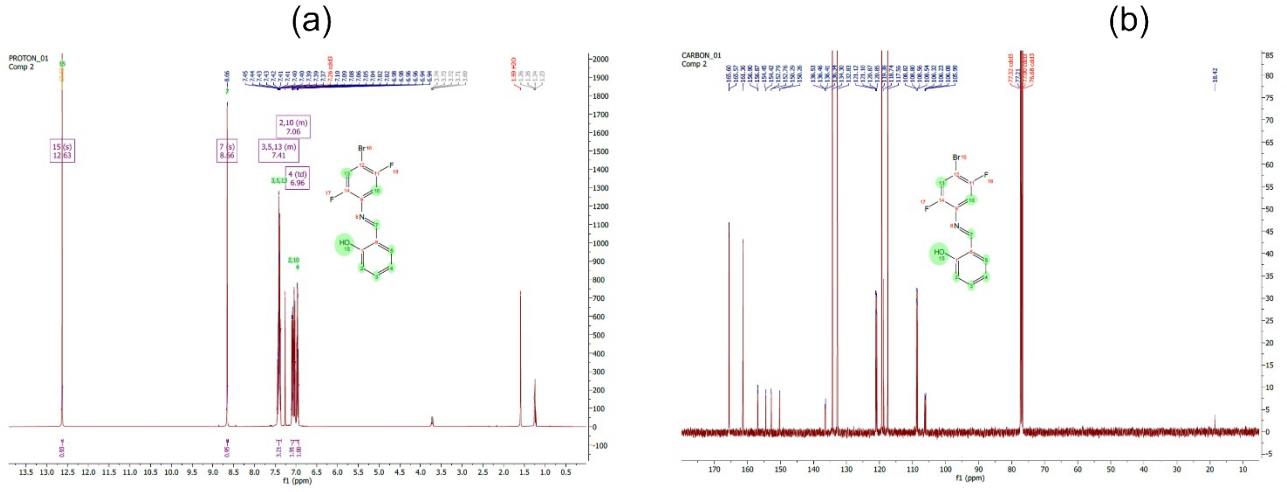

Figure S2. (a) ^{1}HNMR (400 MHz) and (b) ^{13}CNMR (100 MHz) of compound **2** in $CDCl_3$. ^{1}H NMR (400 MHz, $cdcl_3$) δ 12.61 (s, 1H, H15), 8.64 (s, 1H, H7), 7.46 – 7.33 (m, 3H, H3,H5,H13), 7.24 (s, 1H, H2, H10), 7.11 – 6.90 (m, 1H, H4).

^{13}C NMR (101 MHz, $cdcl_3$) δ 165.57 (d, *J* = 3.2 Hz, C11), 161.34 (s, C7, C1), 156.86 (d, *J* = 3.1 Hz, C14), 154.42 (d, *J* = 3.2 Hz), 152.76 (d, *J* = 3.1 Hz), 150.26 (d, *J* = 3.1 Hz), 136.42 (dd, *J* = 12.0, 7.3 Hz,), 134.28 (s, C5), 132.81 (s, C3), 120.97 (dd, *J* = 25.0, 1.3 Hz, C13), 119.36 (s, C4), 118.73 (s, C6), 117.55 (s, C2), 108.67 (dd, *J* = 25.6, 1.8 Hz, C12).

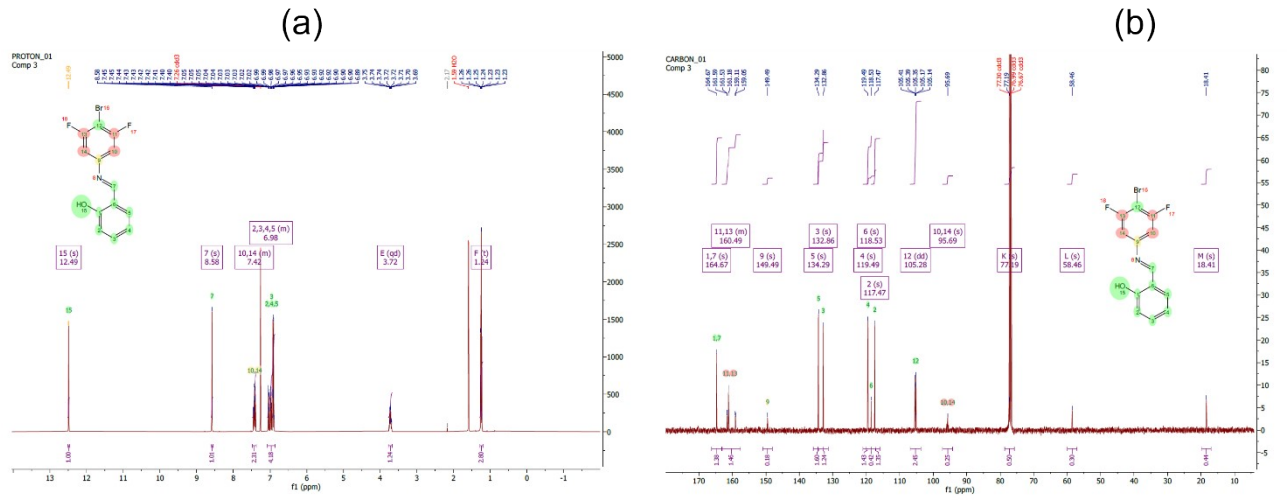

Figure S3. (a) ^{1}HNMR (400 MHz) and (b) ^{13}CNMR (100 MHz) of compound **3** in $CDCl_3$.

^{1}H NMR (400 MHz, $cdcl_3$) δ 12.47 (s, 1H, H15), 8.56 (s, 1H, H7), 7.46 – 7.35 (m, 2H, H13, H14), 7.04 – 6.85 (m, 4H, H2, H3, H4, H5).

^{13}C NMR (101 MHz, $cdcl_3$) δ 164.65 (s, C1, C7), 161.83 – 160.58 (m, C11, C13), 149.48 (s, C9), 134.27 (s, C5), 132.84 (s, C3), 119.48 (s, C4), 118.52 (s, C6), 117.46 (s, C2), 105.26 (dd, *J* = 24.9, 2.7 Hz, C12), 95.67 (s, C10, C14), 77.23 (cdcl3), 58.45 (s), 18.40 (s).

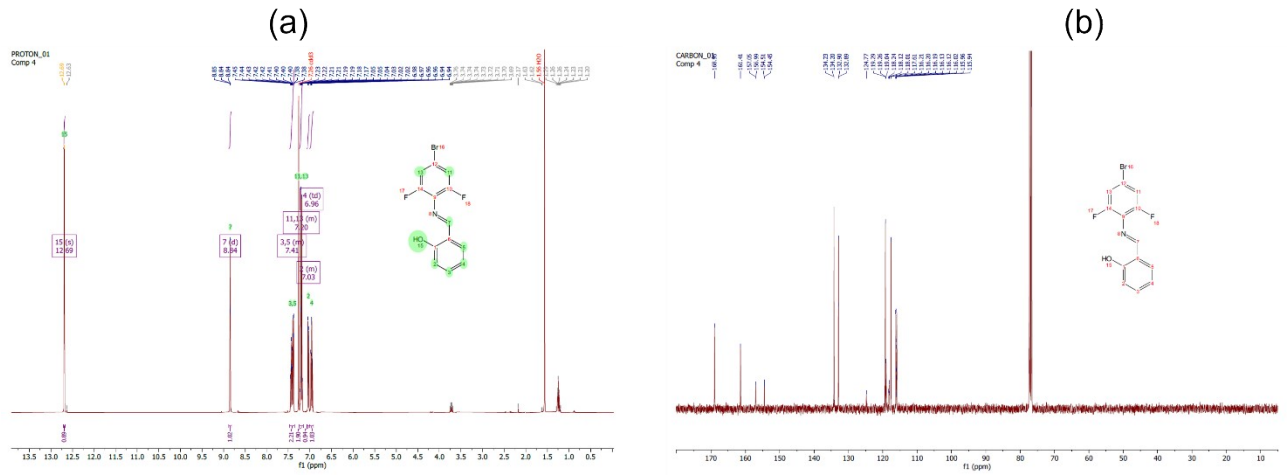

Figure S4. (a) ^{1}HNMR (400 MHz) and (b) ^{13}CNMR (100 MHz) of compound **4** in $CDCl_3$.

^{1}H NMR (400 MHz, $cdcl_3$) δ 12.67 (s, 1H, H15), 8.83 (s, 1H, H7), 7.45 – 7.33 (m, 2H, H3, H5), 7.21 – 7.11 (m, 2H, H11, H13), 7.02 (d, *J* = 8.3 Hz, 1H, H2), 6.94 (td, *J* = 7.7, 1.0 Hz, 1H, H4).

^{13}C NMR (101 MHz, $cdcl_3$) δ 168.93 (t, *J* = 5.1 Hz, C1), 161.39 (s, C7), 157.01 (d, *J* = 6.1 Hz, C10, C14), 154.47 (d, *J* = 6.0 Hz, C9), 134.21 (s, C3), 132.88 (s, C5), 119.24 (s, C6), 119.02 (s, C12), 118.11 (s, C4), 117.59 (s, C2), 116.30 – 115.83 (m, C13, C11).

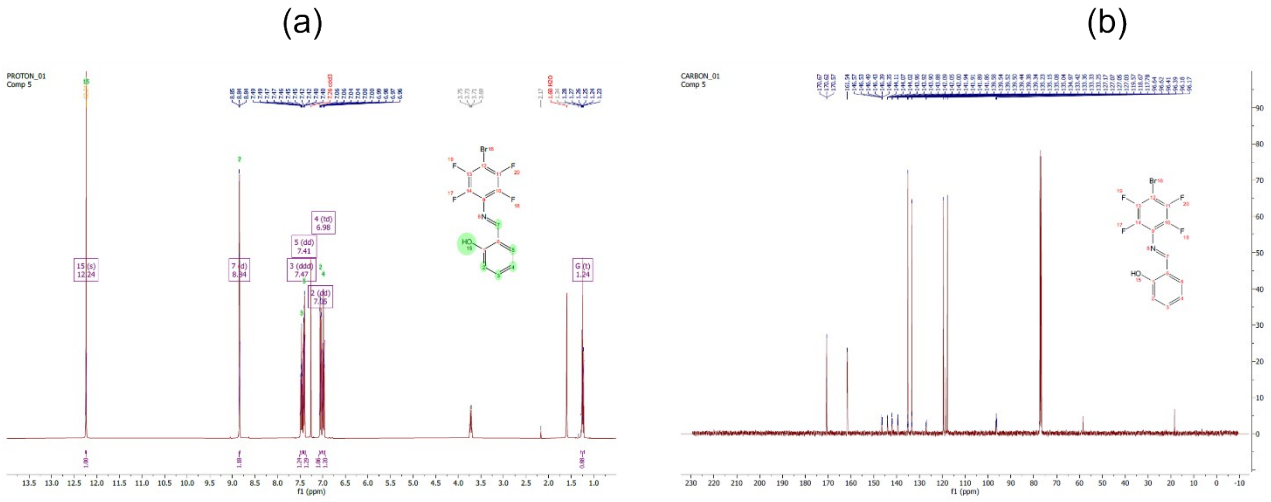

Figure S5. (a) ^{1}HNMR (400 MHz) and (b) ^{13}CNMR (100 MHz) of compound **5** in $CDCl_3$.

^{1}H NMR (400 MHz, cdcl$_3$) δ 12.22 (s, 1H, H15), 8.82 (s, 1H, H7), 7.51 – 7.42 (m, 1H, H3), 7.39 (dd, *J* = 7.7, 1.6 Hz, 1H, H5), 7.03 (d, *J* = 8.3 Hz, 1H, H2), 7.00 – 6.92 (m, 1H, H4).

^{13}C NMR (101 MHz, cdcl$_3$) δ 170.60 (t, *J* = 4.9 Hz, C7), 161.52 (s, C1), 146.51 - 139.37 (m, C13, C11), 135.07 (s, C14, C10), 133.35 (s, C3, C5), 119.55 (s, C9), 118.65 (s, C4), 117.76 (s, C6), 96.38 (s, C2).

Crystal Data and Refinement Details

Table S1. Crystal data and refinement details for compounds **1**-**5** collected at RT.

	1	**2**	**3**	**4**	**5**
Formula	$C_{13}H_{10}BrNO$	$C_{13}H_8BrF_2NO$	$C_{13}H_8BrF_2NO$	$C_{13}H_8BrF_2NO$	$C_{13}H_6BrF_4NO$
FW (g/mol)	276.13	312.11	312.11	312.11	348.10
Crystal System	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space Group	$Pca2_1$	$P2_1$	P-1	P-1	$P2_1$
a/Å	6.2262(3)	5.4360(9)	6.9293(12)	7.2141(6)	6.0196(6)
b/Å	7.0317(4)	19.728(3)	7.4667(9)	7.5974(6)	7.4659(9)
c/Å	26.2485(12)	5.8339(10)	12.746(2)	11.6575(8)	13.8518(9)
α/°	90	90	74.781(13)	79.343(6)	90
β/°	90	105.561(17)	84.546(14)	79.021(6)	95.881(7)
γ/°	90	90	69.627(14)	71.454(7)	90
Volume/Å³	1149.18(10)	602.69(18)	596.53(17)	589.33(8)	619.25(11)
Z	4	2	2	2	2
ρcalc g/cm³	1.596	1.720	1.738	1.759	1.867
μ/mm^{-1}	3.553	3.421	3.457	3.499	3.363
measd rflns	3124	4760	4589	6198	4719
indep rflns	1714	2288	2731	2521	2383
R_1	0.0462	0.0654	0.0518	0.0514	0.0504
wR_2	0.0868	0.1830	0.1001	0.0897	0.1100

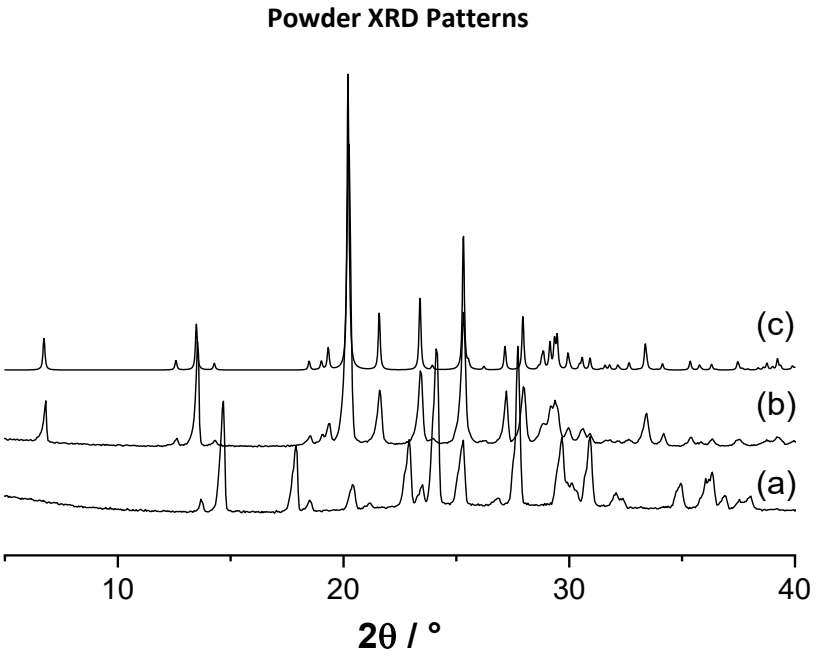

Figure S6. Powder XRD patterns of mechanochemical synthesis of compound **1**. (a) bromoaniline experimental pattern (b) bromoaniline ground with 1 equivalent of salicylaldehyde, and (c) calculated powder pattern for crystalline **1**.

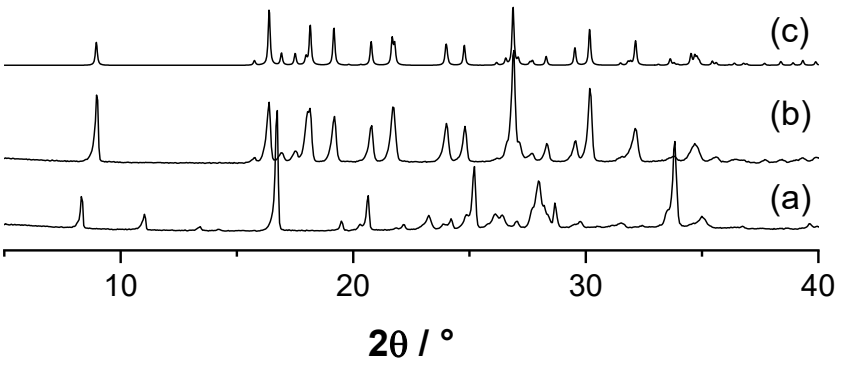

Figure S7. Powder XRD patterns of mechanochemical synthesis of compound **2**. (a) 2,5-dibromoaniline experimental pattern (b) 2,5-dibromoaniline ground with 1 equivalent of salicylaldehyde, and (c) calculated powder pattern for crystalline **2**.

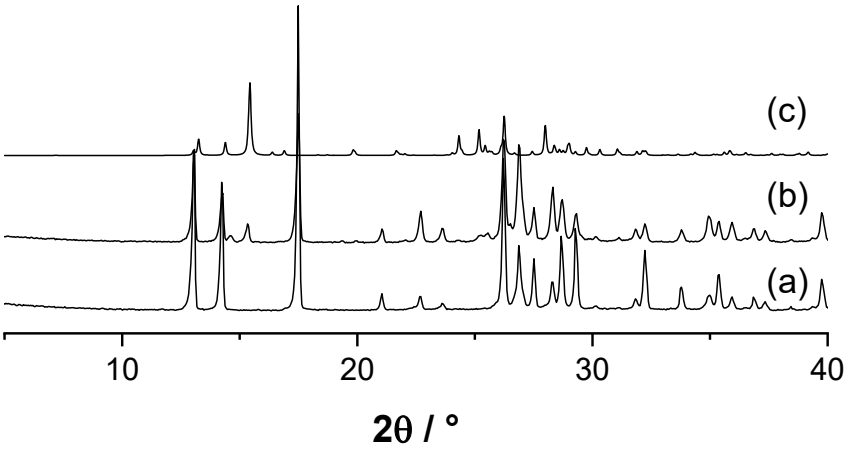

Figure S8. Powder XRD patterns of mechanochemical synthesis of compound **3**. (a) 3,5-dibromoaniline experimental pattern (b) 3,5-dibromoaniline ground with 1 equivalent of salicylaldehyde, and (c) calculated powder pattern for crystalline **3**.

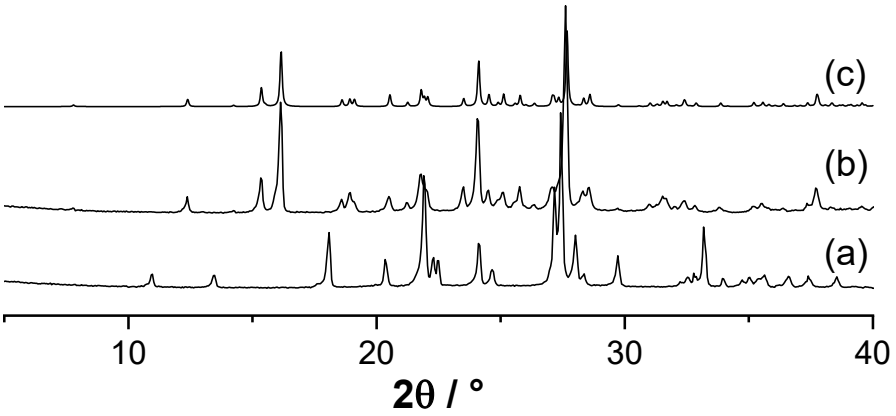

Figure S9. Powder XRD patterns of mechanochemical synthesis of compound **4**. (a) 2,6-dibromoaniline experimental pattern (b) 2,6-dibromoaniline ground with 1 equivalent of salicylaldehyde, and (c) calculated powder pattern for crystalline **4**.

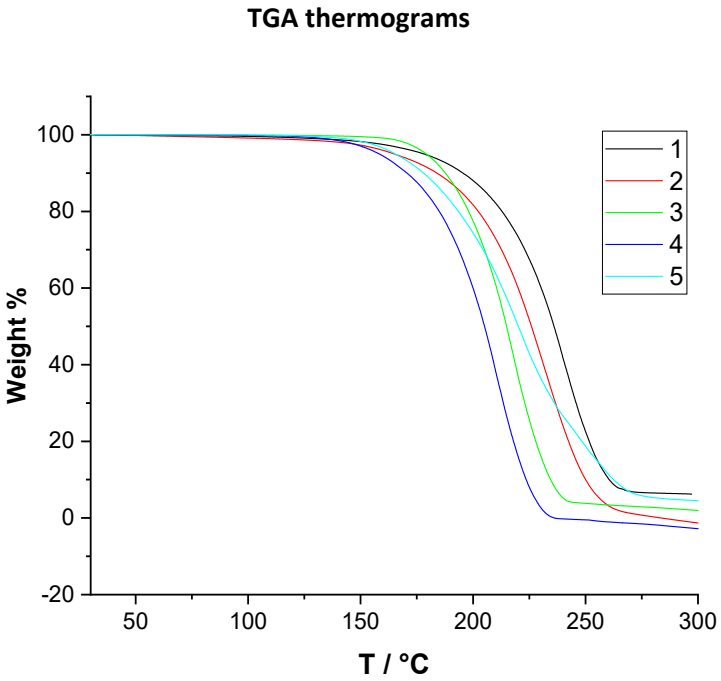

Figure S10. TGA thermograms of compounds **1**-**5**.

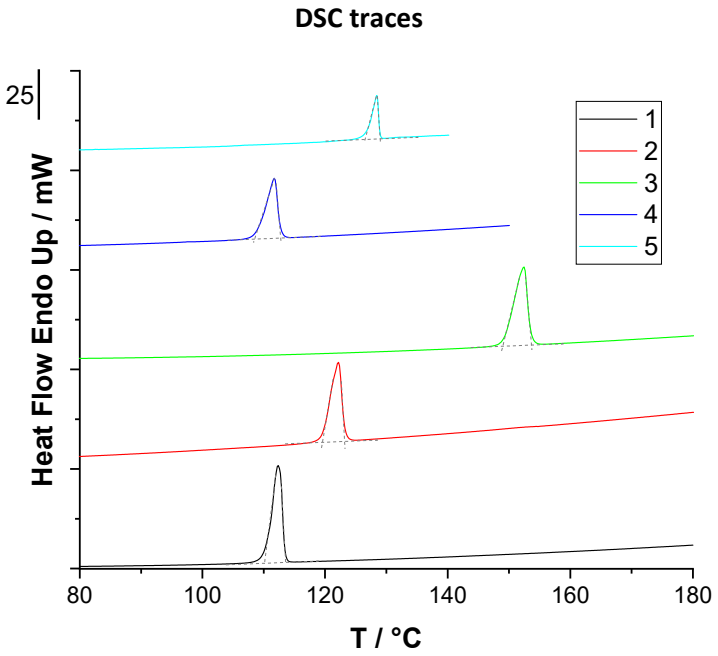

Figure S11. DSC traces of compounds **1**-**5**.

Table S2. DSC data of compounds **1**-**5.**

Compound	Onset (°C)	Peak (°C)	Endpoint (°C)	ΔH (KJ/mol)
1	110	112	113	26
2	119	122	123	25
3	149	152	153	28
4	108	111	112	28
5	126	128	129	27

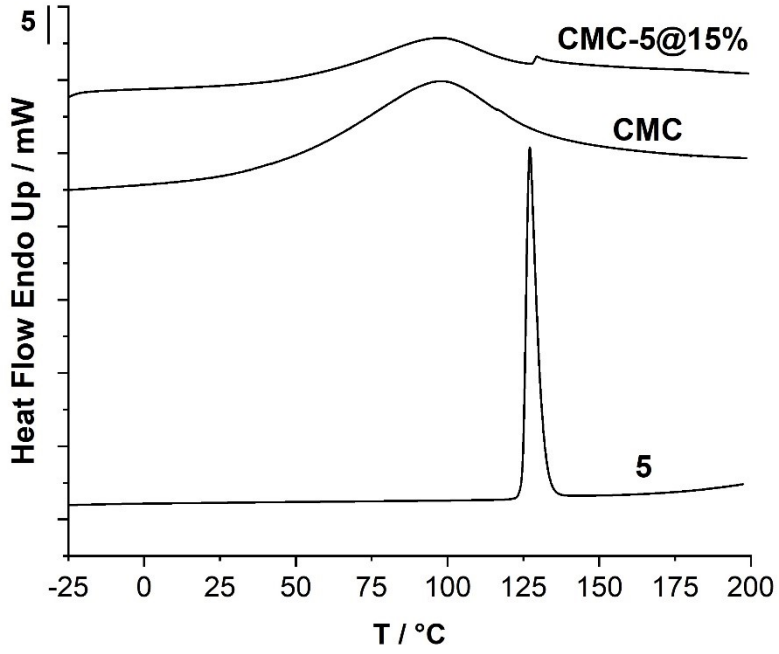

Figure S12. DSC traces of the pristine CMC film, polycrystalline **5**, and the CMC-**5**@15% composite film.

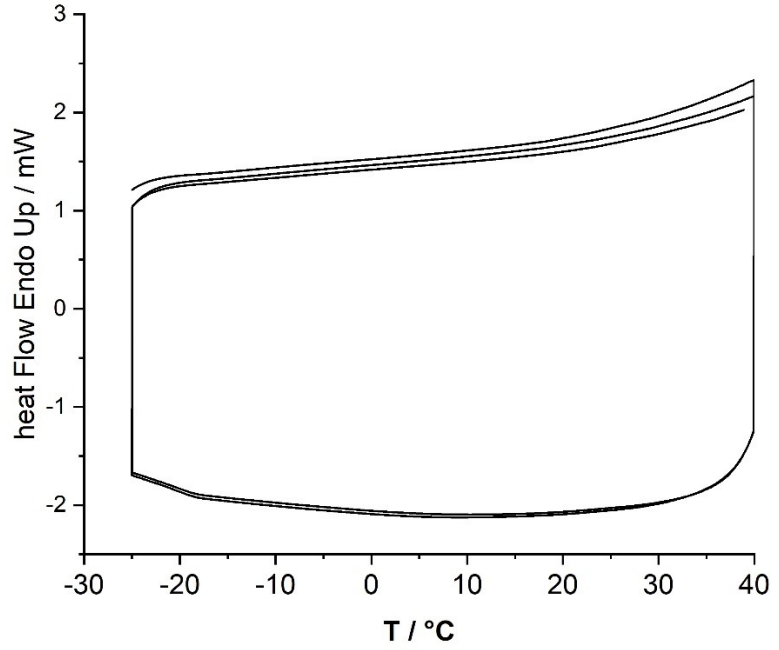

Figure S13. DSC cycles of the CMC-**5**@15% composite film measured from -25°C to 40°C. No degradation of the sample was detected.

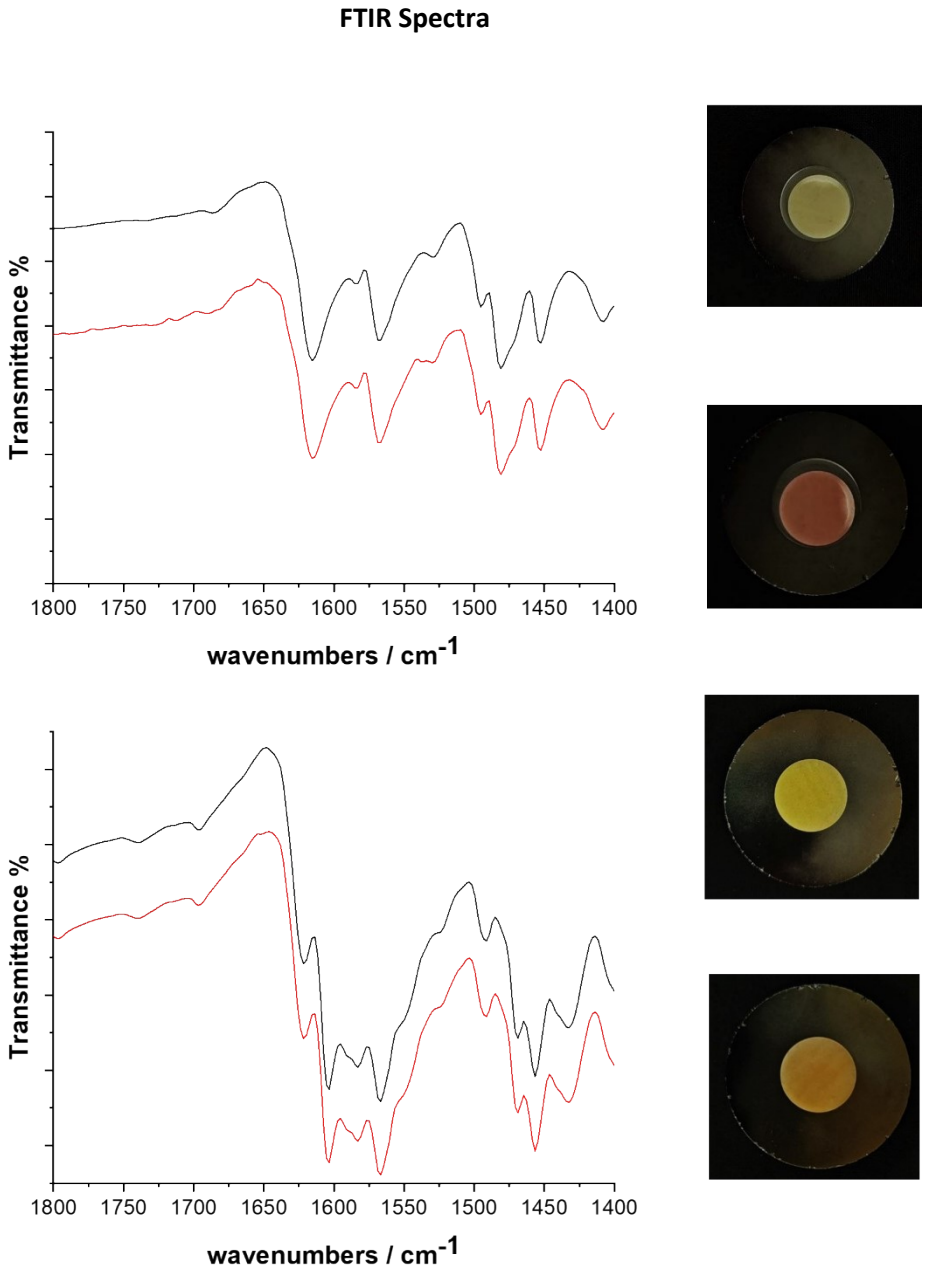

Figure S14. Detail of the FTIR spectra run before (black line) and after UV irradiation (redline) and difference spectra between the untreated and irradiated samples of compounds **1** (top) and **3** (bottom) and photographs of the KBr pellets used for the FTIR measurements. Although they are both photochromic, the trans-keto tautomers were not detected because of fast thermal recovery in **1**, and likely low amount formed in **3**.

Mechanical characterization of the photochromic film CMC-5@15%

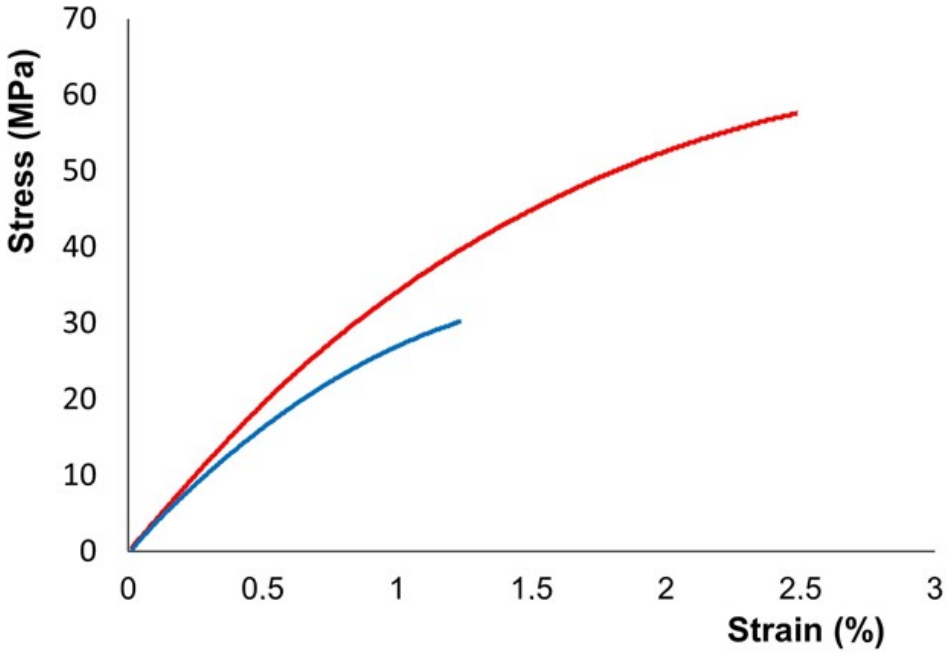

Figure S15. Stress-strain curves of pure CMC (red-line) and CMC-**5**@15% (blue-line).