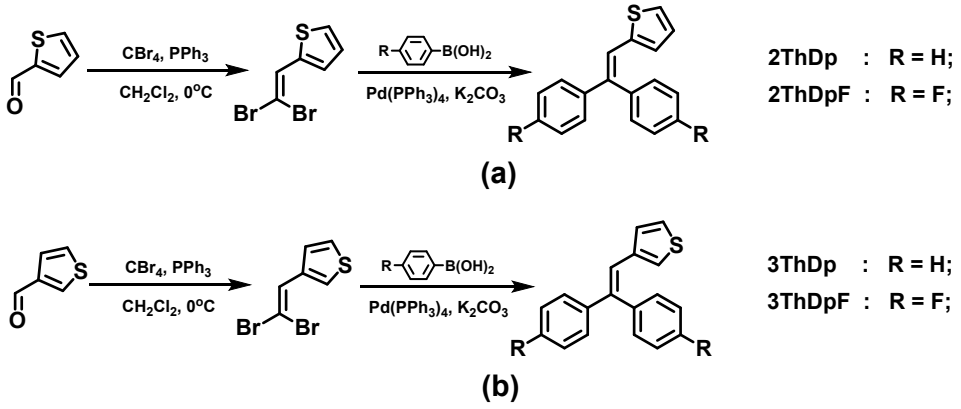
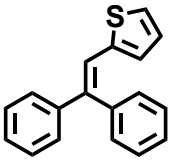
Supporting Information

1 Synthetic details

The details of the synthetic procedures for 2ThDp, 2ThDpF, 3ThDp and 3ThDpF are listed in Scheme S1. Thiophene-2-carbaldehyde, thiophene-3-carbaldehyde, carbon tetrabromide and triphenylphosphine were purchased from Sigma–Aldrich Chemical Co.. Phenylboronic acid, (4-fluorophenyl)boronic acid, $Pd(PPh_3)_4$, and K_2CO_3 were purchased from Aladdin Chemical Co.. All chemicals were of analytical grade and used as received. Compound 2-(2,2-dibromovinyl)thiophene and 3-(2,2-dibromovinyl)thiophene was synthesized according to previous reports.[1] All the final compounds were characterized by ^1H NMR spectroscopy, high-resolution EI mass spectroscopy and elemental analysis. All solvents were distilled and purified according to standard procedures before use.

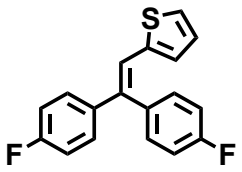


Scheme S1 (a) Synthetic routes for compounds 2ThDp and 2ThDpF; (b) Synthetic routes for compounds 3ThDp and 3ThDpF.

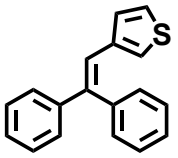


2-(2,2-diphenylvinyl)thiophene (2ThDp) To a mixture of 2-(2,2-dibromovinyl)thiophene (1.34 g, 5.0 mmol) and phenylboronic acid (1.83 g 15.0 mmol) in degassed THF (30 ml) was added 2M K_2CO_3 aqueous solution (10 ml). After degassing for 20 minutes, $Pd(PPh_3)_4$ (100mg, 0.10 mmol) was added to the mixture. The resulting mixture was stirred at reflux for 24 hours under an argon atmosphere.

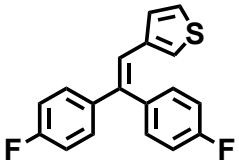
After cooling down to room temperature, the mixture was filtered and the filtrate was purified by column chromatography with hexane as eluent. The residue was purified by recrystallization by CH_2Cl_2-hexane mixed solvent system. Colorless oil was achieved. Yield: 0.76 g (58 %). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ = 7.43–7.49 (m, 3H), 7.28–7.34 (m, 7H), 7.22–7.24 (m, 1H), 7.03–7.04 (m, 1H), 6.91–6.92 (m, 1H), 6.86–6.87 (m, 1H); High solution EI–MS: m/z 262.0809 $[M]^+$; calcd for $C_{18}H_{14}S$: 262.0816. Elemental analyses (%) calcd for $C_{18}H_{14}S$: C 82.40, H 5.38; found: C 82.12, H 5.77.



2-(2,2-bis(4-fluorophenyl)vinyl)thiophene (2ThDpF) This compound was prepared according to the aforementioned procedure for 2ThDp except that phenylboronic acid (1.83 g 15.0 mmol) was replace with (4-fluorophenyl)boronic acid (2.10 g 15.0 mmol). A white solid was achieved. Yield: 1.15 g (77 %). ^{1}H NMR (500 MHz, deutered DMSO, 298 K): δ = 7.50 (s, 1H), 7.31–7.38 (m, 5H), 7.25–7.28 (m, 2H), 7.14–7.19 (m, 3H), 6.94–6.96 (m, 1H). High solution EI–MS: m/z found: 298.0620 $[M]^+$; calcd for $C_{18}H_{12}F_2S$: 298.0628. Elemental analyses (%) calcd for $C_{18}H_{12}F_2S$: C 72.46, H 4.05; found: C 72.12, H 4.32.



3-(2,2-diphenylvinyl)thiophene (3ThDp) This compound was prepared according to the aforementioned procedure for 2ThDp except that 2-(2,2-dibromovinyl)thiophene (1.34 g, 5.0 mmol) was replace with 3-(2,2-dibromovinyl)thiophene (1.34 g, 5.0 mmol). A white solid was achieved. Yield: 0.95 g (72 %). ^{1}H NMR (500 MHz, deutered DMSO, 298 K): δ = 7.42–7.49 (m, 3H), 7.26–7.35 (m, 6H), 7.18–7.21 (m, 3H), 7.13–7.14 (m, 1H), 6.32–6.33 (m, 1H); High solution EI–MS: m/z 262.0809 $[M]^+$; calcd for $C_{18}H_{14}S$: 262.0816. Elemental analyses (%) calcd for $C_{18}H_{14}S$: C 82.40, H 5.38; found: C 81.97, H 5.59.



3-(2,2-bis(4-fluorophenyl)vinyl)thiophene (3ThDpF) This compound was prepared according to the aforementioned procedure for 2ThDp except that 2-(2,2-dibromovinyl)thiophene (1.34 g, 5.0 mmol) and phenylboronic acid (1.83 g 15.0 mmol) were replace with 3-(2,2-dibromovinyl)thiophene (1.34 g, 5.0 mmol) and (4-fluorophenyl)boronic acid (2.10 g 15.0 mmol) respectively. Yield: 1.21 g (81 %). ^{1}H NMR (500 MHz, deutered DMSO, 298 K): δ = 7.29–7.34 (m, 5H), 7.20–7.24 (m, 2H), 7.16–7.19 (m, 4H), 6.35–6.36 (m, 1H); High solution EI–MS: m/z found: 298.0624 $[M]^{+}$; calcd for $C_{18}H_{12}F_2S$: 298.0628. Elemental analyses (%) calcd for $C_{18}H_{12}F_2S$: C 72.46, H 4.05; found: C 72.21, H 4.17.

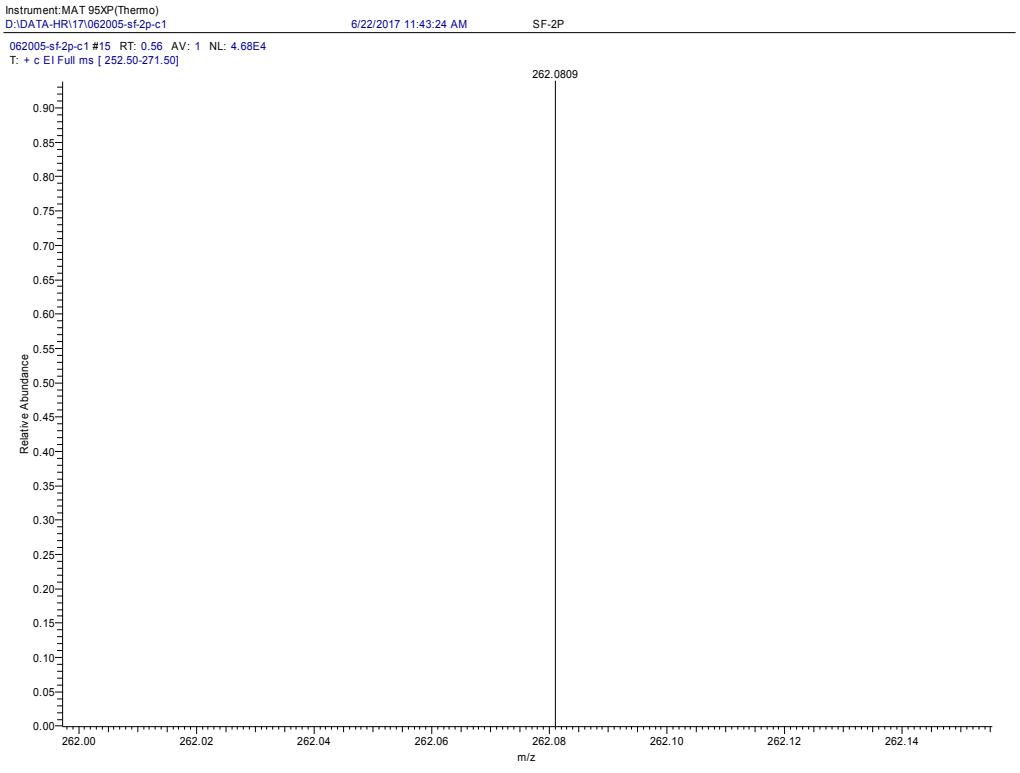


Figure S1 High Resolution EI mass spectrum of compound 2ThDp.

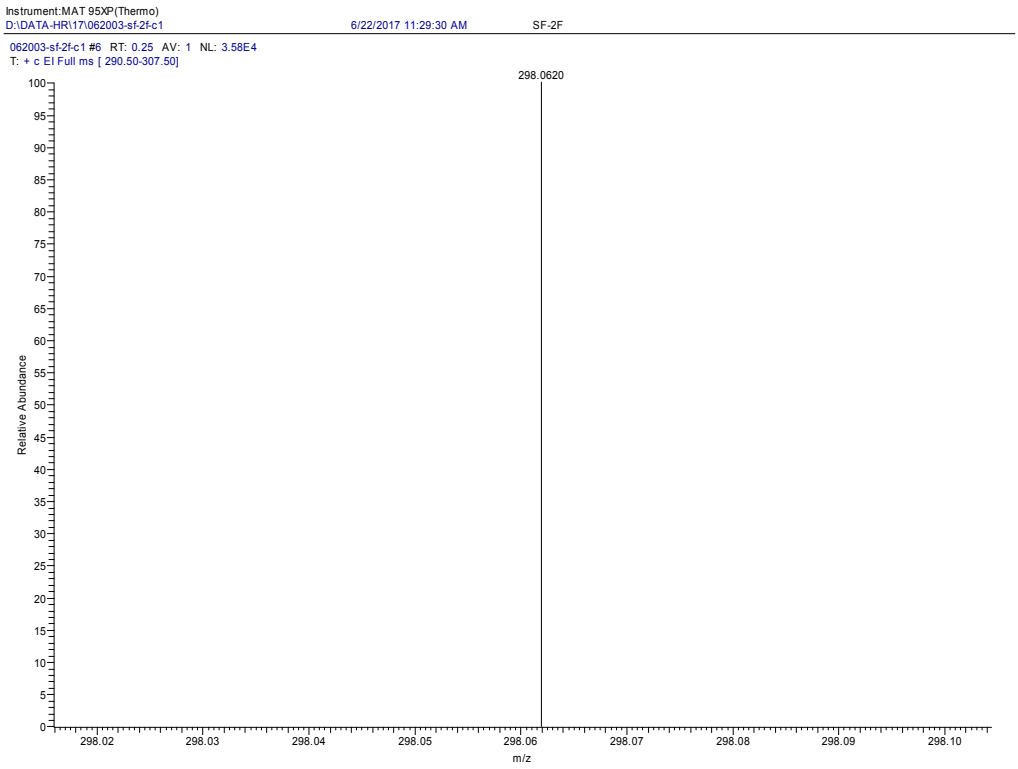


Figure S2 High Resolution EI mass spectrum of compound 2ThDpF.

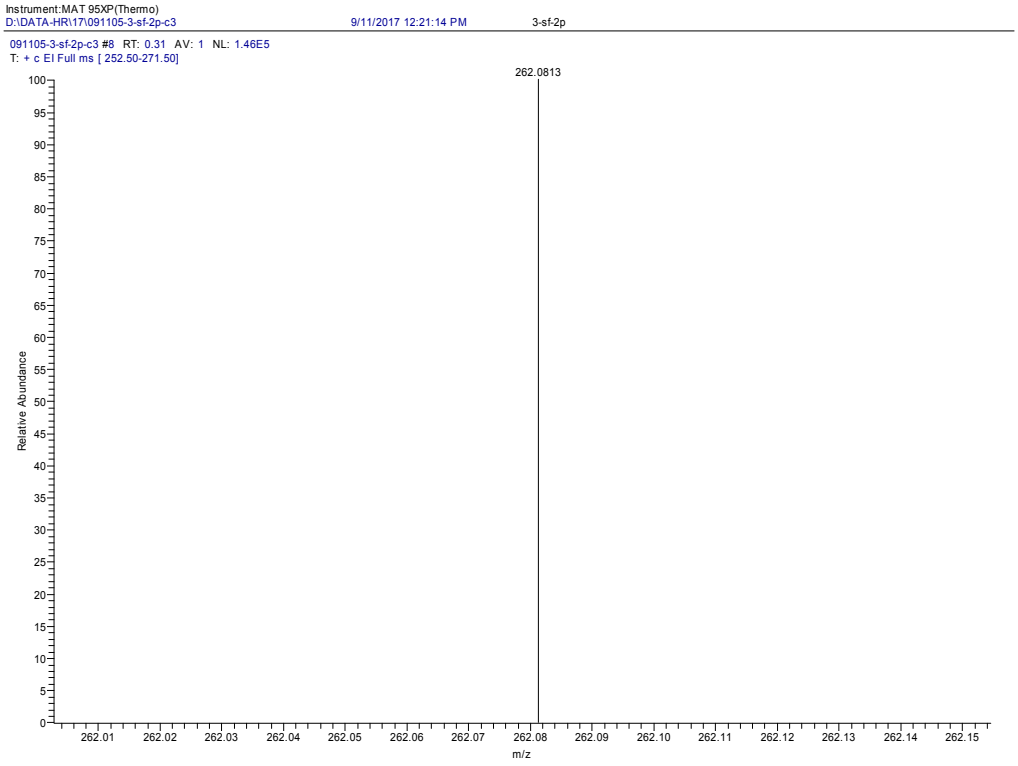


Figure S3 High Resolution EI mass spectrum of compound 3ThDp.

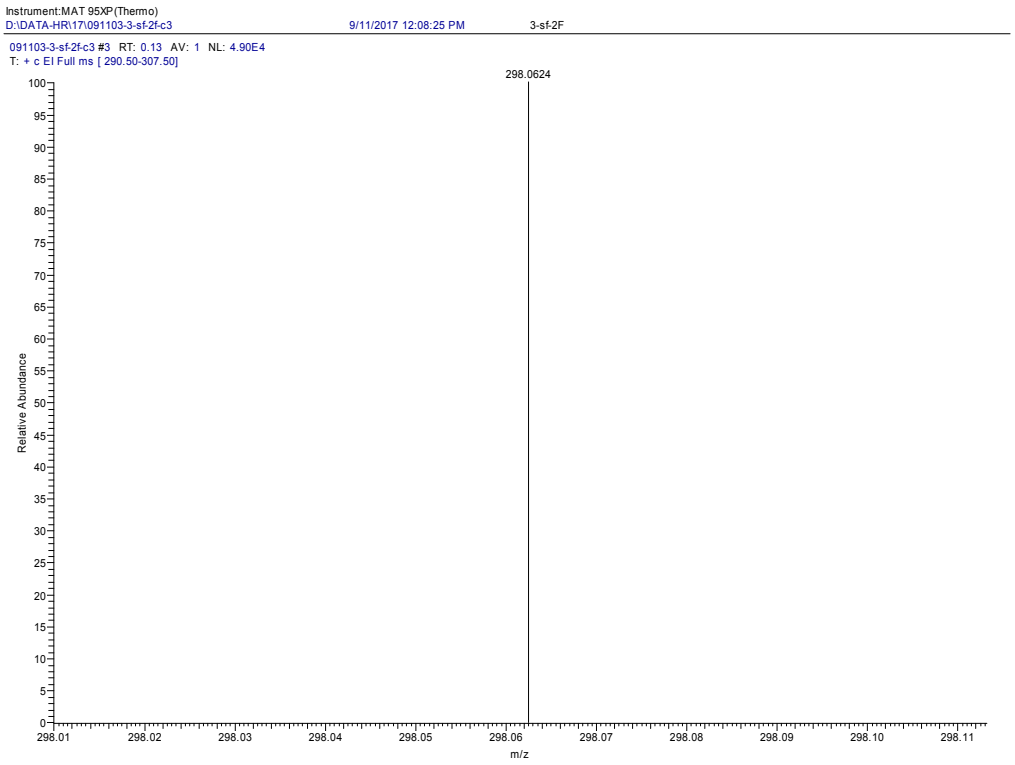


Figure S4 High Resolution EI mass spectrum of compound 3ThDpF.

2 Physical measurements and instrumentations

^{1}H NMR spectra were obtained using a Bruker Avance III 500 NMR (Nuclear Magnetic Resonance Spectrometer) with chemical shifts recorded relative to tetramethylsilane (TMS). ^{1}H–^{1}H COSY spectra were measured with a Bruker AVANCE 600 Nuclear Magnetic Resonance Spectrometer. Positive ion EI mass spectra were performed using a Thermo MAT95XP high resolution mass spectrometer. The elemental analysis was performed using a Vario EL analyzer. Single-crystal X-ray data for 3ThDpF was determined on an Oxford Diffraction Germini S Ultra X-ray Single Crystal Diffractometer using a (Cu) X-ray source. UV-vis reflectance spectra were recorded using an Ocean Optic Maya2000PRO spectrometer with Ocean Optic reflection probes R600-125F. Steady state fluorescence studies were conducted using a Horiba Scientific Fluorolog-3 spectrofluorometer.

3 Photophysical data and spectra

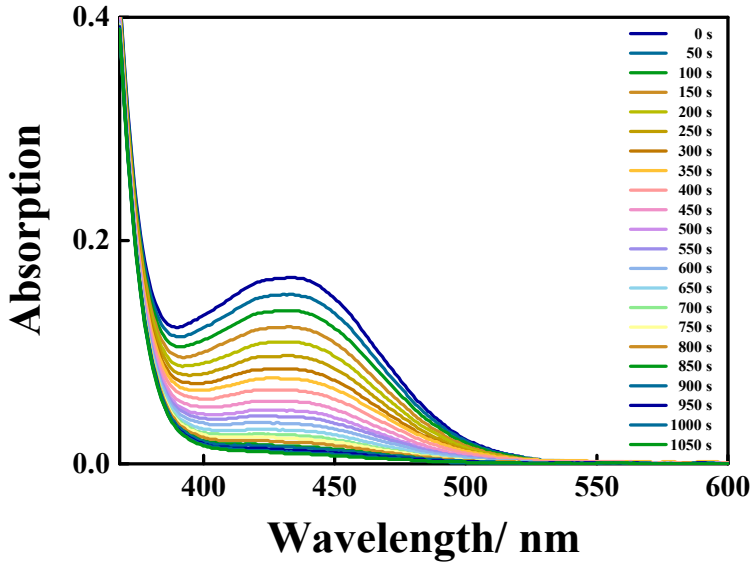


Figure S5 Time-dependent UV-vis absorption spectra of 2ThDpF during the photochromic bleaching process (in degassed THF solution, with concentration of 1.0×10^{-3} M).

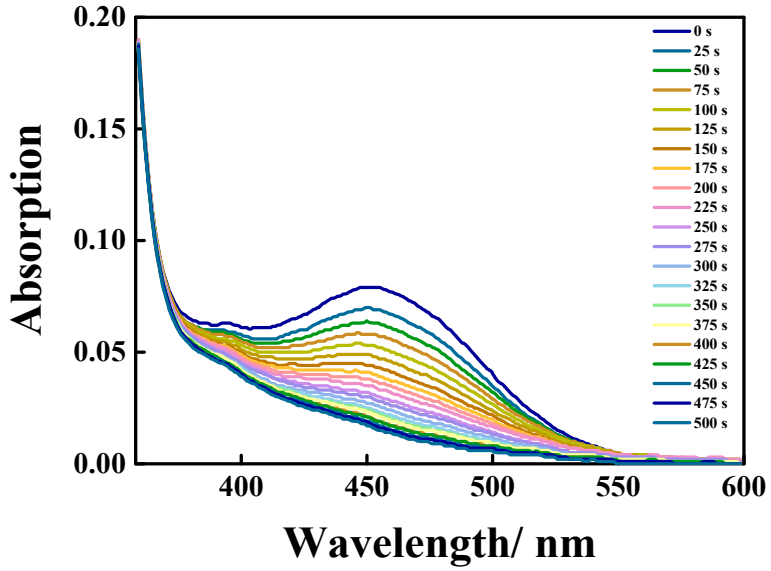


Figure S6 Time-dependent UV-vis absorption spectra of 3ThDpF during the photochromic bleaching process (in degassed THF solution, with concentration of 1.0×10^{-3} M).

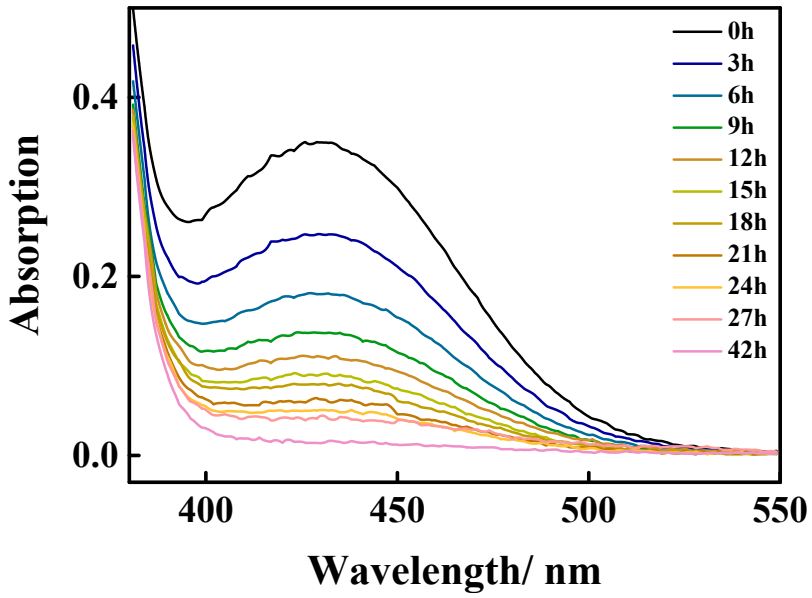


Figure S7 Time-dependent UV-vis absorption spectra of ring-closure state of 2ThDpF in dark at 303 K (in degassed THF solution, with concentration of 1.0×10^{-3} M).

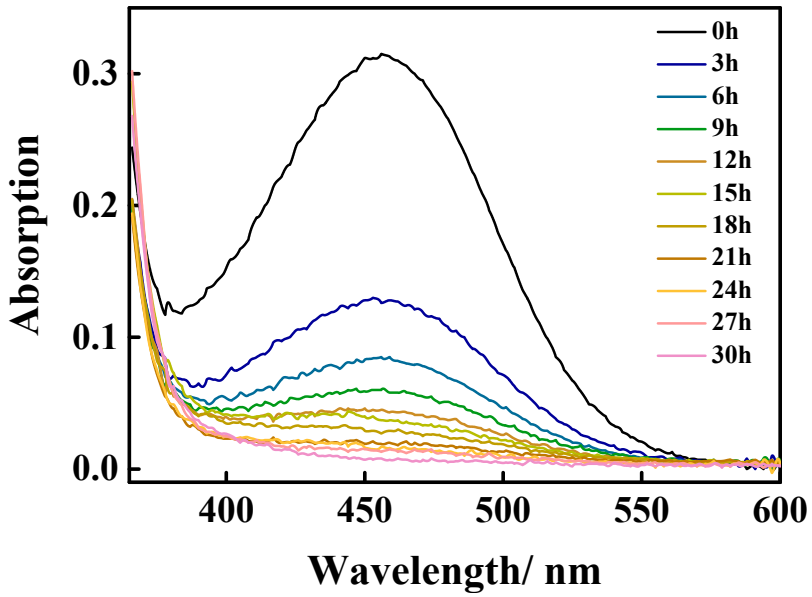


Figure S8 Time-dependent UV-vis absorption spectra of ring-closure state of 3ThDpF in dark at 303 K (in degassed THF solution, with concentration of 1.0×10^{-3} M).

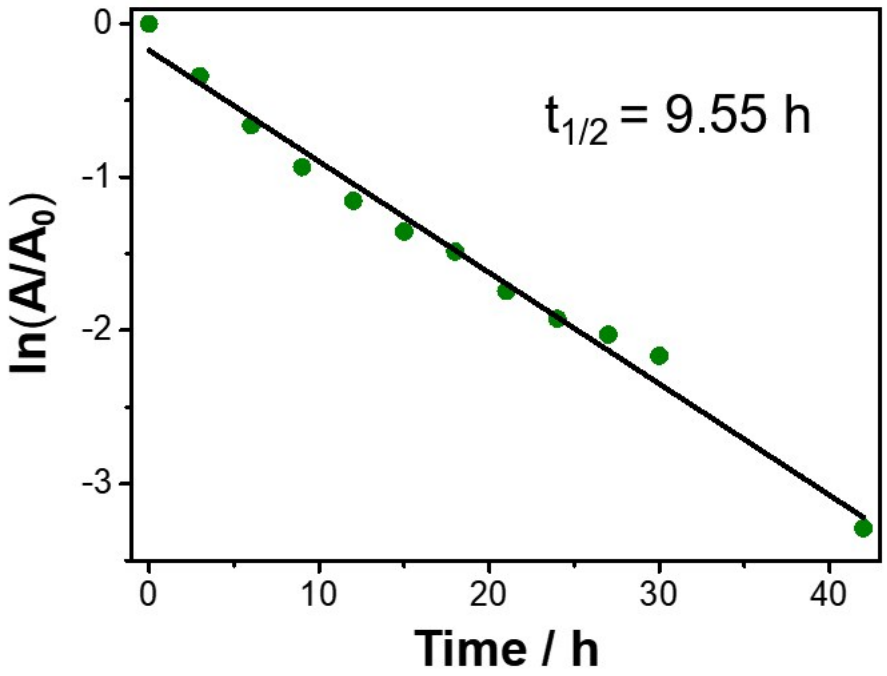


Figure S9 Plot of $\ln(A/A_0)$ versus time for the absorbance decay of 2ThDpF at 430 nm at 303 K in degassed in degassed CH_2Cl_2 solution with concentration of 1.0×10^{-3} M; soild lines represent the theoretical linear fits.

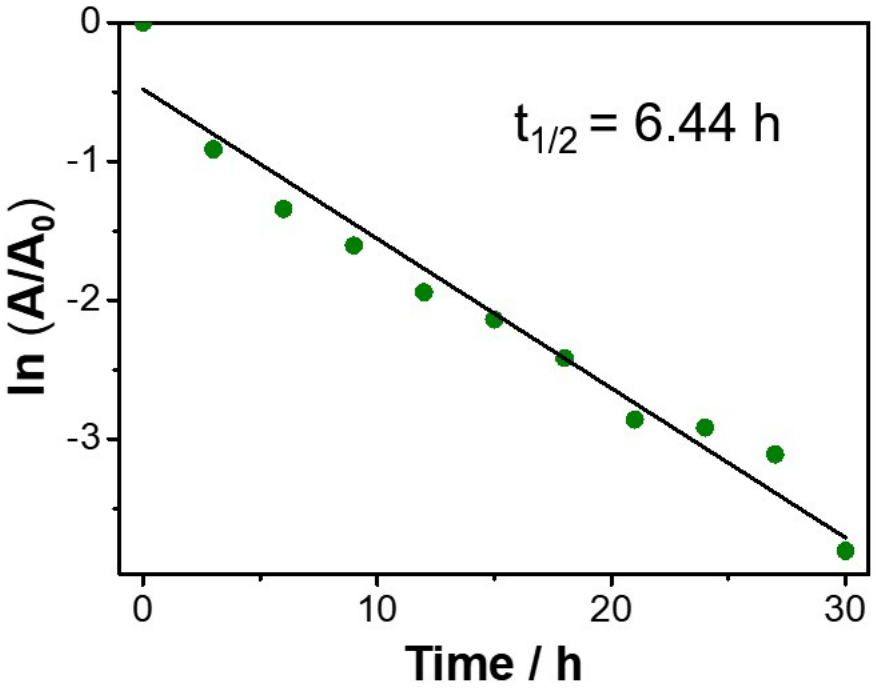


Figure S10 Plot of $\ln(A/A_0)$ versus time for the absorbance decay of 3ThDpF at 457 nm at 303 K in degassed in degassed CH_2Cl_2 solution with concentration of 1.0×10^{-3}

M; soild lines represent the theoretical linear fits.

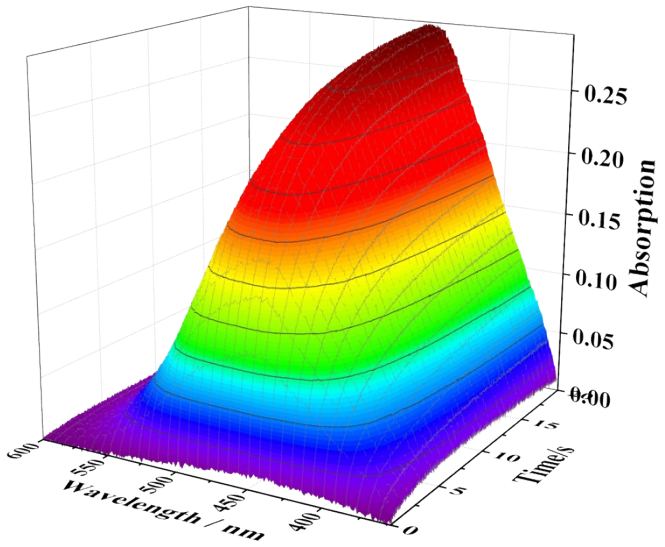


Figure S11 Time dependent UV-vis reflectance spectra of compound 3ThDpF in solid state during the photochromic process.

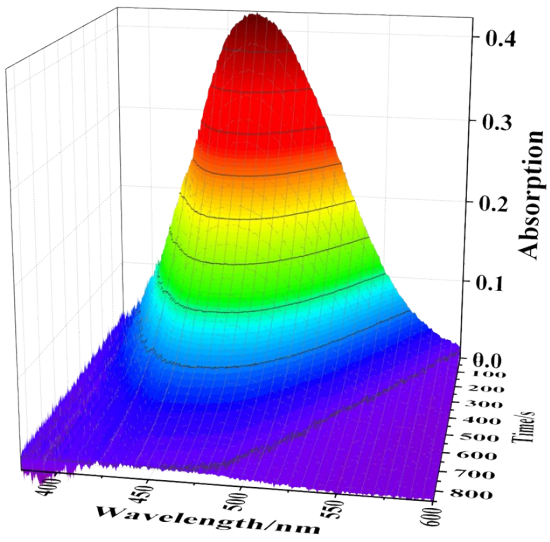


Figure S12 Time dependent UV-vis reflectance spectra of compound 3ThDpF in solid state during the photochromic bleaching process.

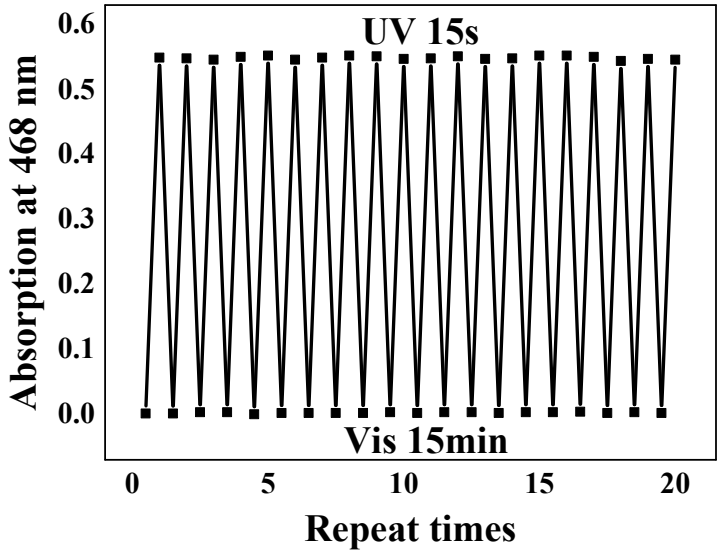


Figure S13 Recycling of the photochromic process of compound 3ThDpF in solid state as a function of exposure to UV-light (365 nm) and white-light for 15 seconds and 15 minutes, respectively.

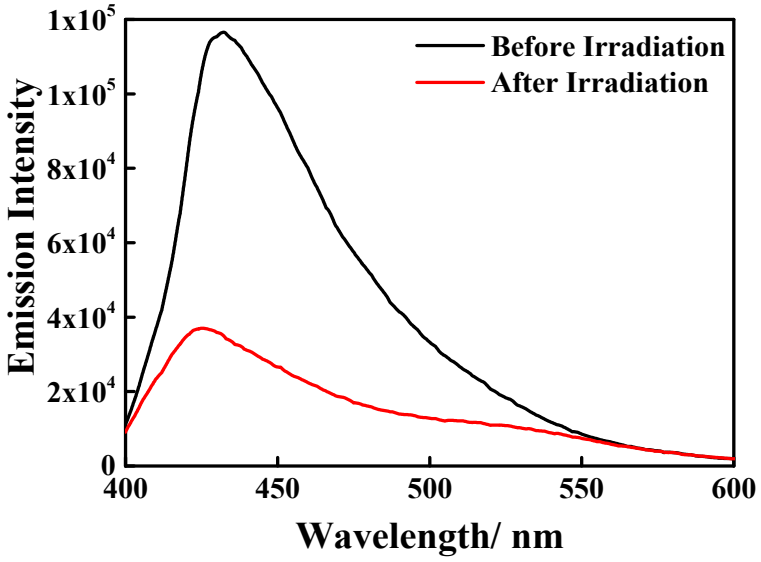


Figure S14 The emission spectra for 2ThDpF in solid state before and after UV-light irradiation.

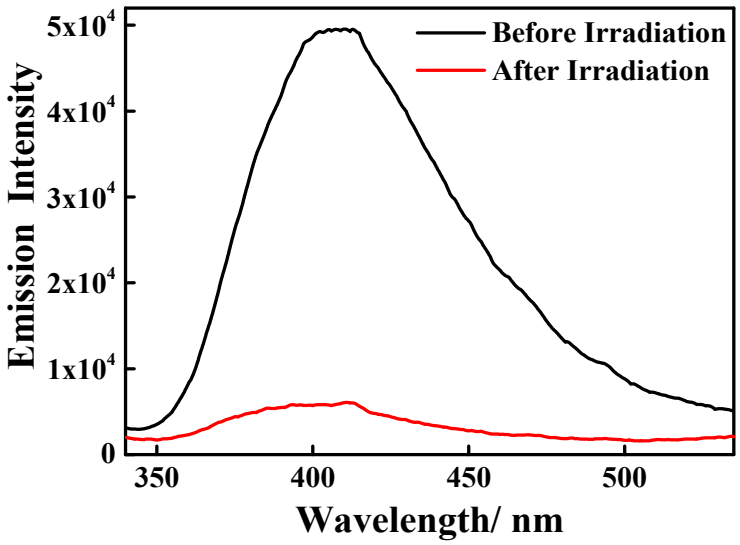


Figure S15 The emission spectra for 3ThDpF in solid state before and after UV-light irradiation.

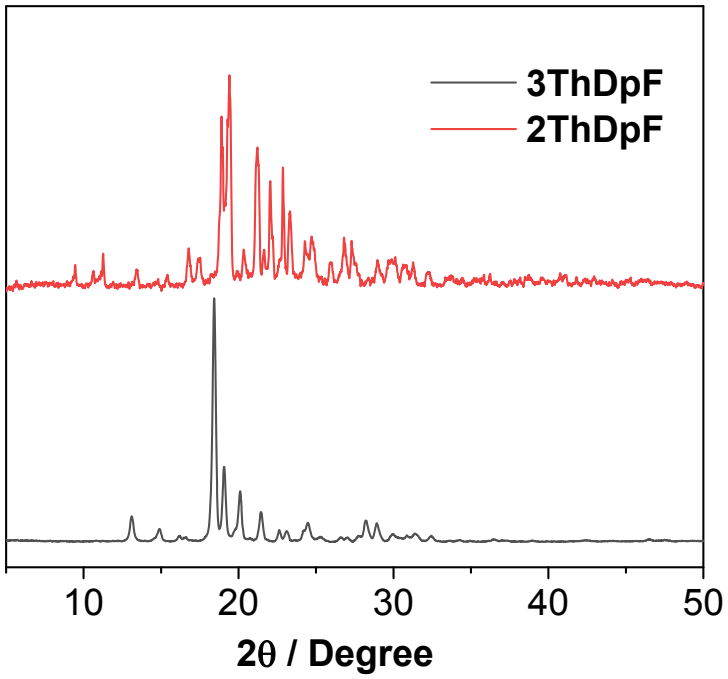


Figure S16 pXRD spectra of 2ThDpF and 3ThDpF powders.

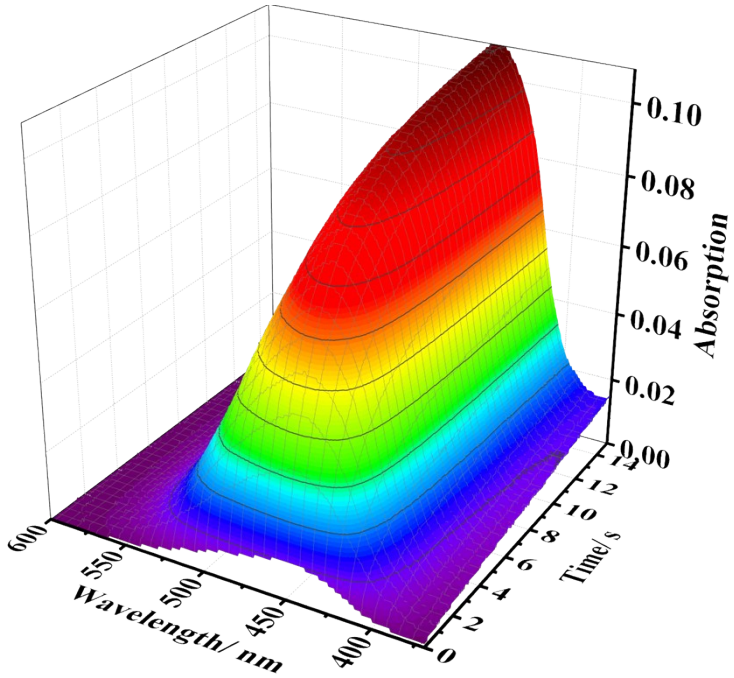


Figure S17 Time dependent UV-vis reflectance spectra of 2ThDpF in single-crystal state during the photochromic process.

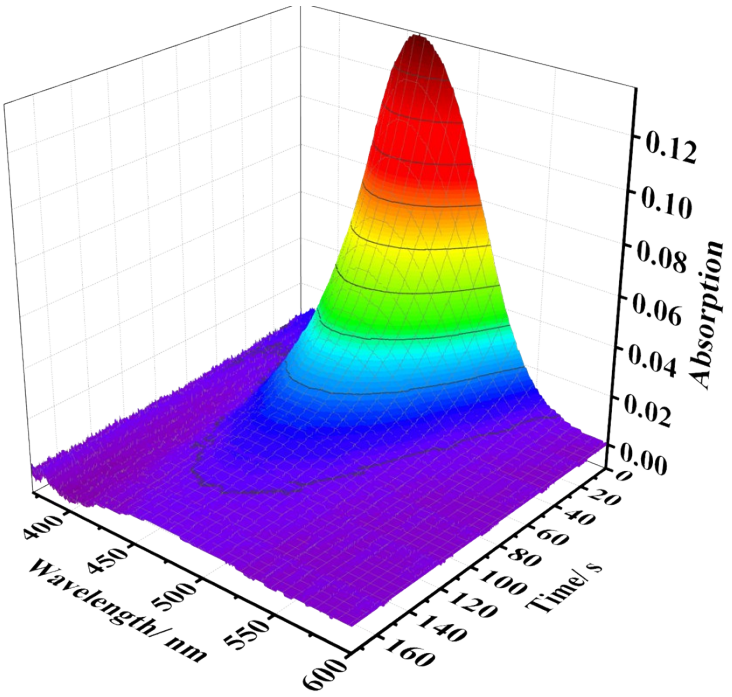


Figure S18 Time dependent UV-vis reflectance spectra of 2ThDpF in single-crystal state during the photochromic bleaching process.

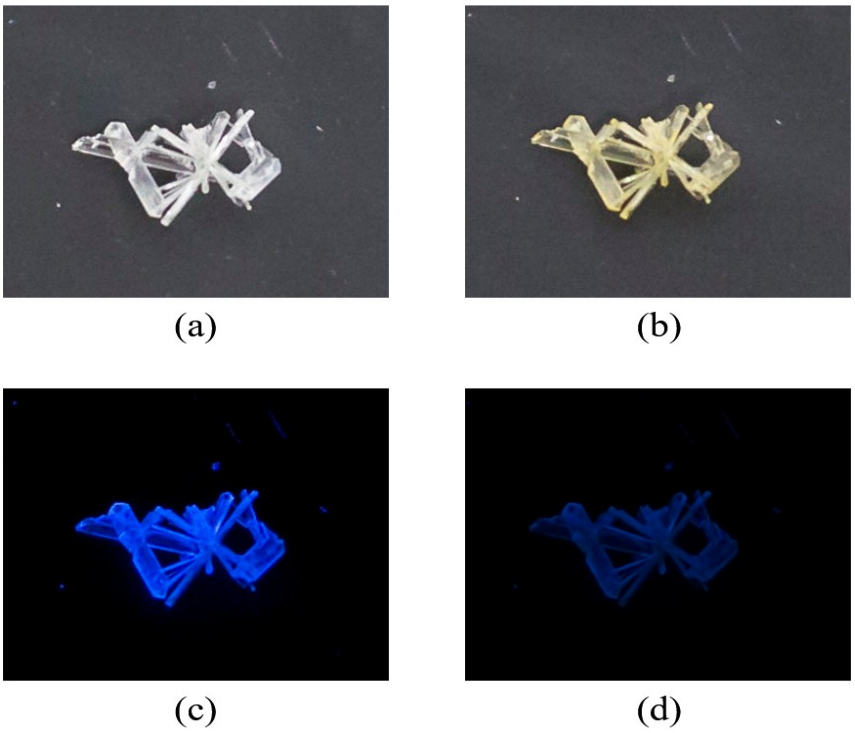


Figure S19 Photos of 2ThDpF: (a) Before UV-irradiated observed under daylight; (b) After UV-irradiated observed under daylight; (c) Before UV-irradiated observed under Uv-light; (d) After UV-irradiated observed under Uv-light.

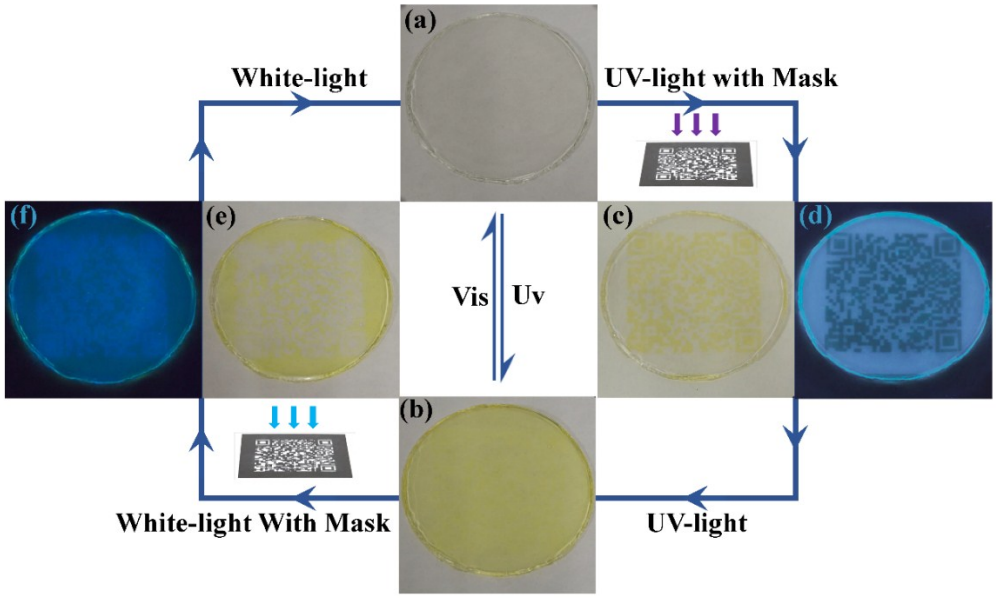


Figure S20 Illustration of the photopatterning processes for polymer films containing 2ThDpF: (a) Before UV-irradiated; (b) After UV-irradiated; (c) After UV-irradiated with mask (observed under daylight); (d) After UV-irradiated with mask (observed under UV-light); (e) The UV-irradiated film further irradiated with white-light with mask (observed under daylight); (f) The UV-irradiated film further irradiated with white-light with mask (observed under UV-light).

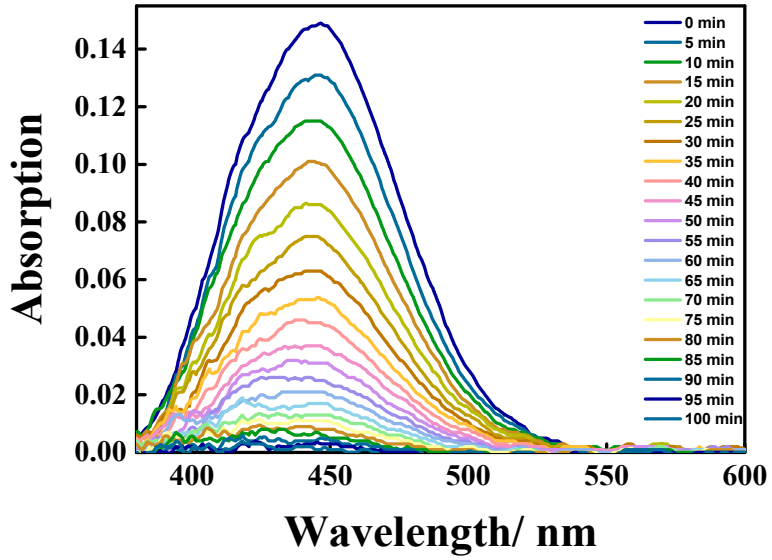


Figure S21 Time dependent UV-vis reflectance spectra of polymer films containing 5 wt% 2ThDpF during the photochromic bleaching process.

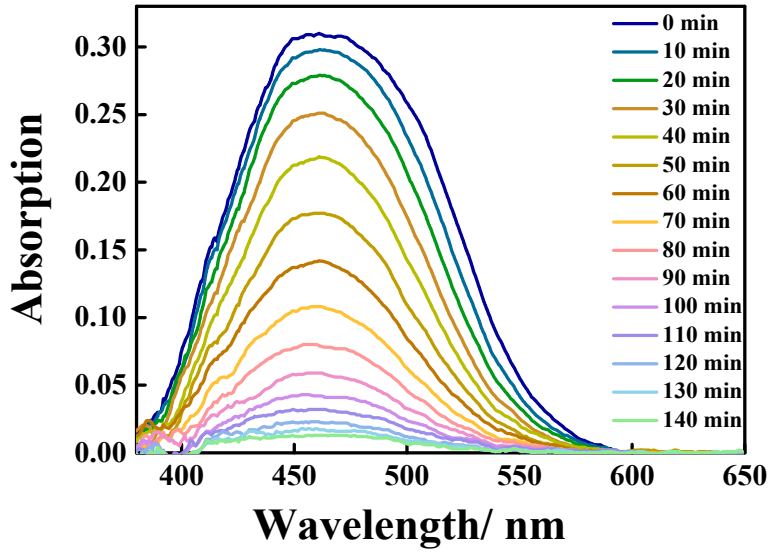


Figure S22 Time dependent UV-vis reflectance spectra of polymer films containing 5 wt% 3ThDpF during the photochromic bleaching process.

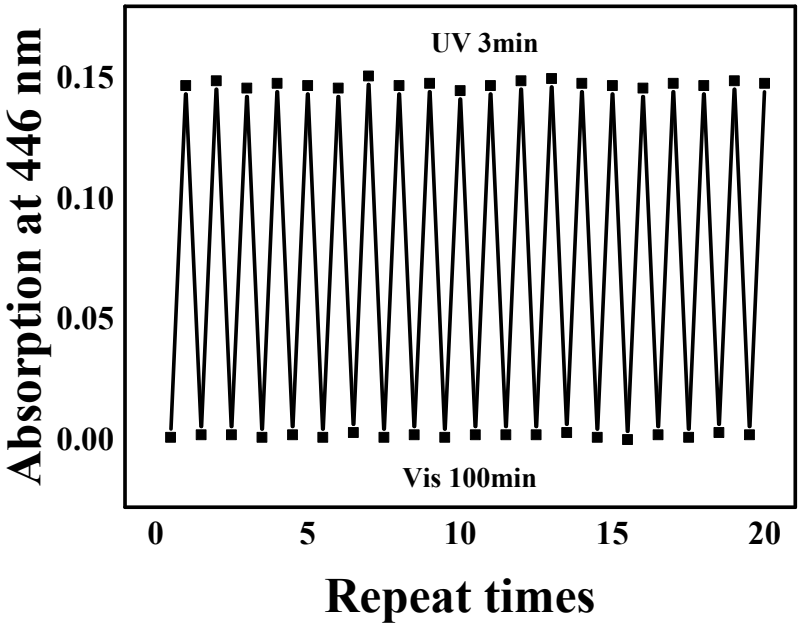


Figure S23 Recycling of the photochromic process of polymer films containing 5 wt% 2ThDpF as a function of exposure to UV-light (365 nm) and white-light for 3 minutes and 100 minutes, respectively.

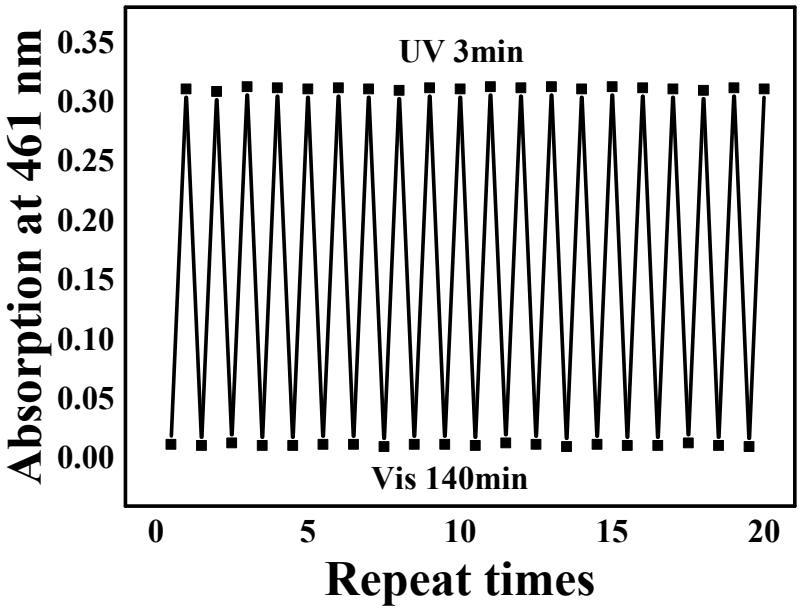
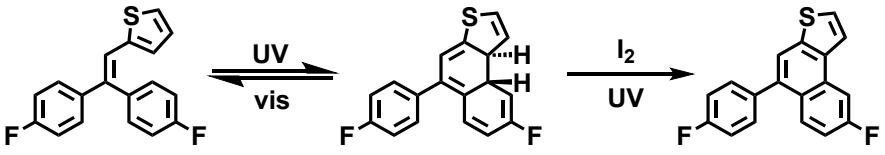


Figure S24 Recycling of the photochromic process of polymer films containing 5 wt% 3ThDpF as a function of exposure to UV-light (365 nm) and white-light for 3 minutes and 140 minutes, respectively.

4 Demonstration of the photochromic mechanism

(1) 2ThDpF



Photochemical reaction procedure of 2ThDpF: A mixture of 2-(2,2-bis(4-fluorophenyl)vinyl)thiophene (30.0 mg, 0.1 mmol) and iodine (51.0 mg, 0.4 mmol) in degassed cyclohexane (5 ml) was irradiated with UV-light in a photochemical reactor (Rayonet RPR200) for 12 h. The mixture was dissolved in 20 ml dichloromethane and washed with Na_2SO_3 aqueous solution for 3 times. The mixture was further purified by column chromatography with hexane as eluent. A white solid named 2ThDpF(O) was obtained. Yield: 26.1 mg (86.6 %).

Charactriztion of 2ThDpF(O): ^{1}H NMR (500 MHz, deutered DMSO, 298 K): δ = 8.43 (dd, 10.6 Hz, 2.7 Hz, 1H), 8.28 (d, 5.0 Hz, 1H), 7.97 (s, 1H), 7.95 (d, 5.4 Hz, 1H), 7.82 (dd, 9.2 Hz, 5.8Hz, 1H), 7.53–7.56 (m, 2H), 7.40–7.44 (m, 1H), 7.35–7.39 (m, 2H); High solution EI–MS: m/z found: 296.0467 $[M]^+$; calcd for $C_{18}H_{10}F_2S$: 296.0471. Elemental analyses (%) calcd for $C_{18}H_{10}F_2S$: C 72.96, H 3.40; found: C 72.65, H 3.60.

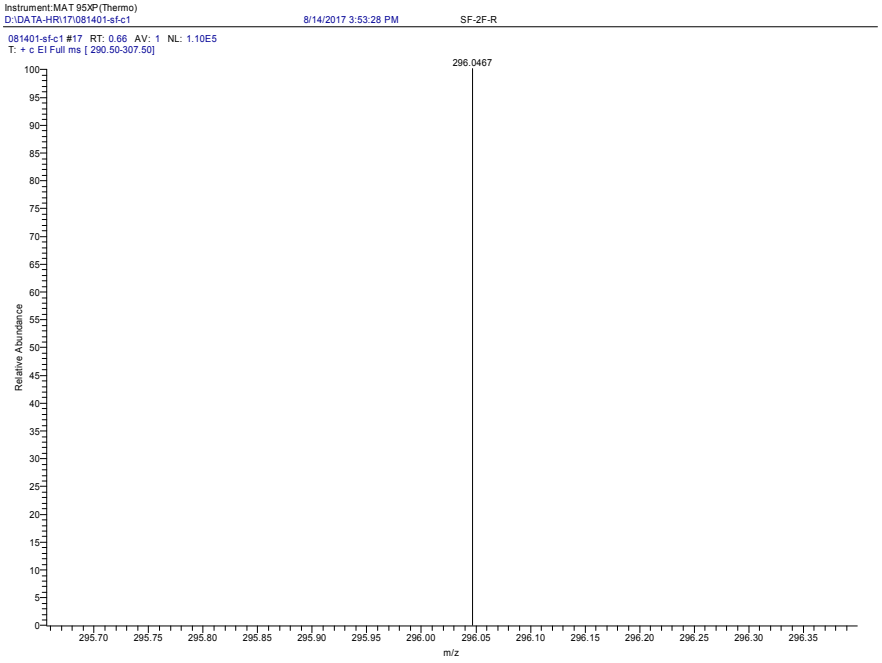


Figure S25 High Resolution EI mass spectrum of compound 2ThDpF(O).

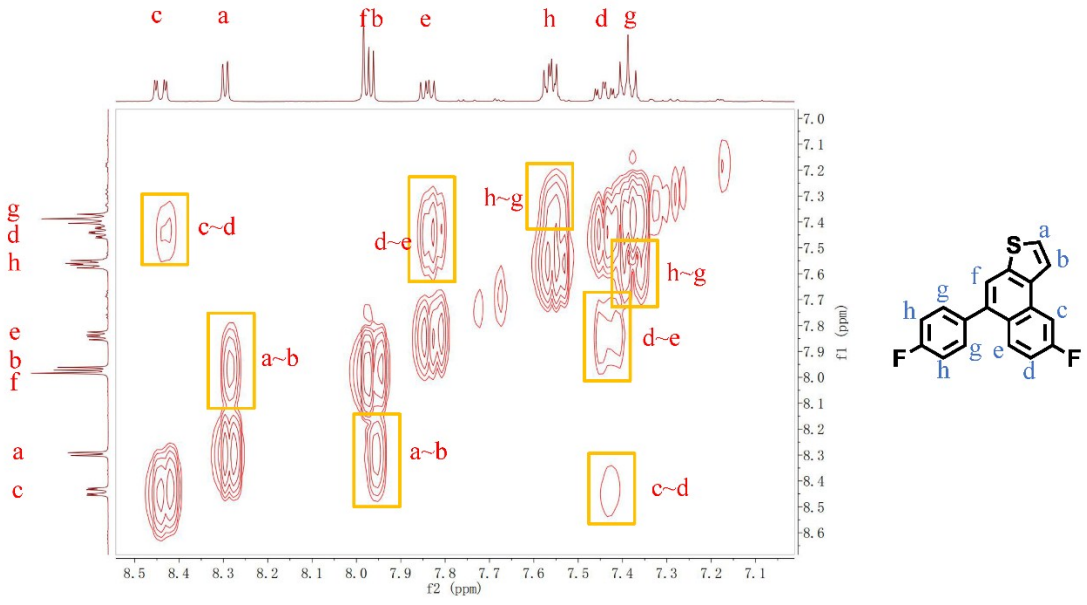
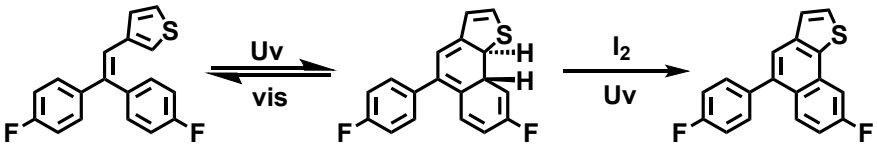


Figure S26. ^{1}H–^{1}H COSY NMR spectrum of 2ThDpF(O) in deutered DMSO solution.

(2) 3ThDpF



3ThDpF 3ThDpF(C) 3ThDpF(O)

Photochemical reaction procedure of 3ThDpF: This compound was prepared according to the aforementioned procedure for 2ThDpF(O) except that 3-(2,2-bis(4-fluorophenyl)vinyl)thiophene (30.0 mg, 0.1 mmol) were used in place of 2-(2,2-bis(4-fluorophenyl)vinyl)thiophene (30.0 mg, 0.1 mmol). A white solid named 2ThDpF(O) was obtained. Yield: 25.7 mg (85.3 %).

Charactriztion of 3ThDpF(O): ^{1}H NMR (500 MHz, deutered DMSO, 298 K): δ = 7.99 (dd, 9.9 Hz, 2.6 Hz, 1H), 7.96 (d, 5.3 Hz, 1H), 7.83–7.86 (m, 2H), 7.64 (d, 5.3 Hz, 1H), 7.54–7.57 (m, 2H), 7.43–7.46 (m, 1H), 7.37–7.41 (m, 2H); High solution EI–MS: m/z found: 296.0464 $[M]^+$; calcd for $C_{18}H_{10}F_2S$: 296.0471. Elemental analyses (%) calcd for $C_{18}H_{10}F_2S$: C 72.96, H 3.40; found: C 72.77, H 3.51.

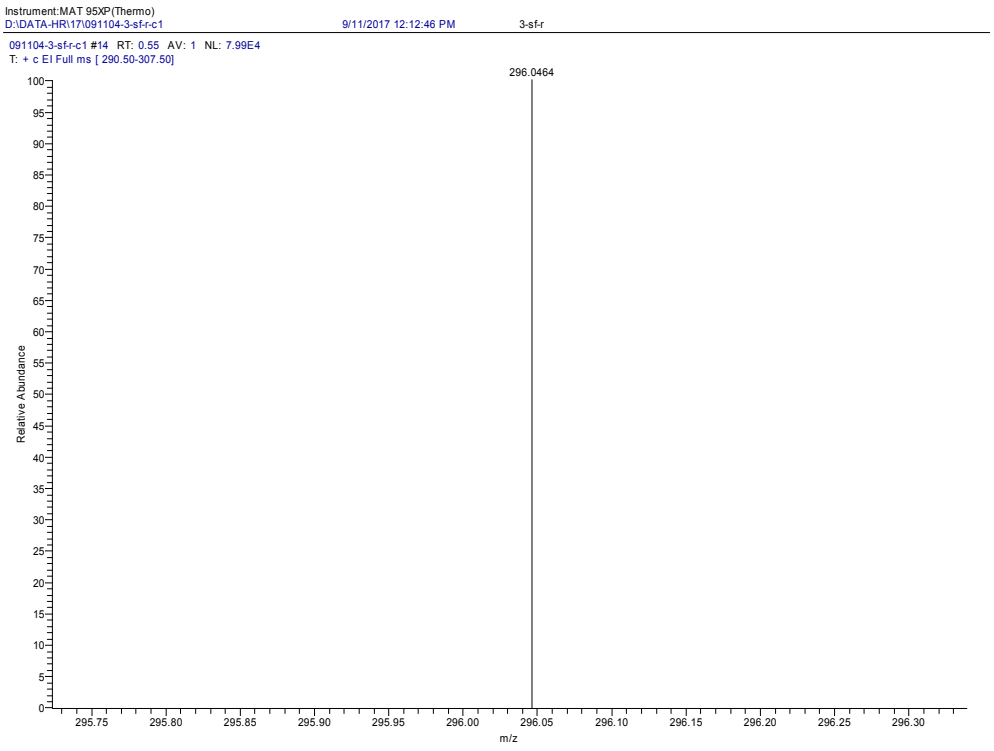


Figure S27 High Resolution EI mass spectrum of compound 3ThDpF(O).

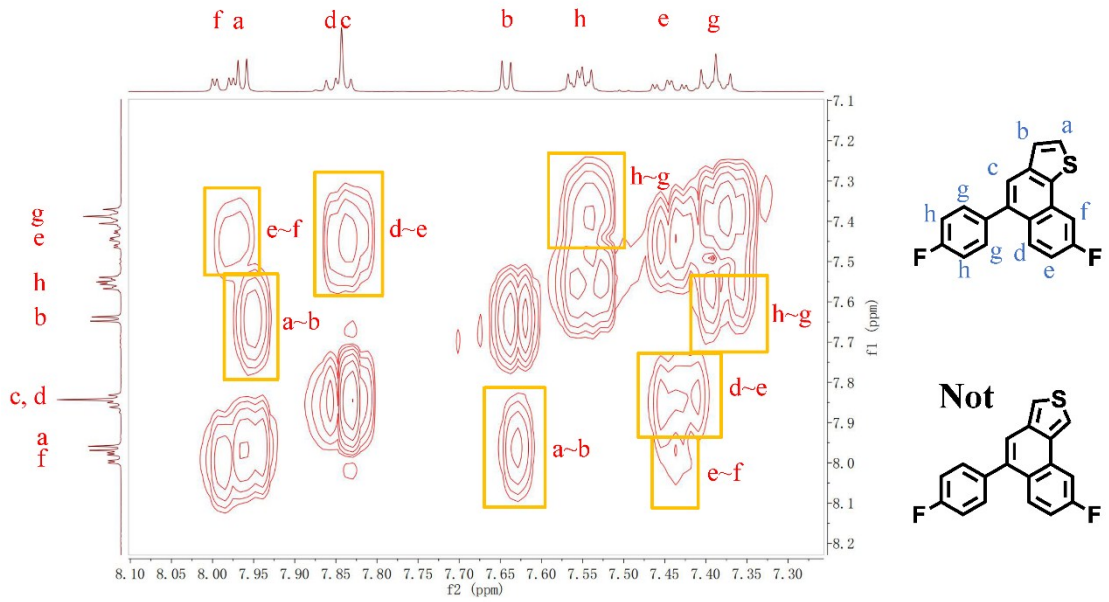


Figure S28. $^{1}H–^{1}H$ COSY NMR spectrum of 3ThDpF(O) in deutered DMSO solution.

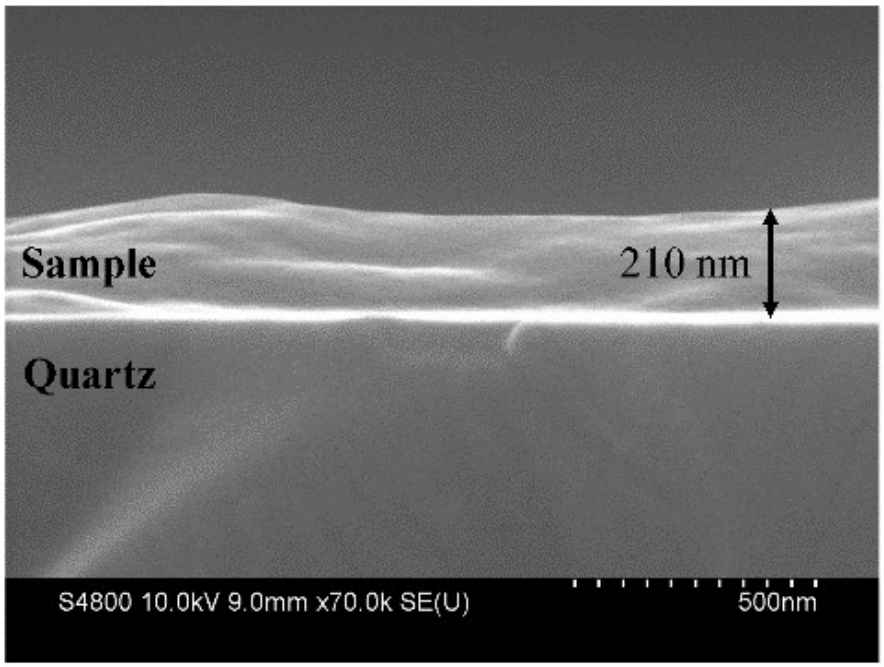


Figure S29 SEM image for the cross sections of surface-2ThDpF.

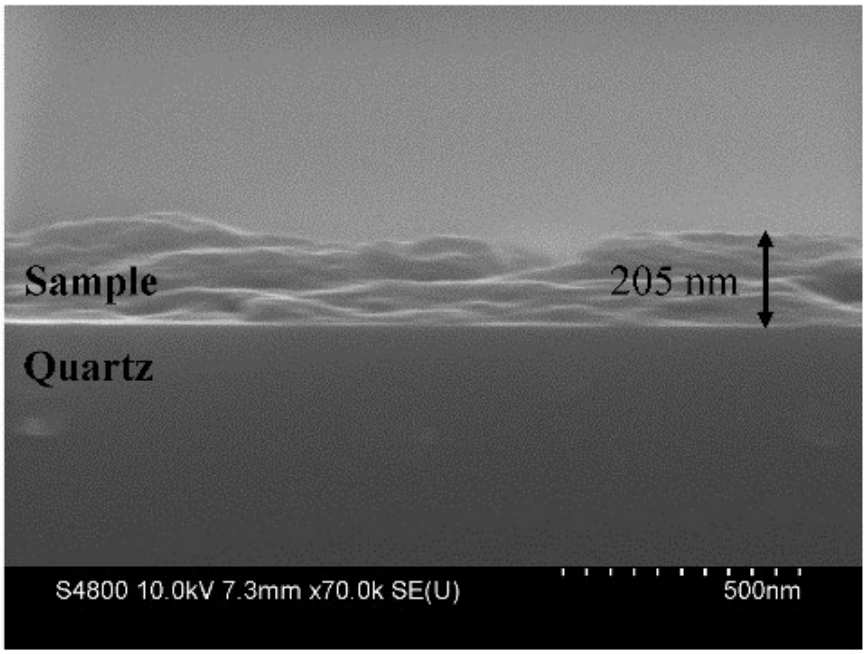


Figure S30 SEM image for the cross sections of surface-3ThDpF.

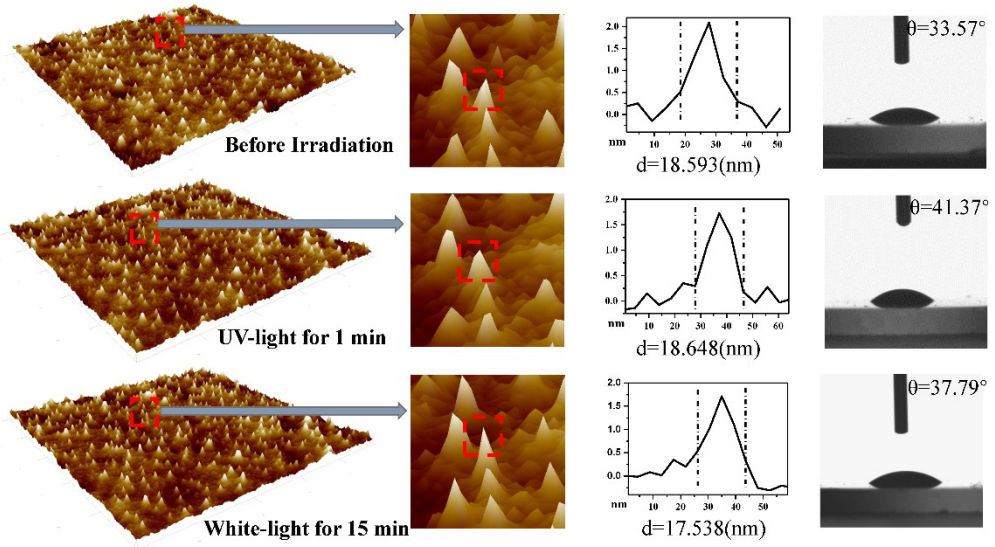


Figure S31 AFM images and contact angles for the surface-3ThDpF before, after UV-light irradiation (1 minute) and further white-light irradiation for 15 minutes.

5. Single crystal data of 2ThDpF

Single-crystal X-ray analyses for **2ThDpF** were performed on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer with graphite-monochromatized Cu-Kα radiation (λ = 1.54184 Å). The structure was solved with Olex2 v1.2 program

and expanded using Fourier techniques. Non-H atoms of this compound was further refined with anisotropic thermal parameters. The hydrogen atoms were added in idealized positions and refined with fixed geometry according to their carrier atoms.

Crystal data for **2ThDpF**; $C_{18}H_{12}F_2S$, Formula Weight = 298.84 g/mol, orthorhombic, space group Pbca, T = 293 K, Z = 16, a = 9.2899(3) Å, b = 19.4917(7) Å, c = 31.1683(11) Å, α = 90 °, β = 90°, γ = 90 °, V = 5643.8(3) Å^3, ρ_c = 1.407 g cm^{-3}, μ($Cu_{K\alpha}$) = 2.152 mm^{-1}, F(000) = 2472. Reflections collected 13309, Independent reflections 5534 (R_{int}

Table S1. Bond distances (Å) for **2ThDpF**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S2	C22	1.726(3)	C26	C27	1.382(5)
S2	C19	1.718(4)	C6	C13	1.490(5)
S1	C4	1.729(4)	C6	C5	1.347(5)
S1	C1	1.703(4)	C13	C14	1.415(5)
F4	C28	1.360(4)	C13	C18	1.396(5)
F3	C34	1.361(4)	C30	C29	1.381(5)
F2	C16	1.355(4)	C27	C28	1.372(5)
F1	C10	1.361(4)	C28	C29	1.380(5)
C3	C4	1.427(5)	C36	C35	1.391(5)
C3	C2	1.439(5)	C14	C15	1.379(5)
C23	C24	1.362(5)	C12	C11	1.391(5)
C23	C22	1.441(5)	C21	C20	1.416(5)
C24	C31	1.482(4)	C33	C34	1.362(6)
C24	C25	1.488(5)	C4	C5	1.446(5)
C31	C32	1.395(5)	C34	C35	1.378(6)
C31	C36	1.397(5)	C16	C15	1.368(6)

C25	C26	1.398(5)	C16	C17	1.375(5)
C25	C30	1.389(5)	C10	C11	1.392(6)
C32	C33	1.397(5)	C10	C9	1.345(6)
C22	C21	1.390(5)	C19	C20	1.350(6)
C7	C6	1.501(5)	C2	C1	1.351(5)
C7	C12	1.393(5)	C8	C9	1.391(5)
C7	C8	1.385(5)	C17	C18	1.389(6)

Table S2. Bond Angles (°) for **2ThDpF**

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C19	S2	C22	92.43(18)	C27	C28	C29	122.9(3)
C1	S1	C4	92.54(18)	C35	C36	C31	120.9(3)
C4	C3	C2	110.0(3)	C15	C14	C13	120.7(4)
C24	C23	C22	129.1(3)	C11	C12	C7	120.2(4)
C23	C24	C31	119.7(3)	C22	C21	C20	113.5(3)
C23	C24	C25	122.4(3)	C34	C33	C32	118.4(4)
C31	C24	C25	118.0(3)	C28	C29	C30	118.4(3)
C32	C31	C24	121.9(3)	C3	C4	S1	110.8(3)
C32	C31	C36	118.2(3)	C3	C4	C5	122.3(3)
C36	C31	C24	119.9(3)	C5	C4	S1	126.7(3)
C26	C25	C24	119.2(3)	F3	C34	C33	119.0(4)
C30	C25	C24	121.5(3)	F3	C34	C35	118.3(4)
C30	C25	C26	119.3(3)	C33	C34	C35	122.7(3)
C31	C32	C33	121.2(4)	C6	C5	C4	130.2(3)
C23	C22	S2	127.3(3)	F2	C16	C15	119.1(3)
C21	C22	S2	109.5(2)	F2	C16	C17	118.7(4)
C21	C22	C23	123.1(3)	C15	C16	C17	122.3(4)
C12	C7	C6	120.1(3)	C34	C35	C36	118.6(4)

C8	C7	C6	120.1(3)	F1	C10	C11	117.2(4)
C8	C7	C12	119.7(3)	C9	C10	F1	120.1(4)
C27	C26	C25	120.7(3)	C9	C10	C11	122.7(3)
C13	C6	C7	116.8(3)	C20	C19	S2	112.1(3)
C5	C6	C7	121.5(3)	C1	C2	C3	114.1(3)
C5	C6	C13	121.6(3)	C16	C15	C14	119.4(3)
C14	C13	C6	120.2(3)	C7	C8	C9	120.1(4)
C18	C13	C6	122.1(3)	C12	C11	C10	117.9(4)
C18	C13	C14	117.8(3)	C19	C20	C21	112.5(4)
C29	C30	C25	120.6(3)	C10	C9	C8	119.4(4)
C28	C27	C26	118.2(3)	C2	C1	S1	112.5(3)
F4	C28	C27	118.2(3)	C16	C17	C18	118.5(4)
F4	C28	C29	118.9(3)	C17	C18	C13	121.4(3)

6 Computational Details

Calculations were carried out using Gaussian 09 software package. Geometry optimizations were performed for **2ThDpF** and **3ThDpF** in both open forms and closed form using density functional theory (DFT) at B3LYP/6-31G* level. On the basis of the ground state optimized geometries in the gas phase, the time-dependent density functional theory (TDDFT) method at the same level was employed to compute the low-energy singlet–singlet transitions for the complexes.

Table S3. Bond angles and Bond distances (Å) for **2ThDpF**

Tag	**Symbol**	**NA**	**NB**	**NC**	**Bond**	**Angle**	**Dihedral**	**X**	**Y**	**Z**
1	C							1.723321	-1.95978	0.132812
2	C	1			1.448767			0.310109	-1.64871	0.203516
3	C	2	1		1.358996	131.8624		-0.36699	-0.47567	0.092326
4	C	3	2	1	1.48584	119.9222	172.7396	-1.85218	-0.47844	0.048429

5	C	3	2	1	1.493414	123.1905	-8.48409	0.307625	0.855494	0.035789
6	C	5	3	2	1.404421	120.7899	-65.1531	1.031341	1.342018	1.136665
7	C	6	5	3	1.394258	121.1713	-178.225	1.633483	2.599171	1.105878
8	C	7	6	5	1.389391	118.6228	-0.10888	1.506968	3.369789	-0.04327
9	C	8	7	6	1.390748	121.9969	0.518122	0.792075	2.928391	-1.15155
10	C	9	8	7	1.393045	118.6308	-0.02994	0.188077	1.674155	-1.10004
11	C	4	3	2	1.408228	120.7679	147.7888	-2.59091	0.590836	0.590678
12	C	11	4	3	1.392329	121.5054	-178.579	-3.98322	0.59054	0.584034
13	C	12	11	4	1.389786	118.8055	-0.51701	-4.64995	-0.48929	0.017506
14	C	13	12	11	1.390062	121.7	-0.41899	-3.96267	-1.55781	-0.54657
15	C	14	13	12	1.392231	118.7745	0.351865	-2.5706	-1.54139	-0.53305
16	F	13	12	11	1.34966	119.1776	-179.673	-5.9995	-0.49424	0.001035
17	F	8	7	6	1.349317	119.0335	-179.881	2.088442	4.58674	-0.08296
18	S	1	2	3	1.759003	126.4491	-8.05636	3.014124	-0.85769	-0.32906
19	C	18	1	2	1.733888	91.83231	-176.313	4.202646	-2.11539	-0.21965
20	C	19	18	1	1.368515	111.986	-0.22252	3.650724	-3.31083	0.153366
21	C	1	2	3	1.383495	123.8716	176.1337	2.246636	-3.22233	0.347652
22	H	2	1	21	1.088543	111.7109	-5.31856	-0.29207	-2.54309	0.353151
23	H	6	5	3	1.085351	119.2423	1.70013	1.12074	0.726666	2.026235
24	H	7	6	5	1.084457	121.683	179.8078	2.191578	2.98428	1.952204
25	H	9	8	7	1.084483	119.6488	179.7803	0.714807	3.562911	-2.02763
26	H	10	9	8	1.08562	119.4945	179.4399	-0.38106	1.319518	-1.95379
27	H	11	4	3	1.084667	119.363	0.561597	-2.06527	1.428367	1.036483
28	H	12	11	4	1.084587	121.5507	179.3202	-4.55296	1.408628	1.011193
29	H	14	13	12	1.084608	119.6393	-178.431	-4.51662	-2.37128	-1.00239
30	H	15	14	13	1.085082	118.9804	-177.576	-2.03061	-2.35422	-1.00753
31	H	19	18	1	1.081348	119.6961	-179.654	5.239752	-1.89207	-0.42905
32	H	20	19	18	1.083831	123.5911	-179.693	4.224031	-4.22136	0.283542
33	H	21	1	2	1.084719	121.9901	-2.94665	1.622304	-4.0623	0.632742

Table S4. Bond angles and Bond distances (Å) for **2ThDpF(C)**

Tag	Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
1	C							-1.44047	-1.78184	0.003935
2	C	1			1.348696			-0.1192	-1.61035	0.213266
3	C	2	1		1.460358	120.5217		0.481368	-0.28294	0.113576
4	C	3	2	1	1.487647	116.4021	-166.596	1.966924	-0.2318	0.053572
5	C	3	2	1	1.377651	119.5153	14.65594	-0.33008	0.830354	0.106732
6	C	5	3	2	1.543789	118.2068	7.391215	-1.83714	0.636523	0.379656
7	C	6	5	3	1.509778	114.0999	-169.157	-2.6768	1.859443	0.098813
8	C	7	6	5	1.338002	120.6383	-12.1365	-2.10061	3.048575	-0.11148
9	C	8	7	6	1.445549	123.6261	5.365903	-0.67063	3.240739	-0.20006
10	C	9	8	7	1.356911	119.7488	1.963281	0.159468	2.171409	-0.1069
11	C	4	3	2	1.40624	121.908	-127.294	2.719058	0.570104	0.930357
12	C	11	4	3	1.393744	121.3517	178.1784	4.112138	0.580691	0.888687
13	C	12	11	4	1.389624	118.7459	-0.39848	4.759211	-0.22848	-0.03738
14	C	13	12	11	1.390062	121.814	-0.35126	4.055725	-1.04808	-0.91239
15	C	14	13	12	1.393019	118.6772	0.265856	2.663857	-1.04758	-0.85578
16	F	13	12	11	1.34936	119.0972	-179.921	6.107802	-0.22497	-0.08279
17	F	8	7	6	1.353486	120.7939	-176.93	-2.85154	4.158356	-0.3023
18	S	1	2	3	1.771062	126.9681	-178.147	-2.35016	-3.29663	0.124624
19	C	18	1	2	1.7826	90.3099	166.2456	-3.88377	-2.38807	0.109949
20	C	19	18	1	1.335538	114.794	5.524811	-3.75459	-1.07444	-0.09341
21	C	20	19	18	1.510426	114.7373	3.542739	-2.3412	-0.61167	-0.35716
22	H	6	5	3	1.110083	106.1022	72.49583	-1.92708	0.407887	1.46221
23	H	21	20	19	1.109725	107.9643	103.3233	-2.24139	-0.41974	-1.44559
24	H	2	1	21	1.085602	121.2088	-179.024	0.525497	-2.44948	0.455683
25	H	7	6	5	1.084234	119.3774	172.2243	-3.75761	1.783127	0.13856
26	H	9	8	7	1.08436	118.2349	178.8043	-0.29837	4.240845	-0.39253
27	H	10	9	8	1.083821	119.2358	175.0864	1.223821	2.313095	-0.25436

28	H	11	4	3	1.085177	119.3578	-0.51561	2.205575	1.177455	1.668646
29	H	12	11	4	1.084549	121.6034	-179.533	4.696424	1.19188	1.567881
30	H	14	13	12	1.084538	119.6588	-179.87	4.596514	-1.66717	-1.61984
31	H	15	14	13	1.08586	119.2888	179.6623	2.104211	-1.67989	-1.53847
32	H	19	18	1	1.083106	118.0513	-175.516	-4.80494	-2.94146	0.245296
33	H	20	19	18	1.084264	122.635	177.8897	-4.6061	-0.40649	-0.1597

Table S5. Bond angles and Bond distances (Å) for **3ThDpF**

Tag	**Symbol**	**NA**	**NB**	**NC**	**Bond**	**Angle**	**Dihedral**	**X**	**Y**	**Z**
1	C							1.796488	-1.7586	0.081111
2	C	1			1.464066			0.34663	-1.56957	0.156385
3	C	2	1		1.356935	130.624		-0.40338	-0.44253	0.063879
4	C	3	2	1	1.487458	119.9016	173.3974	-1.88721	-0.54013	0.028274
5	C	3	2	1	1.493935	123.2625	-8.21328	0.182758	0.93116	0.028573
6	C	5	3	2	1.404643	120.8413	-60.0439	0.964534	1.4081	1.093644
7	C	6	5	3	1.393721	121.197	-178.928	1.496572	2.696184	1.078405
8	C	7	6	5	1.390348	118.6784	-0.00679	1.2397	3.511246	-0.0183
9	C	8	7	6	1.390087	121.9219	0.391456	0.464662	3.080378	-1.08882
10	C	9	8	7	1.394313	118.6359	0.027674	-0.06706	1.791932	-1.05296
11	C	4	3	2	1.407798	120.8392	145.6066	-2.69008	0.448954	0.627443
12	C	11	4	3	1.392364	121.4647	-178.32	-4.07914	0.353127	0.631946
13	C	12	11	4	1.389983	118.7903	-0.55298	-4.67661	-0.74176	0.018513
14	C	13	12	11	1.389869	121.729	-0.36804	-3.92466	-1.73256	-0.60167
15	C	14	13	12	1.392635	118.7488	0.348212	-2.53649	-1.62124	-0.59751
16	F	13	12	11	1.349685	119.1458	-179.637	-6.02284	-0.83811	0.012205
17	F	8	7	6	1.349482	119.0383	-179.902	1.752946	4.759101	-0.04153
18	C	1	2	3	1.380258	128.2717	-19.2937	2.742854	-0.9083	-0.45415
19	S	18	1	2	1.728388	112.4082	-177.464	4.337306	-1.57221	-0.38873
20	C	19	18	1	1.736044	91.65587	0.134868	3.75613	-3.02435	0.364499

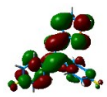
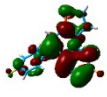
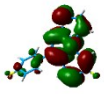
21	C	20	19	18	1.362672	111.2201	0.200383	2.405796	-2.98133	0.542324
22	H	2	1	18	1.088355	113.1465	160.1202	-0.19909	-2.49985	0.302269
23	H	6	5	3	1.085099	119.1991	1.267001	1.158331	0.758077	1.940611
24	H	7	6	5	1.08454	121.6676	179.7441	2.097744	3.07364	1.898373
25	H	9	8	7	1.084536	119.668	179.7439	0.284099	3.748294	-1.92398
26	H	10	9	8	1.08569	119.419	179.4243	-0.68203	1.445661	-1.87797
27	H	11	4	3	1.084795	119.3727	0.866117	-2.21737	1.298798	1.108155
28	H	12	11	4	1.08458	121.5731	179.3026	-4.69894	1.108441	1.10275
29	H	14	13	12	1.084598	119.645	-178.508	-4.42693	-2.5599	-1.09115
30	H	15	14	13	1.085118	119.102	-177.79	-1.94526	-2.37233	-1.11112
31	H	18	1	21	1.078974	128.0745	178.5575	2.58968	0.063856	-0.89645
32	H	20	19	18	1.080737	120.2919	-179.765	4.444404	-3.81479	0.628094
33	H	21	20	19	1.084719	123.3094	179.8918	1.838524	-3.78777	0.994507

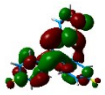
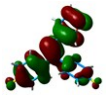
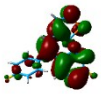
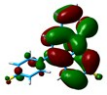
Table S6. Bond angles and Bond distances (Å) for **3ThDpF(C)**

Tag	Symbol	NA	NB	NC	Bond	Angle	Dihedral	X	Y	Z
1	C							-1.32713	-1.9393	0.012913
2	C	1			1.359007			0.004052	-1.72085	0.177642
3	C	2	1		1.451401	121.6049		0.571393	-0.38722	0.099412
4	C	3	2	1	1.488807	116.6479	-169.234	2.056485	-0.29528	0.048477
5	C	3	2	1	1.381425	119.7496	11.96755	-0.26291	0.713811	0.101036
6	C	5	3	2	1.543854	118.4851	8.149043	-1.76628	0.498044	0.378165
7	C	6	5	3	1.509349	114.2008	-168.009	-2.62917	1.699939	0.079829
8	C	7	6	5	1.337885	120.5272	-13.2041	-2.07486	2.899701	-0.12812
9	C	8	7	6	1.445453	123.5313	5.546648	-0.64787	3.118171	-0.20088
10	C	9	8	7	1.357469	119.8015	2.368783	0.201895	2.064139	-0.10269
11	C	4	3	2	1.405999	121.8544	-126.451	2.782027	0.501422	0.951635
12	C	11	4	3	1.393766	121.3506	178.0769	4.174617	0.549011	0.9198
13	C	12	11	4	1.389661	118.7362	-0.33933	4.847888	-0.21684	-0.02431

14	C	13	12	11	1.389969	121.8192	-0.32252	4.171149	-1.02866	-0.92707
15	C	14	13	12	1.393208	118.6717	0.227582	2.779238	-1.06557	-0.87966
16	F	13	12	11	1.34936	119.0947	-179.948	6.196165	-0.17705	-0.06087
17	F	8	7	6	1.352794	120.8701	-176.765	-2.844	3.993795	-0.33168
18	C	1	2	3	1.439957	129.2511	-176.757	-2.06841	-3.16932	0.117969
19	C	18	1	2	1.353236	113.6866	168.5031	-3.41032	-2.99552	0.135644
20	S	19	18	1	1.761009	115.4791	-0.33842	-3.95923	-1.32514	0.03736
21	C	1	2	3	1.518718	118.758	3.59063	-2.22211	-0.76441	-0.34082
22	H	21	1	2	1.102257	109.1328	83.75066	-2.19007	-0.60106	-1.43044
23	H	6	5	3	1.110878	106.3835	73.4526	-1.85674	0.280662	1.463805
24	H	2	1	18	1.086281	120.067	3.012743	0.671763	-2.55419	0.376931
25	H	7	6	5	1.085056	119.1125	171.2773	-3.70876	1.594884	0.108315
26	H	9	8	7	1.084368	118.2202	179.1608	-0.29218	4.125537	-0.38677
27	H	10	9	8	1.083807	119.2314	175.0292	1.264696	2.226602	-0.23942
28	H	11	4	3	1.08525	119.3548	-0.68024	2.248279	1.075825	1.701929
29	H	12	11	4	1.084545	121.6096	-179.538	4.738773	1.156335	1.619175
30	H	14	13	12	1.084542	119.6504	-179.956	4.732106	-1.6123	-1.64882
31	H	15	14	13	1.085848	119.2996	179.609	2.239943	-1.69137	-1.58436
32	H	18	1	2	1.08471	123.0153	-8.82416	-1.59305	-4.13902	0.219503
33	H	19	18	1	1.08341	126.125	-179.162	-4.15466	-3.77807	0.221447

Table S7. Calculated HOMO, LUMO distributions, energy levels, energy gap and vertical excitation wavelengths for **2ThDpF**, **2ThDpF(C)**, **3ThDpF** and **3ThDpF(C)**.

Sample	LUMO	HOMO	E_{LUMO} (eV)	E_{HOMO} (eV)	ΔE_g (eV)	Vertical excitation wavelength (nm)
2ThDpF			-1.91	-5.82	3.91	338
2ThDpF(C)			-2.32	-5.31	2.99	480

3ThDpF			-1.76	-5.94	4.18	323
3ThDpF(C)			-2.51	-5.29	2.78	512

Reference:

[1] T. Gibtner, F. Hampel, J.-P. Gisselbrecht, A. Hirsch, *Chem. Eur. J.*, **2002**, 8, 408.