Supporting Information for

Diarylethene-based conjugated polymer networks for ultrafast photochromic films

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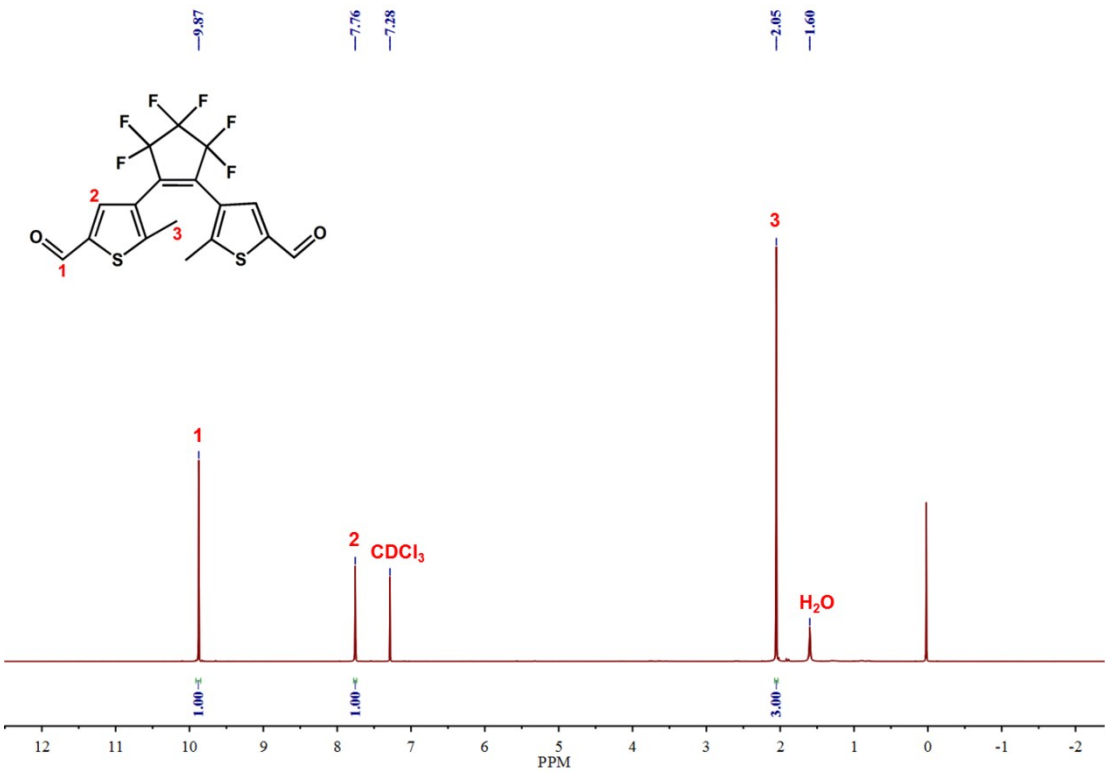

Fig. S1 ^{1}H NMR spectrum of DEA-CHO.

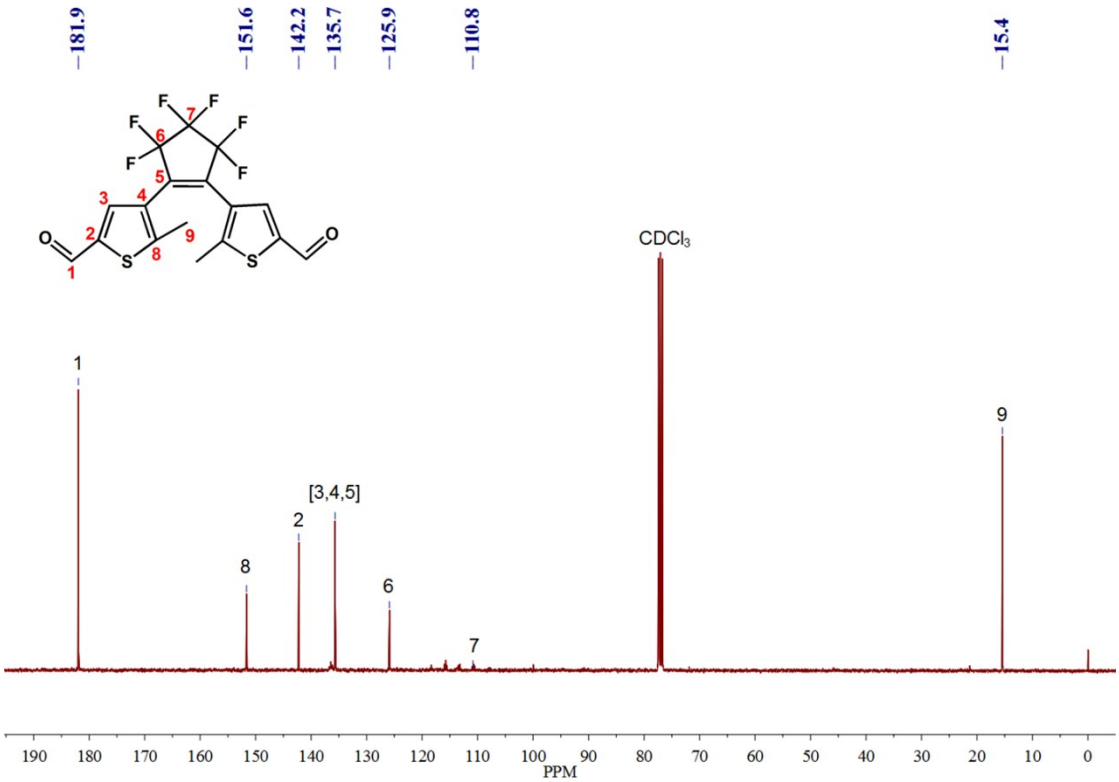

Fig. S2 ^{13}C NMR spectrum of DEA-CHO.

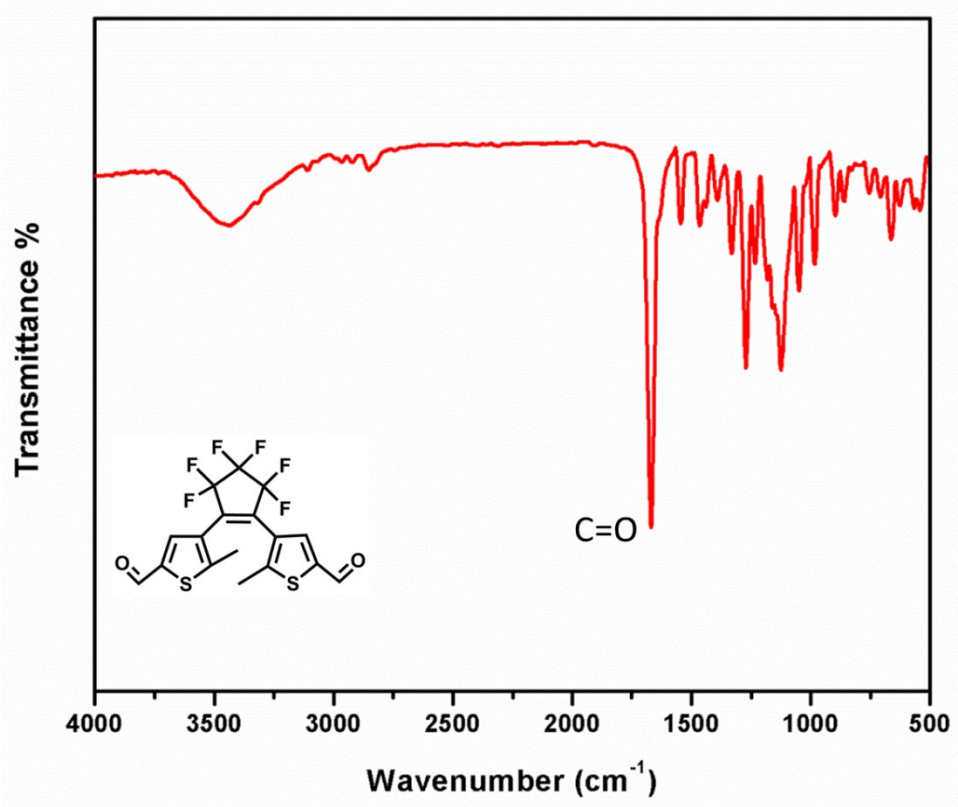

Fig. S3 FT-IR spectrum of DEA-CHO.

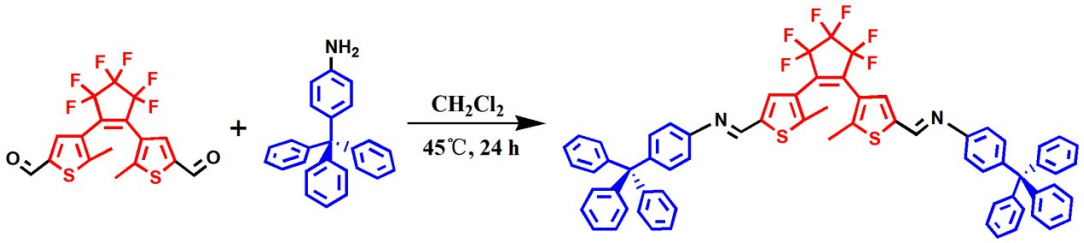

Fig. S4 Synthesis of MC.

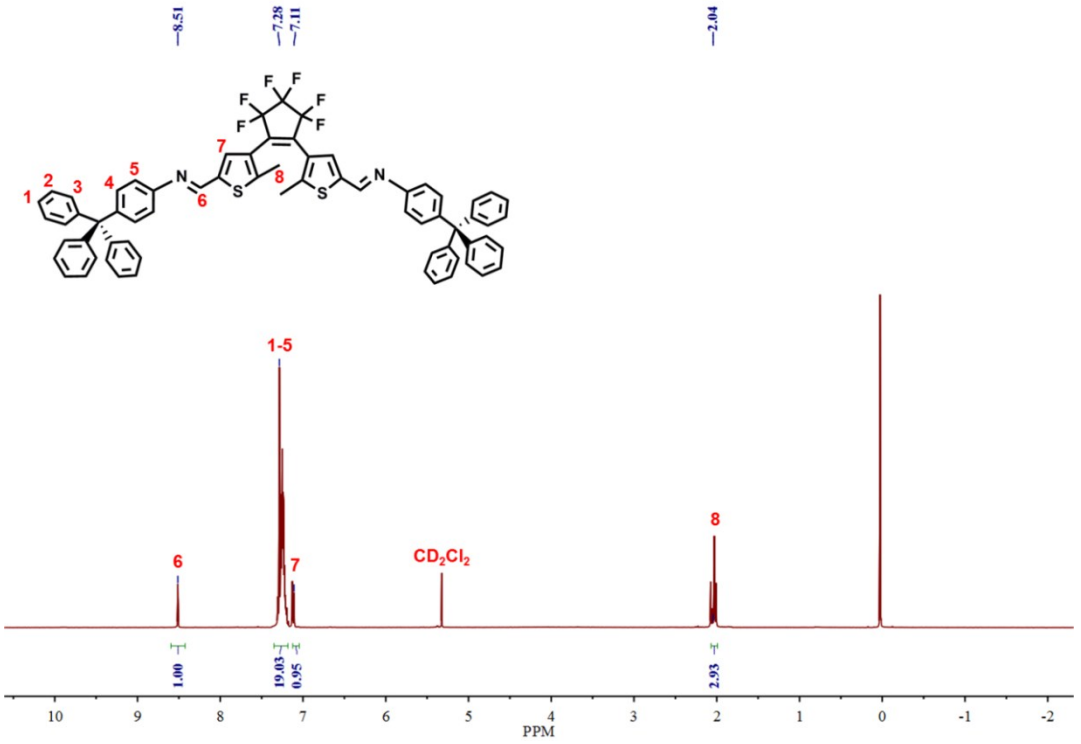

Fig. S5 ^{1}H NMR spectrum of MC.

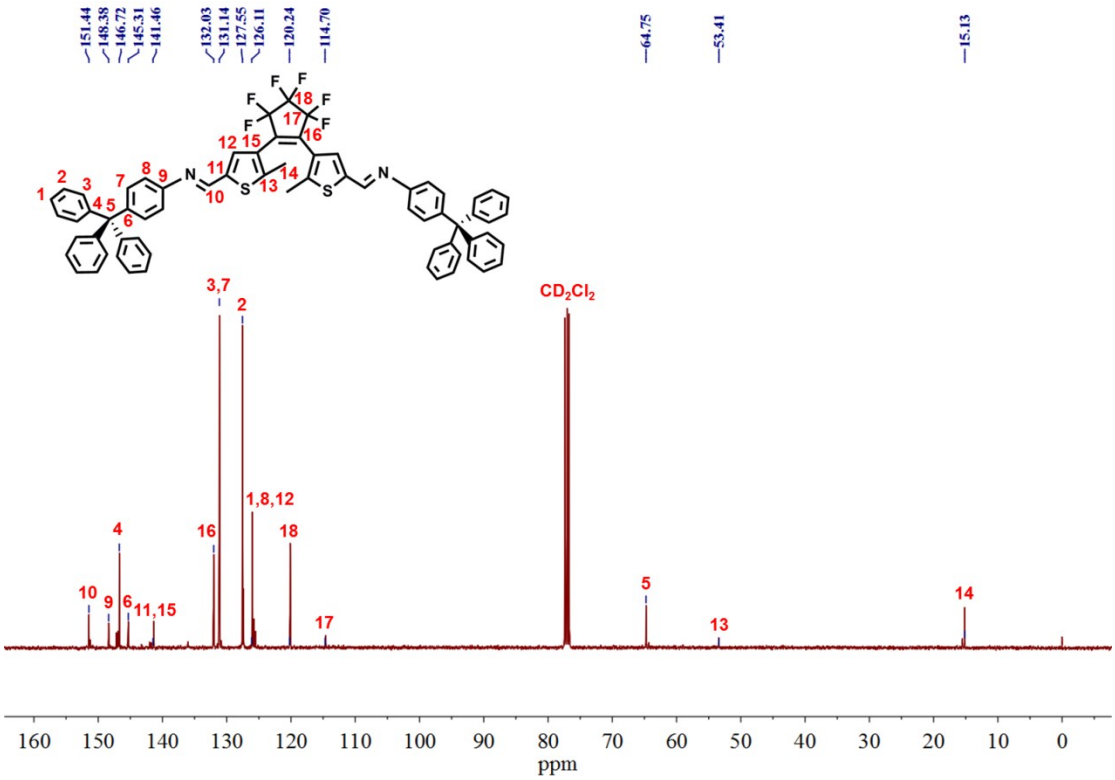

Fig. S6 ^{13}C NMR spectrum of MC.

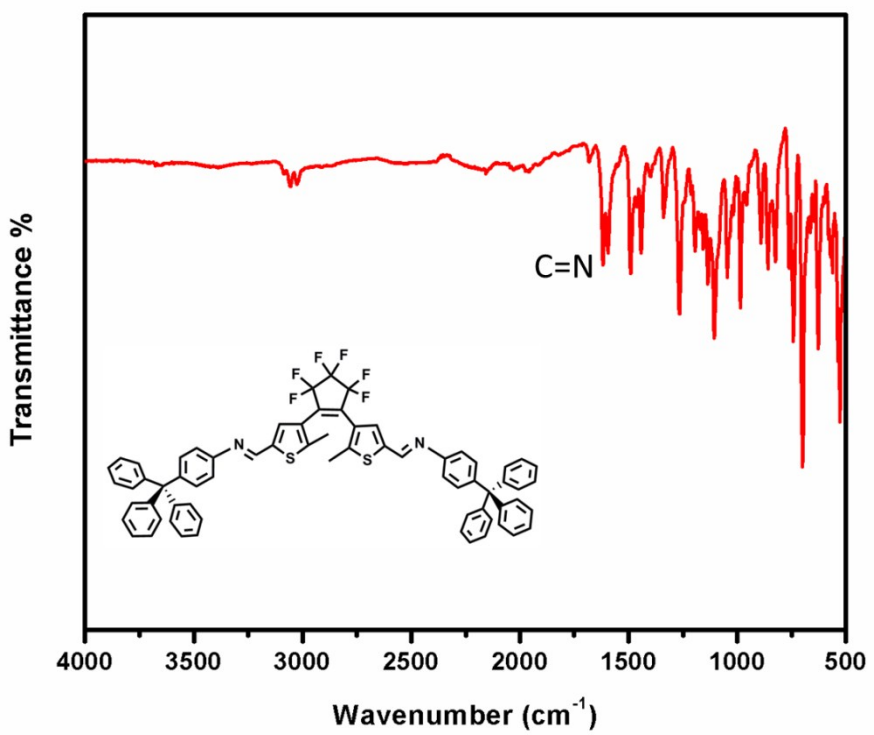

Fig. S7 FT-IR spectrum of MC.

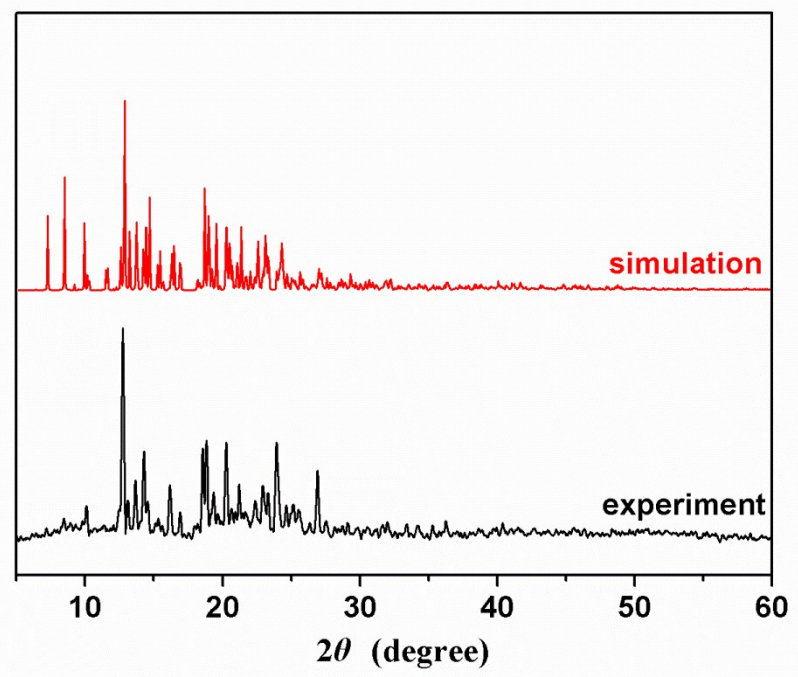

Fig. S8 Powder X-ray diffraction (PXRD) patterns of MC.

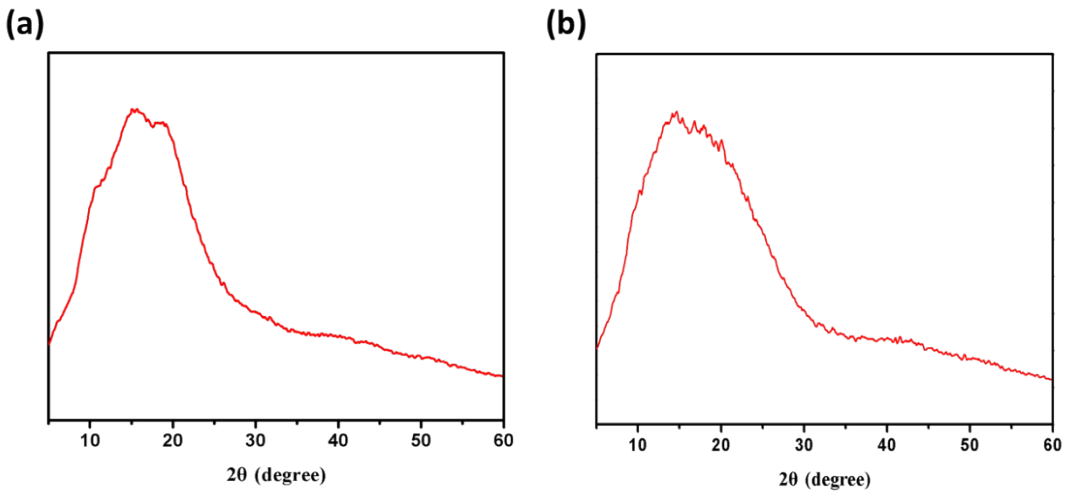

Fig. S9 PXRD patterns of (a) **DPP-1** and (b) **DPP-2**.

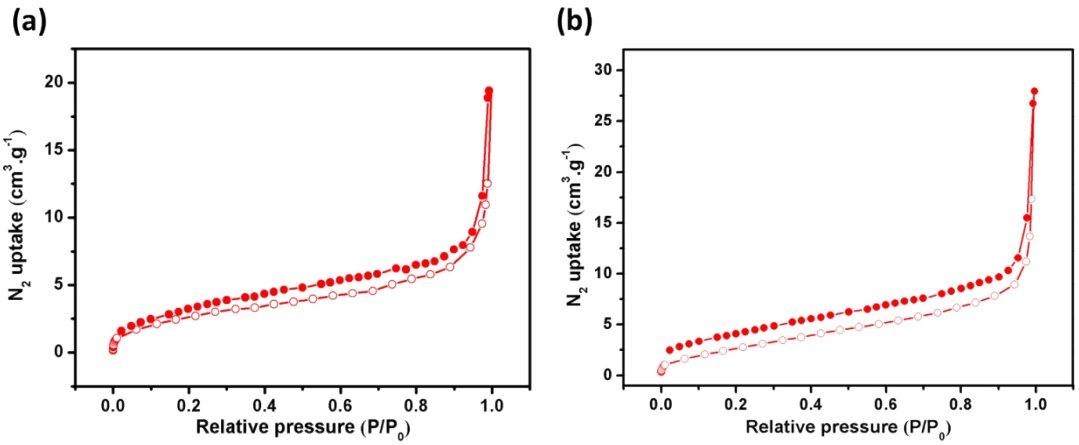

Fig. S10 N_2 adsorption/desorption isotherms of (a) **DPP-1** and (b) **DPP-2**.

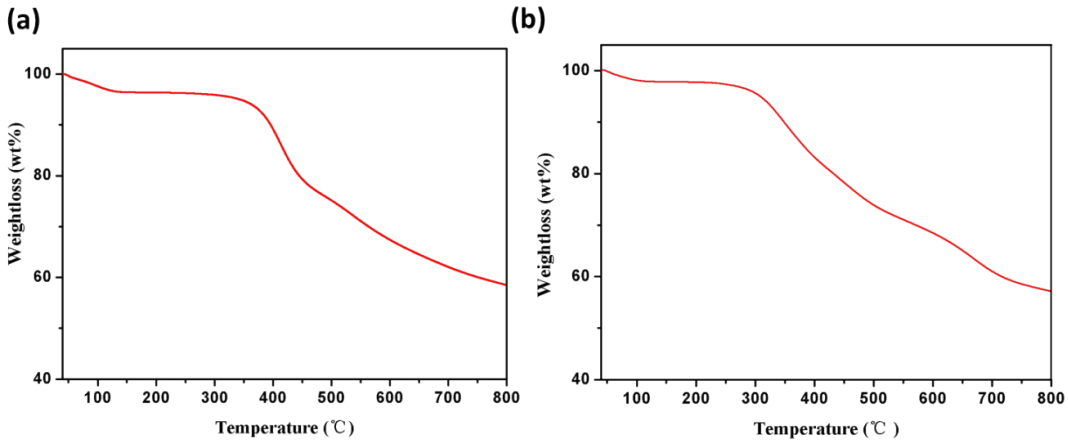

Fig. S11 TGA profiles of (a) **DPP-1** and (b) **DPP-2** under N_2 atmosphere.

Table S1 Screening of synthesis conditions of **DPP-1** and **DPP-2**.

Entry	Solvent combination and ratio	Catalyst	Temperature (°C)	Reaction time (days)	XRD results
1	Mesitylene/Dioxane=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
2	Mesitylene/EtOH=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
3	Mesitylene/MeOH=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
4	Mesitylene/o-DCB=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
5	o-DCB/BuOH=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
6	o-DCB/EtOH=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
7	DMAC/Mesitylene=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
8	DMAC/Dioxane=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous
9	DMAC/o-DCB=10:0~0:10	3~6 M HOAc or 0.06-0.15 mmol TsOH	120~180	5~7	amorphous

We have made a lot of efforts to test a serious of reaction conditions through controlling the solvents composition and ratio range, catalyst, reaction temperature and reaction time. Detailed conditions are as follows. The total amount of solvent was 2 mL, and solvent ratio included 10:0, 9:1, 7:1, 5:1, 3:1, 1:1, 1:3, 1:5, 1:7, 1:9, 0:10. For catalyst, the total amount of HOAc catalyst was 0.2 mL, and concentration included 3, 4, 5, 6 M; the amount of TsOH included 0.06, 0.09, 0.12, 0.15 mmol. Temperature included 120, 140, 160, 180 °C. Reaction time included 5, 6, 7 days. However, the experiment results were disappointing, and the products checked by the XRD all shown amorphous structure. The screening of the reaction conditions was based on whether the product could undergo photochromism and photochromic properties. For **DPP-1**, the optimum reaction conditions were mesitylene/dioxane = 5:1, 3 M HOAc, 120 °C for 5 days. For **DPP-2**, the optimum reaction conditions were o-DCB/EtOH = 1:3, 0.12 mmol TsOH, 120 °C for 5 days.

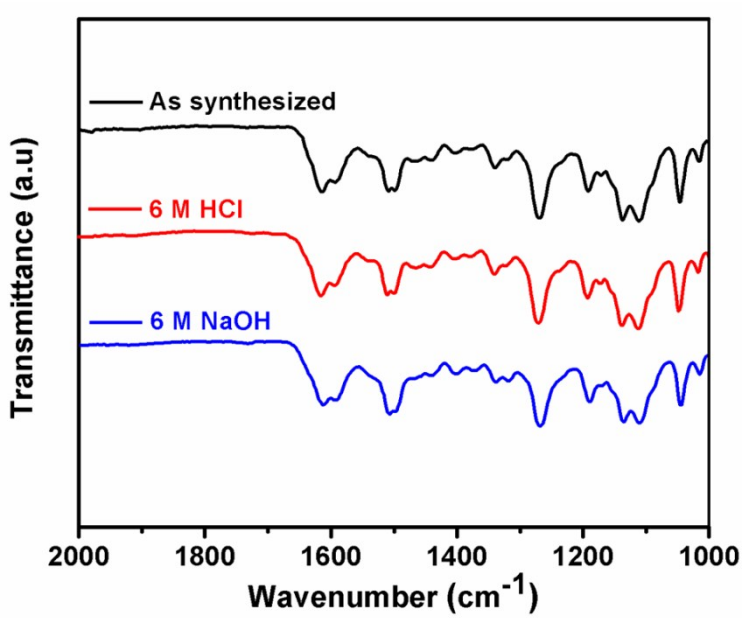

Fig. S12 FT-IR spectra of **DPP-1**: pristine (black); treated in 6 M HCl solution for 5 days (red); treated in 6 M NaOH solution for 5 days (blue).

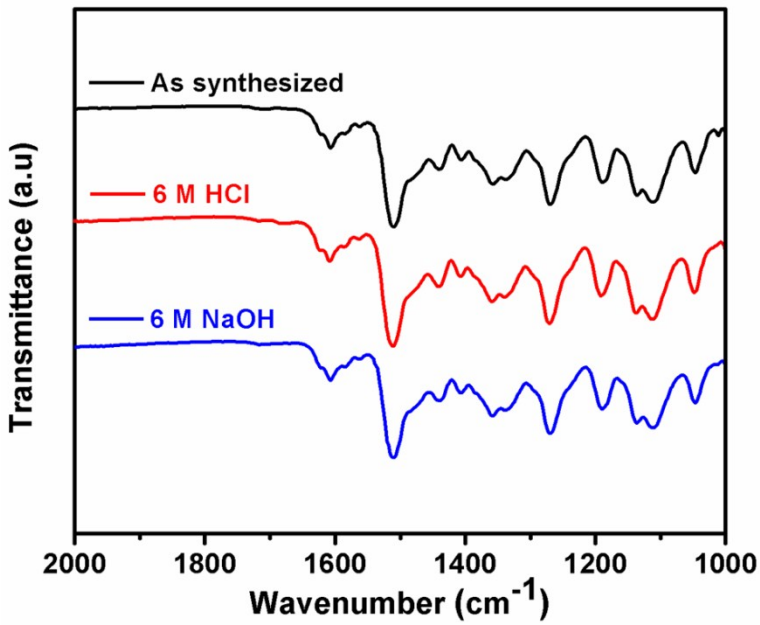

Fig. S13 FT-IR spectra of **DPP-2**: pristine (black); treated in 6 M HCl solution for 5 days (red); treated in 6 M NaOH solution for 5 days (blue).

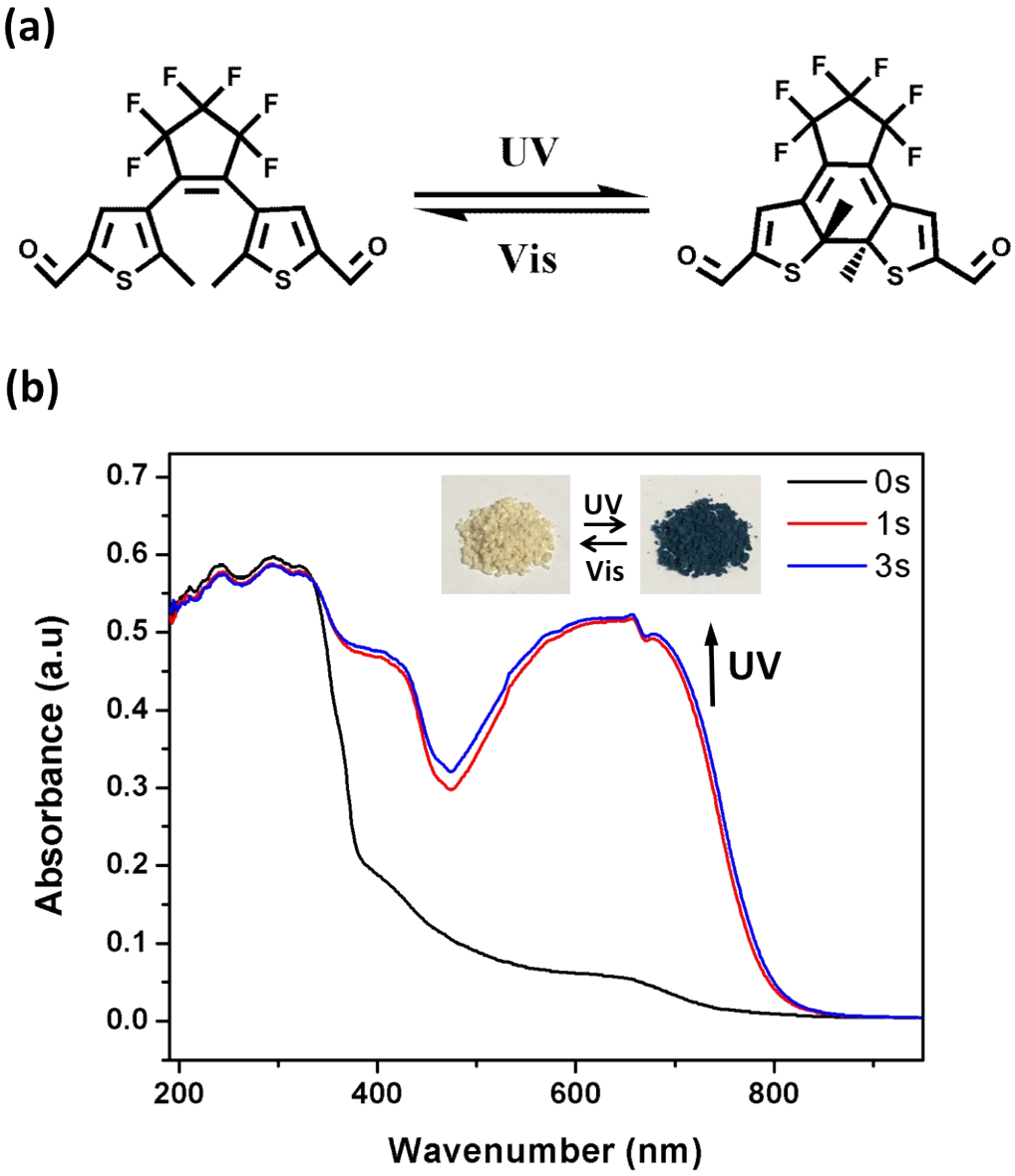

Fig. S14 (a) Molecular structures of the open and closed forms of DEA-CHO. (b) Time-dependent UV-vis-NIR absorption spectra of DEA-CHO upon irradiation with UV light (λ = 365 nm).

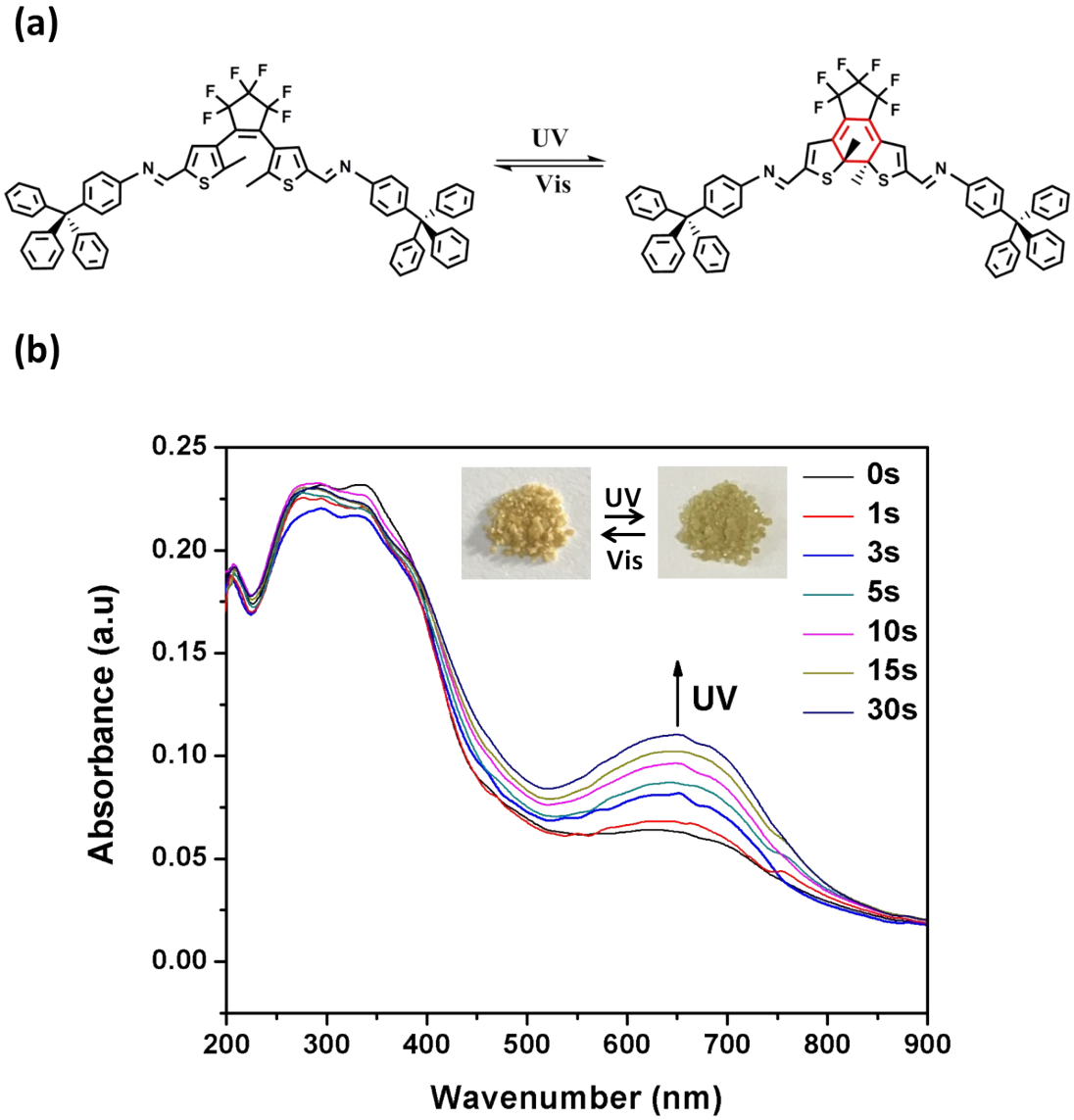

Fig. S15 (a) Molecular structures of the open and closed forms of MC. (b) Time-dependent UV-vis-NIR absorption spectra of MC upon irradiation with UV light (λ = 365 nm).

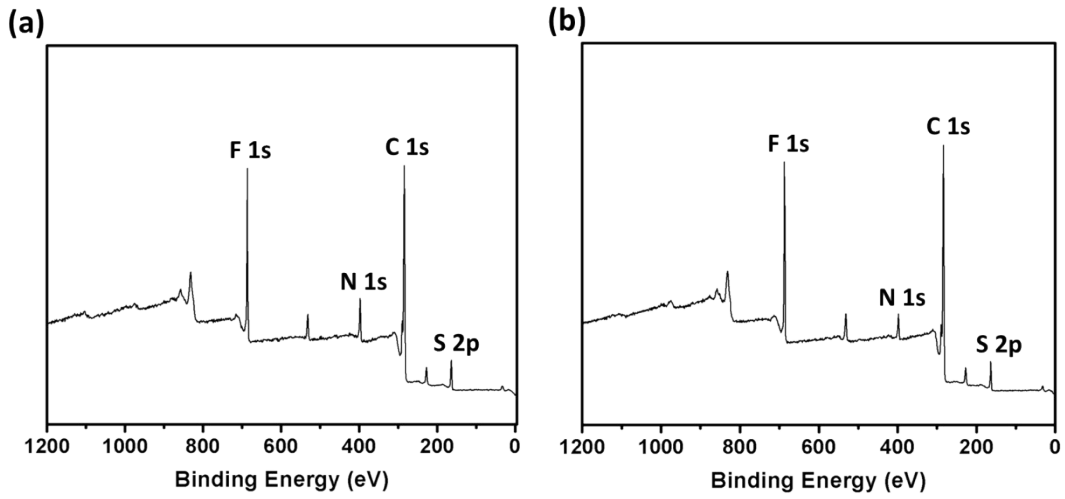

Fig. S16 (a) XPS survey spectrum of **DPP-1**. (b) XPS survey spectrum of **DPP-2**.

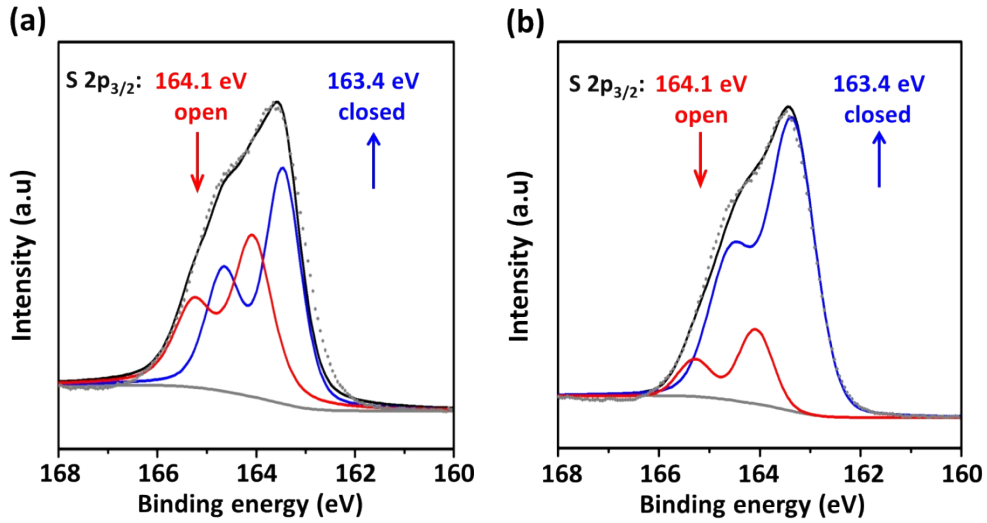

Fig. S17 S 2p XPS spectrum of **DPP-2** before (a) and after (b) UV irradiation at 365 nm for 5 min.

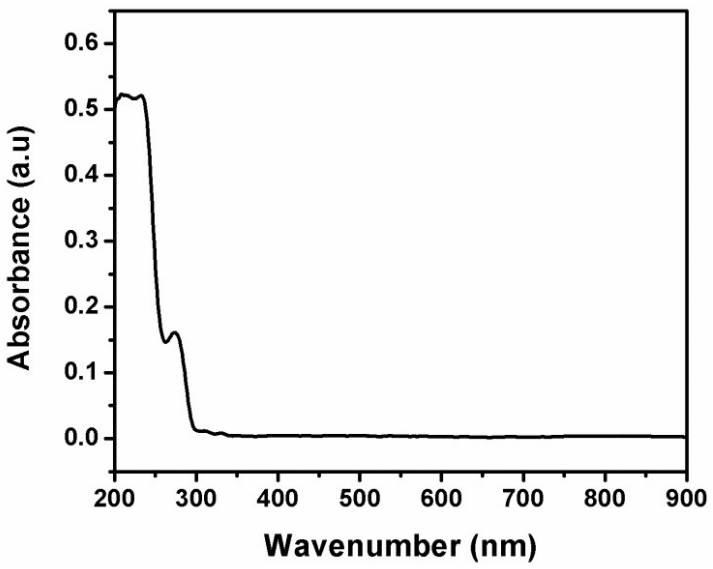

Fig. S18 UV-vis-NIR absorption spectrum of PMMA.

Table S2 Summary of crystallographic data for DEA-CHO and MC.

	DEA-CHO	MC
Formula	$C_{17}H_{10}F_6O_2S_2$	$C_{67}H_{48}C_{l0}F_6N_2S_2$ 0.5(C_4H_8O)
Fw	424.37	1095.24
T (K)	153	173
λ (Å)	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	*Pbcn*	*C2/c*
a (Å)	12.065(3)	39.4752(11)
b (Å)	8.649(2)	9.6754(3)
c (Å)	16.450(4)	28.3165(9)
α (°)	90	90
β (°)	90	99.622(3)
γ (°)	90	90
V (Å^3)	1716.6(7)	10663.0(6)
Z	4	8
D_{calc} (g/cm^3)	1.642	1.364
μ (mm^{-1})	0.382	0.169
F (000)	856	4560
θ (°)	2.5-25.5	2.3-27.0
index ranges	-10≤ h ≤14 -10≤ k ≤10 -19≤ l ≤12	-50≤ h ≤47 -12≤ k ≤12 -34≤ l ≤36
reflections collected	7129	53316
GOF (F^2)	1.034	1.079
R_1[a],wR_2[b] (I>2σ(I))	0.0352, 0.0720	0.0531, 0.1526
R_1[a],wR_2[b] (all data)	0.0620, 0.0823	0.0708, 0.1623

$R_1{}^a = \Sigma||F_o| - |F_c||/\Sigma F_o|$. $wR_2{}^b = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)]^{1/2}$

Table S3 Selected bond lengths [Å] and angles [°] for DEA-CHO and MC.

DEA-CHO			
S1-C5	1.721(3)	C4-C7	1.468(3)
S1-C8	1.717(2)	C4-C4_a	1.348(4)
F1-C1	1.341(9)	C5-C6	1.365(3)
F2-C1	1.357(9)	C5-C9	1.453(3)
F3-C2	1.348(7)	C6-C7	1.418(3)
F4-C2	1.339(10)	C7-C8	1.383(3)
F5-C3	1.358(9)	C8-C10	1.496(3)
F6-C3	1.356(8)	C1-C4_a	1.527(7)
O1-C9	1.211(3)	C2-C3	1.533(9)
C1-C2	1.536(9)	C3-C4	1.482(7)
MC			
S1-C6	1.721(2)	C1-C2	1.342(3)
S1-C9	1.715(2)	C2-C3	1.501(3)
S2-C37	1.720(2)	C3-C4	1.541(4)
S2-C40	1.717(2)	C4-C5	1.531(4)
F1-C3	1.348(4)	C6-C7	1.363(3)
F2-C3	1.351(4)	C7-C8	1.431(3)
F3-C4	1.332(5)	C8-C9	1.370(3)
F4-C4	1.338(4)	C11-C12	1.386(3)
F5-C5	1.349(4)	C12-C13	1.384(3)
F6-C5	1.370(4)	C13-C14	1.401(3)
N1-C10	1.263(3)	C14-C17	1.549(2)
N1-C11	1.425(2)	C17-C24	1.549(2)

Symmetry transformations used to generate equivalent atoms for DEA-CHO: a = 1-x, y, 3/2-z.