Supporting Information

Photo-induced room temperature phosphorescence and thermally activated photochromism based on thianthrene derivatives

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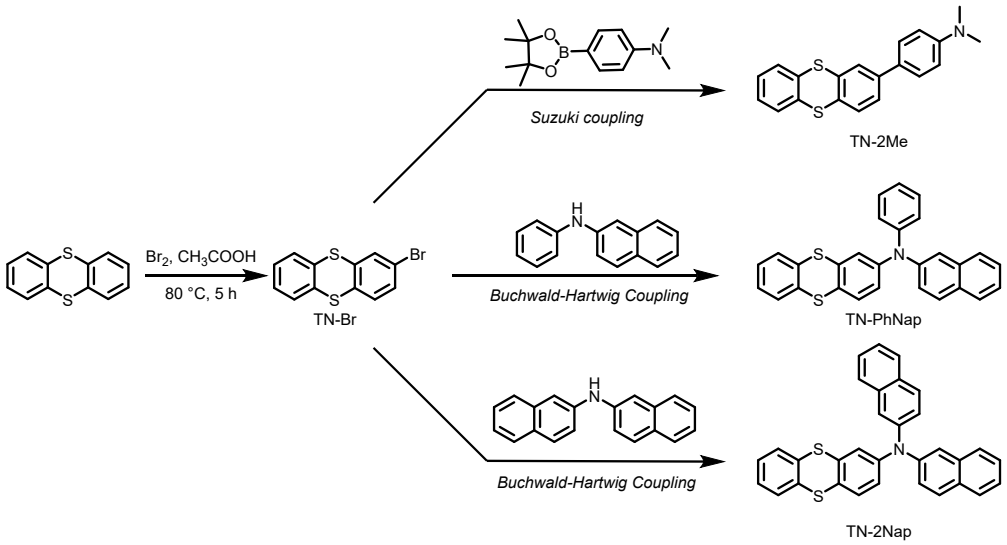
1. Experimental section

1.1 Instrumentation and materials

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on 600 MHz JEOL nuclear magnetic resonance spectrometer. High resolution mass spectra (HRMS) were measured on a UHPLC/ Q-TOF MS. High-performance liquid chromatogram (HPLC) spectra were recorded on Shimadzu LC-2050. UV-vis spectra were measured on a Shimadzu UV-2600. Photoluminescence spectra were performed on a Hitachi F-4600 fluorescence spectrophotometer. The single-crystal X-ray diffraction data were collected in XtaLAB SuperNova X-ray diffractometer. Fluorescence quantum yields and lifetimes were determined with FLS1000 spectrometer. Electron paramagnetic resonance (EPR) measurements at X-band (9.5 GHz, actual: 9430.72 MHz, power: 0.998 mW, sweep time: 1.0 min) were performed using a JES-FA200 spectrometer, and the spectra were obtained using electron paramagnetic resonance (JES-FA200) with a xenon lamp (500 W Xe-Hg lamp and equipped with filters) as the excitation source. The reagents were all purchased from commercial sources and used without further purification. Gaussian 09 program was used to perform TD-DFT calculations. The ground state (S_0) geometries were optimized for gas-phase molecular structures based on the B3LYP/6-311G (d) level. The reorganization energy (λ) was computed from the neutral and cationic geometries obtained at the B3LYP/6-31G (d) level. The spin density/odd electron density was completed with the assistance of Multiwfn[1].

1.2 Synthesis



Scheme S1 The synthetic routes of TN-2Me, TN-PhNap and TN-2Nap[2-4].

2-bromothianthrene (**TN-Br**)

To a CH_3COOH solution (60 mL) containing thianthrene (6.50 g, 30.0 mmol) at 0 °C, Br_2 (5.76 g, 36.0 mmol) was added dropwise. After heated to 80 °C and stirred for 5 h, the mixture was allowed to cool to room temperature and poured into the $NaHSO_3$ solution. Then, the mixture was extracted with CH_2Cl_2 several times. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified on a silica column to give the target product (7.35 g, 83%).

***N*, *N*-dimethyl-4-(thianthren-2-yl) aniline** (**TN-2Me**)

Under a N_2 atmosphere, TN-Br (1.48 g, 5 mmol), 4-(*N*,*N*-Dimethylamino)benzeneboronic acid pinacol ester (1.10 g, 5 mmol), and Pd $(PPh_3)_4$ (0.29 g, 0.25 mmol) were added to the mixture of THF (30 mL) and 2 M K_2CO_3 (20 mL). The mixture was stirred at 110 °C for 12 h. After cooled to room temperature, the mixture was poured into water (50 mL) and extracted with CH_2Cl_2 several times. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane=10:1 as eluent to afford a white solid (1.09 g, 65%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.68 (m, 1H), 7.52-7.45 (m, 4H), 7.44-7.40 (m, 1H), 7.26-7.23 (m, 2H), 6.80-6.76 (m, 2H), 3.00 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 150.34, 141.24, 136.02, 135.99, 135.79, 132.59, 128.99, 128.92, 128.85, 127.77, 127.74, 127.70, 127.45, 126.40, 125.71, 112.77, 40.63. HRMS (ESI): m/z calculated for $C_{20}H_{18}NS_2$: 336.0875 $[M+H]^+$, found: 336.0837.

***N*-(naphthalen-2-yl)-*N*-phenylthianthren-2-amine** (**TN-PhNap**)

N-phenylnaphthalen-2-amine (1.10 g, 5 mmol), TN-Br (1.48 g, 5 mmol), potassiumtert-butoxide (1.12 g, 10 mmol), palladium acetate (56 mg, 0.25 mmol) and tri-tert-butylphosphine solution (0.14 mL, 0.06 mmol) were dissolved in toluene (30 mL) in a Schlenk tube. The resultant mixture was refluxed for 12 hours under nitrogen, then concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane=10:1 as eluent to afford a white solid (1.84 g, 85%).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.77 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.52-7.47 (m, 1H), 7.46-7.43 (m, 1H), 7.43-7.35 (m, 3H), 7.33 (d, J = 8.5 Hz, 1H), 7.30-7.20 (m, 6H), 7.14-7.09 (m, 2H), 7.09 – 7.04 (m, 1H),

7.00 (dd, *J* = 8.4, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.98, 147.30, 144.96, 136.99, 136.23, 135.63, 134.46, 130.41, 129.61, 129.38, 129.30, 128.94, 128.83, 128.17, 127.83, 127.74, 127.17, 126.54, 124.97, 124.80, 124.60, 123.69, 123.22, 121.13. HRMS (ESI): m/z calculated for $C_{28}H_{19}NS_2$:434.1032 $[M+H]^+$, found: 434.0955.

***N*, *N*-di(naphthalen-2-yl) thianthren-2-amine (TN-2Nap)**

Following the similar synthetic method for TN-PhNap to give TN-2Nap (2.13 g, 88%) as white solid. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.80-7.76 (m, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.63-7.55 (m, 2H), 7.53-7.48 (m, 1H), 7.46 (d, *J* = 2.2 Hz, 2H), 7.45-7.37 (m, 5H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.32-7.27 (m, 3H), 7.27-7.20 (m, 2H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 147.90, 144.95, 137.10, 136.17, 135.60, 134.46, 130.51, 129.46, 129.39, 128.97, 128.84, 128.53, 127.85, 127.76, 127.21, 126.60, 125.07, 124.67, 123.97, 123.49, 121.29. HRMS (ESI): m/z calculated for $C_{32}H_{21}NS_2$: 484.1188 $[M+H]^+$, found: 484.1116.

1.3 Preparation of the doped films

Dissolve 1.00 g PMMA and 0.03 mmol TN-2Me/TN-PhNap/TN-2Nap in 10 mL THF solution. The solution was placed in an evaporating dish with a flat bottom, then stood for ~48 hours until the solvent was evaporated and the doping system was solidified. After drying at 60℃ for 24 hours, the film was cut and its photophysical properties were studied. The preparation of the polystyrene-doped system, utilizing polystyrene as a rigid polymer matrix, follows a similar procedure to that of the PMMA-doped system.

2. Photophysical properties

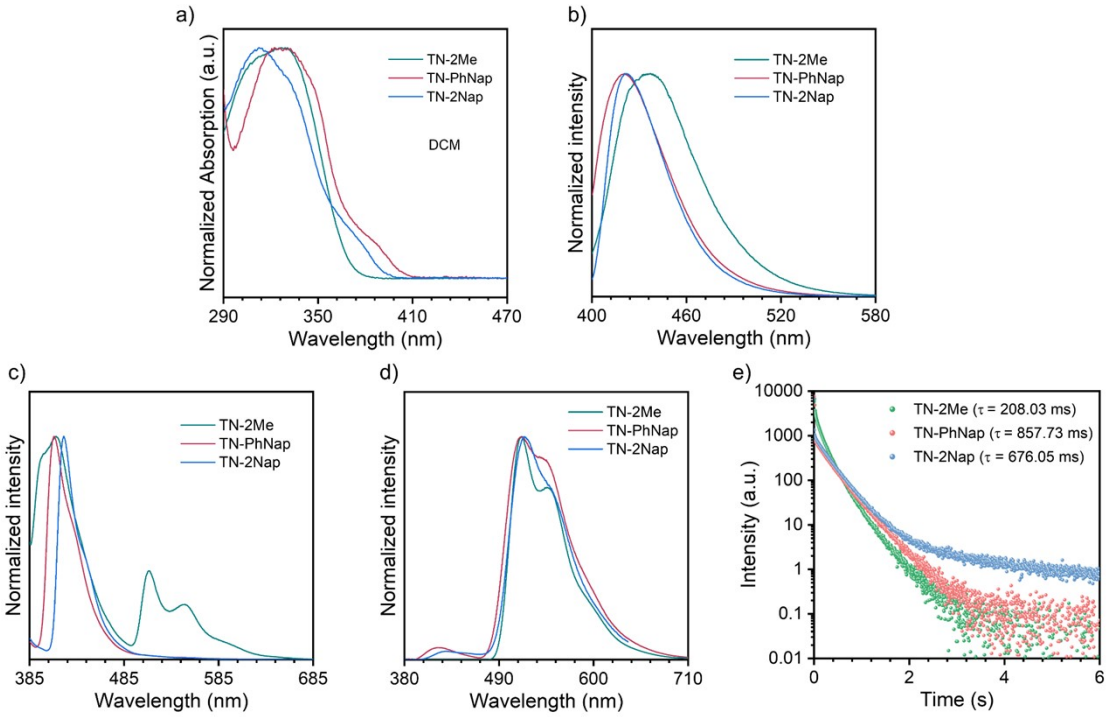


Fig. S1 (a) Absorption spectra of TN-2Me, TN-PhNap, and TN-2Nap in dichloromethane (DCM) solution (c = 1.0 × 10^{-5} mol L^{-1}) at room temperature. (b) Normalized steady-state photoluminescence (PL) spectra of TN-2Me, TN-PhNap, and TN-2Nap in DCM solution at room temperature and (c) 77 K. (d) Normalized delayed (1.0 ms) PL spectra of TN-2Me, TN-PhNap, and TN-2Nap in dichloromethane (DCM) solution at 77 K. (e) PL intensity decay curves of TN-2Me, TN-PhNap, and TN-2Nap in DCM solution at 77 K (λ_{em} = 520 nm).

m

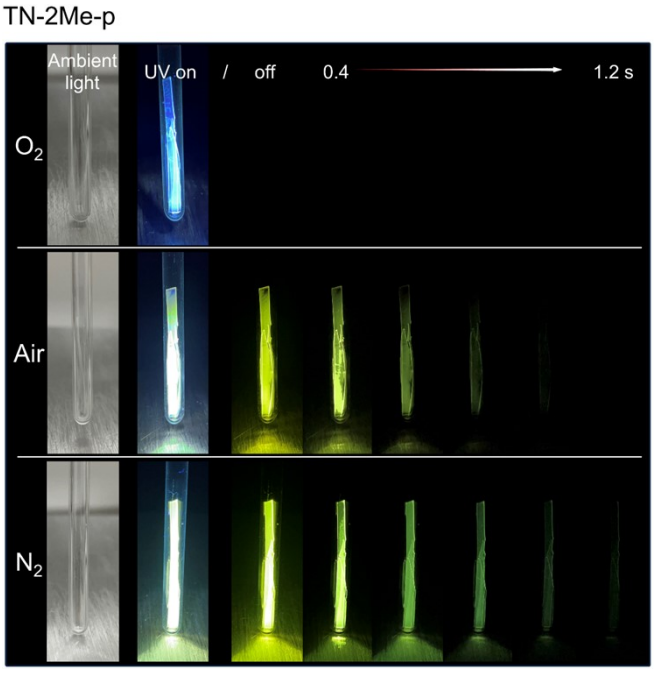


Fig. S2 Comparison of photo-induced room-temperature phosphorescence characteristics of doped films TN-2Me-p in nitrogen versus oxygen environments. Samples exposed to an oxygen atmosphere exhibit significantly reduced UV light activation efficiency.

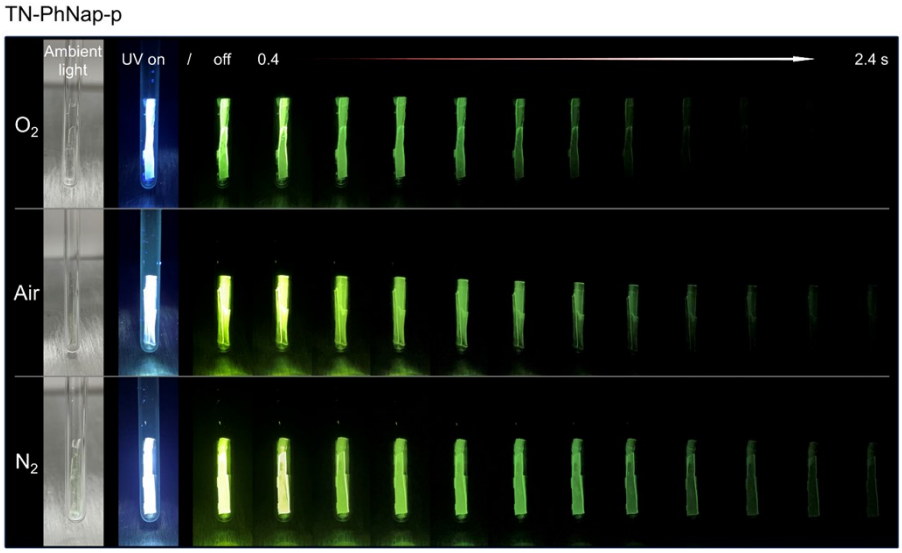


Fig. S3 Comparison of photo-induced room-temperature phosphorescence characteristics of doped films TN-PhNap-p in nitrogen versus oxygen environments. Samples exposed to an oxygen atmosphere exhibit significantly reduced UV light activation efficiency.

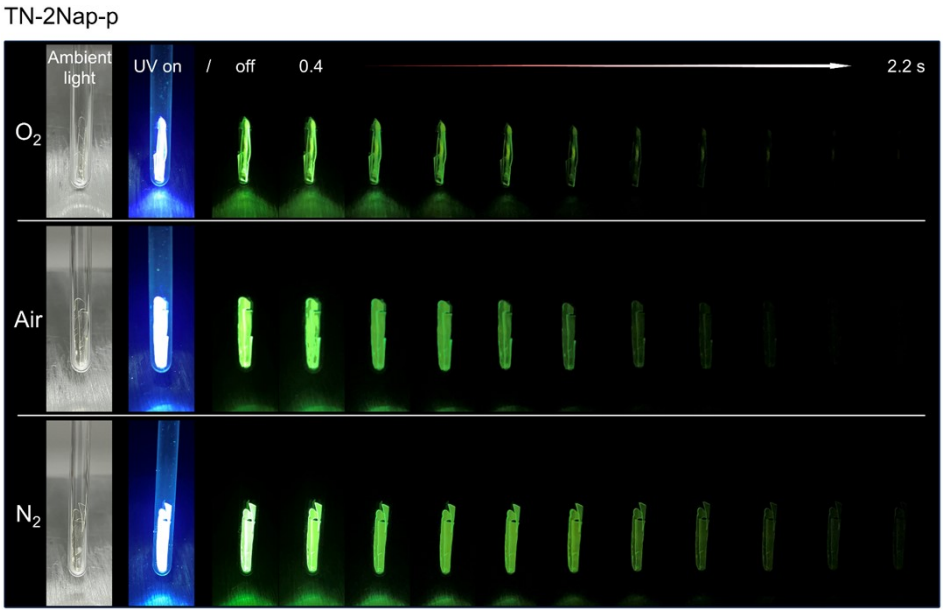


Fig. S4 Comparison of photo-induced room-temperature phosphorescence characteristics of doped films TN-2Nap-p in nitrogen versus oxygen environments. Samples exposed to an oxygen atmosphere exhibit significantly reduced UV light activation efficiency.

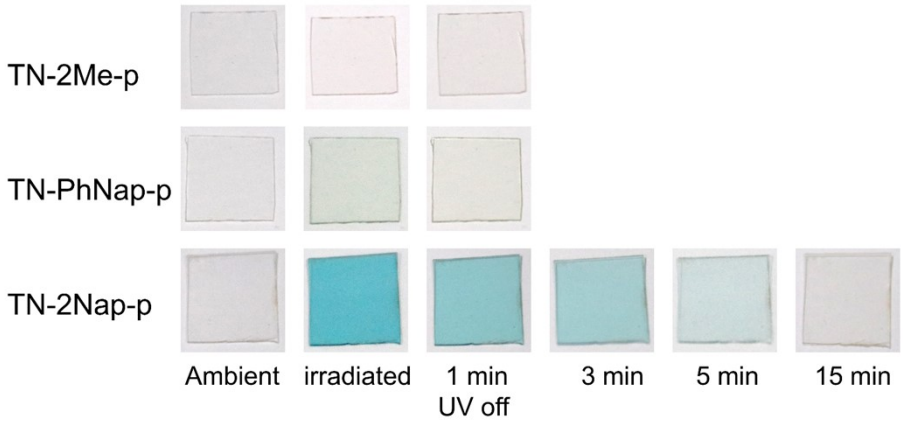


Fig. S5 Photographs of the photochromic recovery process.

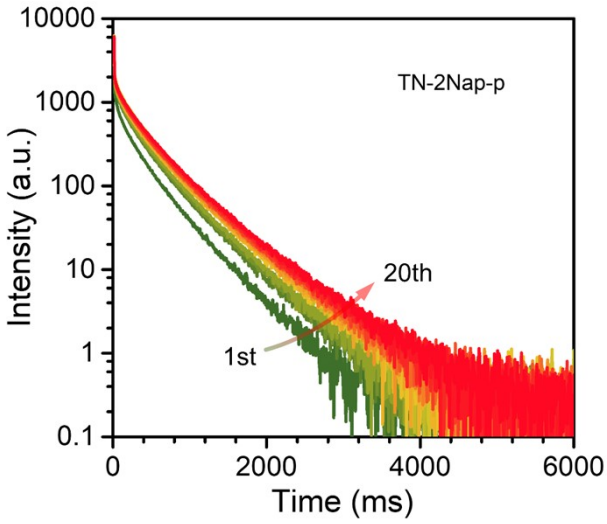


Fig. S6 Photoluminescence decay curves of TN-2Nap-p measured for each cycle from the 1st to the 20th. Before capturing and recording each afterglow decay curve, the doped film was continuously irradiated with UV light for 30 seconds.

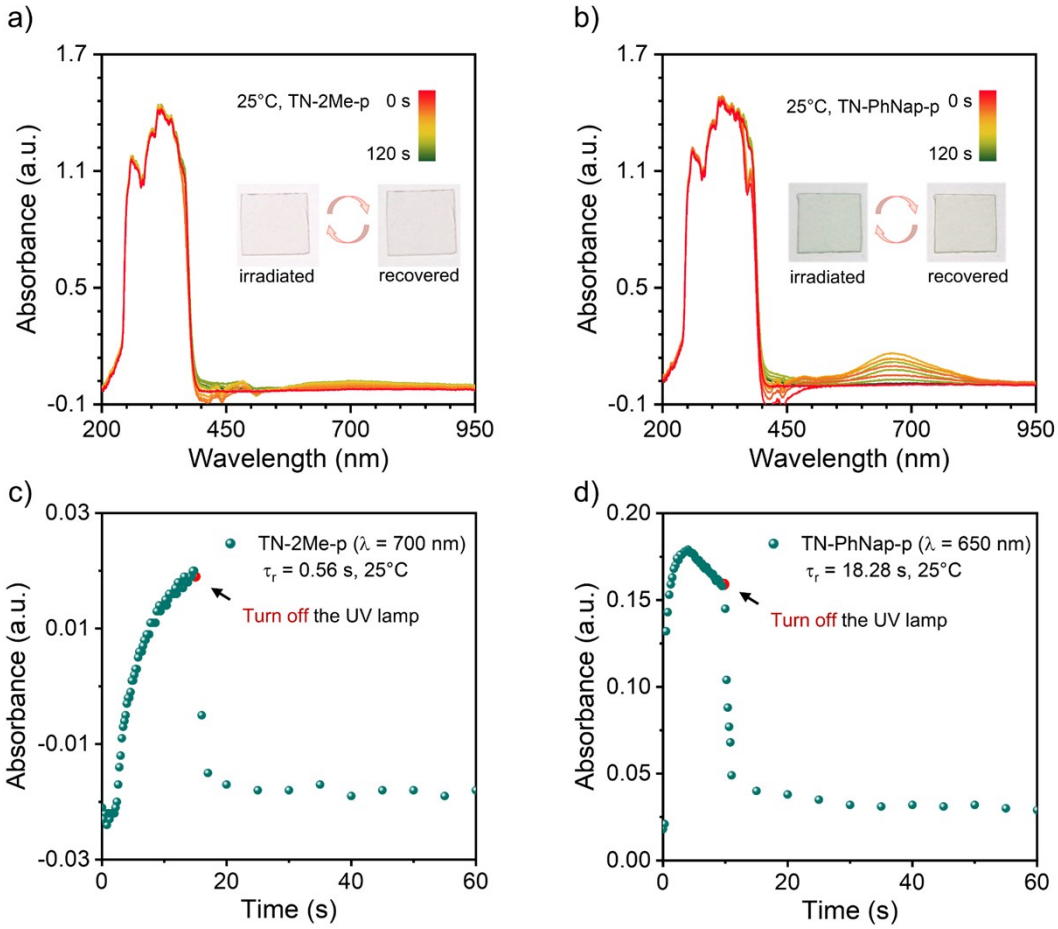


Fig. S7 In situ monitoring of absorption spectra and absorbance decay curves of (a, c) TN-2Me-p, (b, d) TN-PhNap-p during continuous exposure to 365 nm UV light (500 μW cm^{-2}) and subsequent recovery in air after the UV source is turned off, recorded at temperatures of 25 °C.

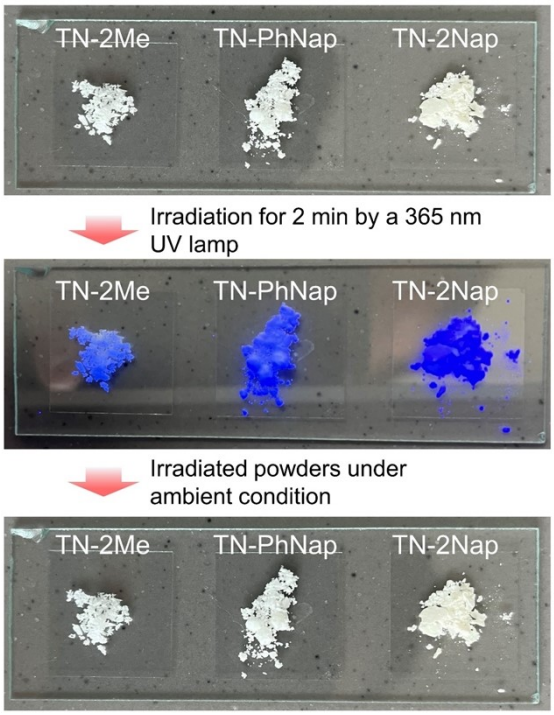


Fig. S8 The photographs of the powders (TN-2Me, TN-PhNap and TN-2Nap) before and after under continuous UV irradiation.

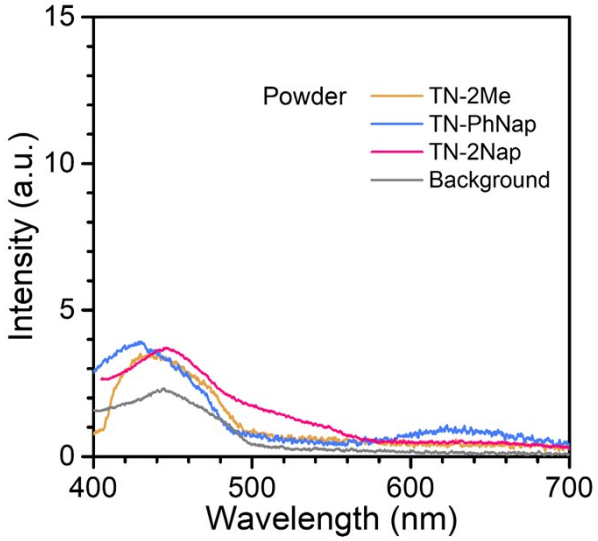


Fig. S9 Delayed PL spectra of the powders TN-2Me, TN-PhNap, and TN-2Nap (Excitation slit: 20 nm. Emission slit: 20 nm).

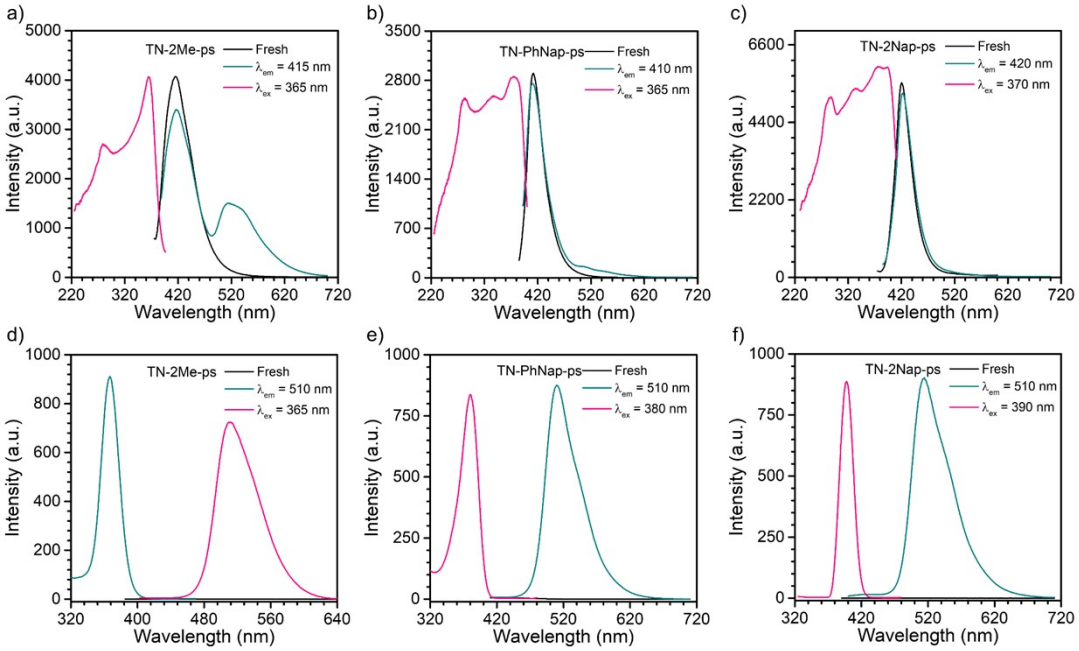


Fig. S10 (a), (b), (c) Excitation and steady-state PL spectra (before/after UV irradiation) of TN-2Me, TN-PhNap, and TN-2Nap doped in polystyrene (TN-2Me-ps, TN-PhNap-ps, and TN-2Nap-ps). (d), (e), (f) Excitation and delayed (1.0 ms) PL spectra of TN-2Me-ps, TN-PhNap-ps, and TN-2Nap-ps before/after UV irradiation.

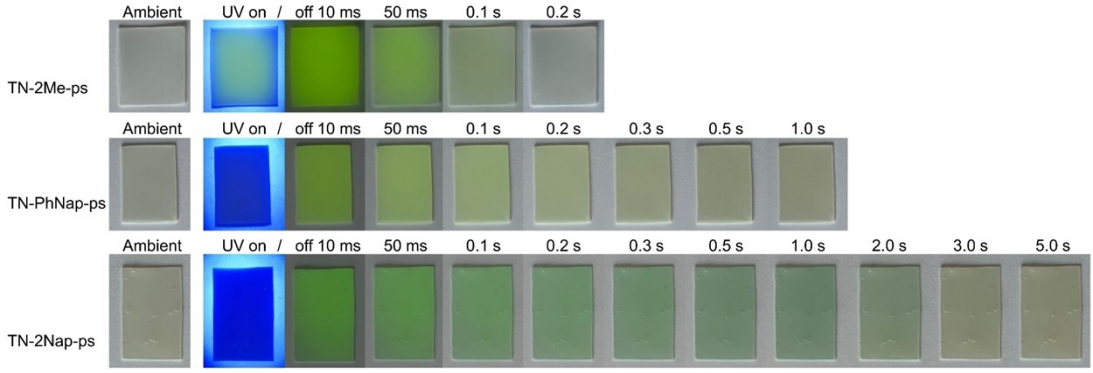


Fig. S11 Comparison of photochromic images of doped films based on polystyrene matrix (TN-2Me-ps, TN-PhNap-ps and TN-2Nap-ps), taken under bright field conditions.

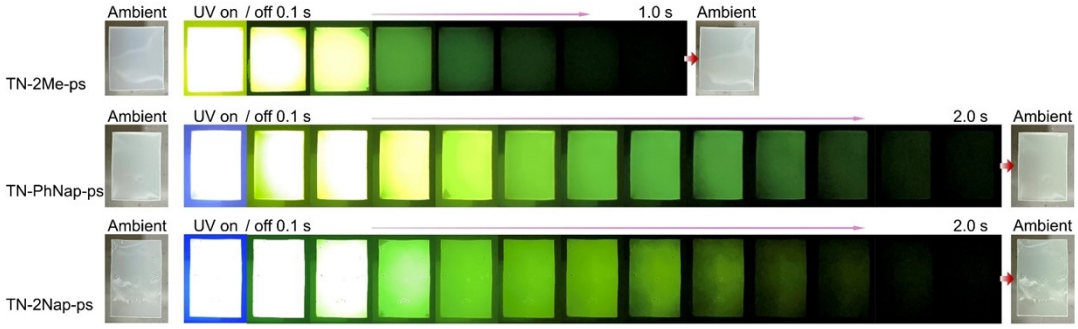


Fig. S12 Comparison of afterglow properties of the doped films with a polystyrene matrix (TN-2Me-ps, TN-PhNap-ps and TN-2Nap-ps). The afterglow of the films was photographed under dark field conditions.

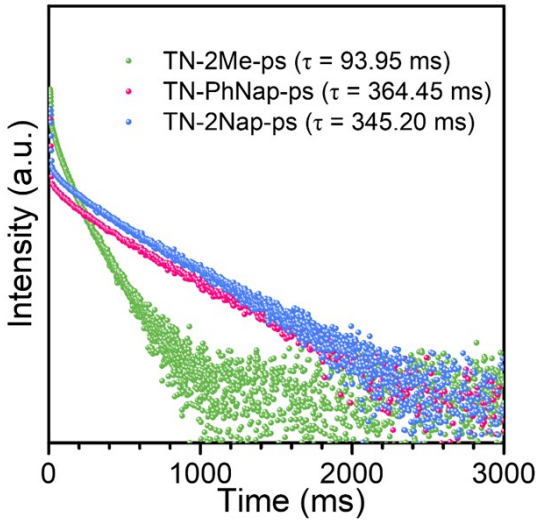


Fig. S13 PL intensity decay curves of **TN-2Me-ps**, **TN-PhNap-ps**, and **TN-2Nap-ps**.

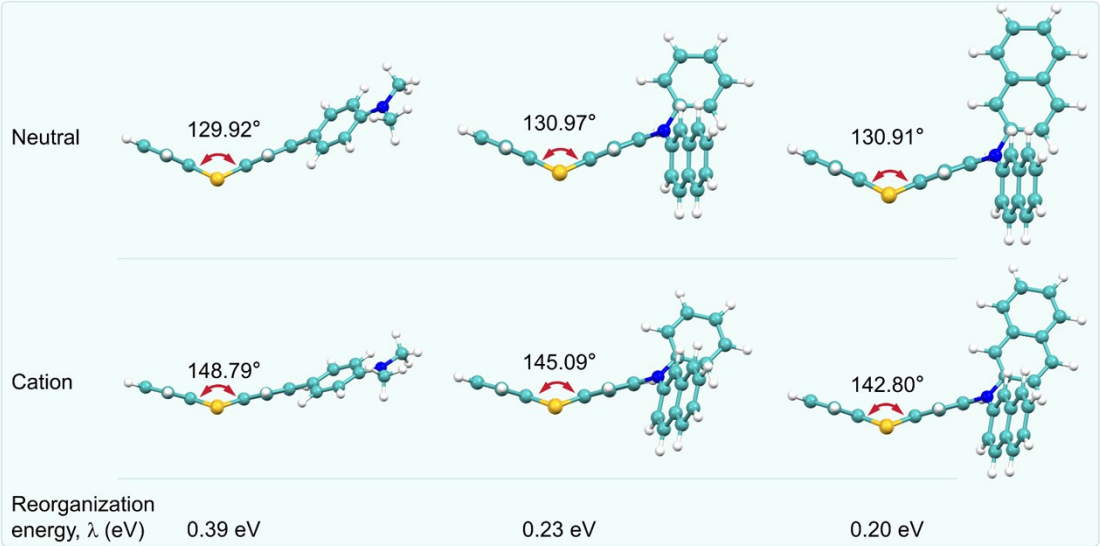


Fig. S14 Optimized molecular structures of the neutral and radical cation states for TN-2Me, TN-PhNap, and TN-2Nap. The calculated reorganization energies (λ) for the photo-generated radical processes are 0.39 eV, 0.23 eV, and 0.2 eV, respectively.

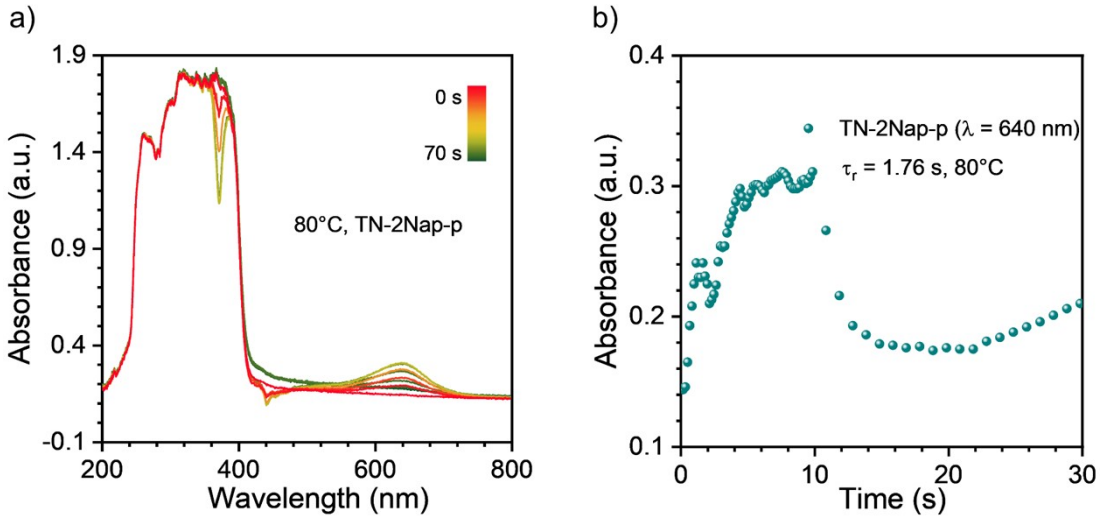


Fig. S15 In situ monitoring of absorption spectra and absorbance decay curves of TN-2Nap-p during continuous exposure to 365 nm UV light (500 μW cm^{-2}) and subsequent recovery in air after the UV source is turned off, recorded at temperatures of 80 °C.

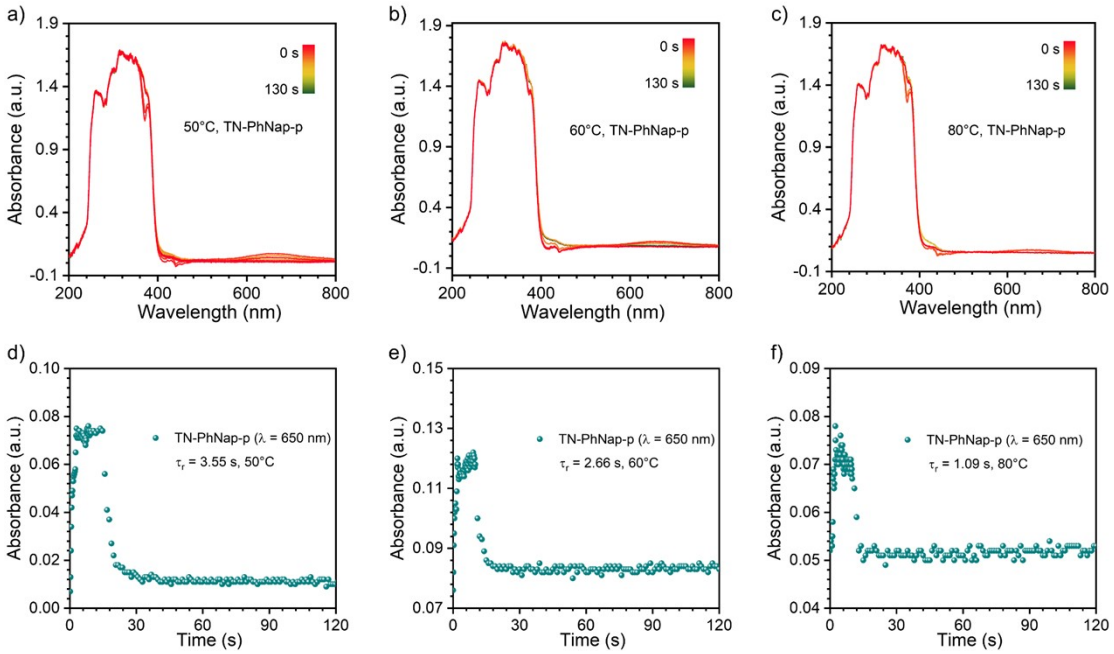


Fig. S16 In situ monitoring of absorption spectra and absorbance decay curves of TN-PhNap-p during continuous exposure to 365 nm UV light (500 μW cm^{-2}) and subsequent recovery in air after the UV source is turned off, recorded at temperatures of 50 °C, 60 °C, and 80 °C.

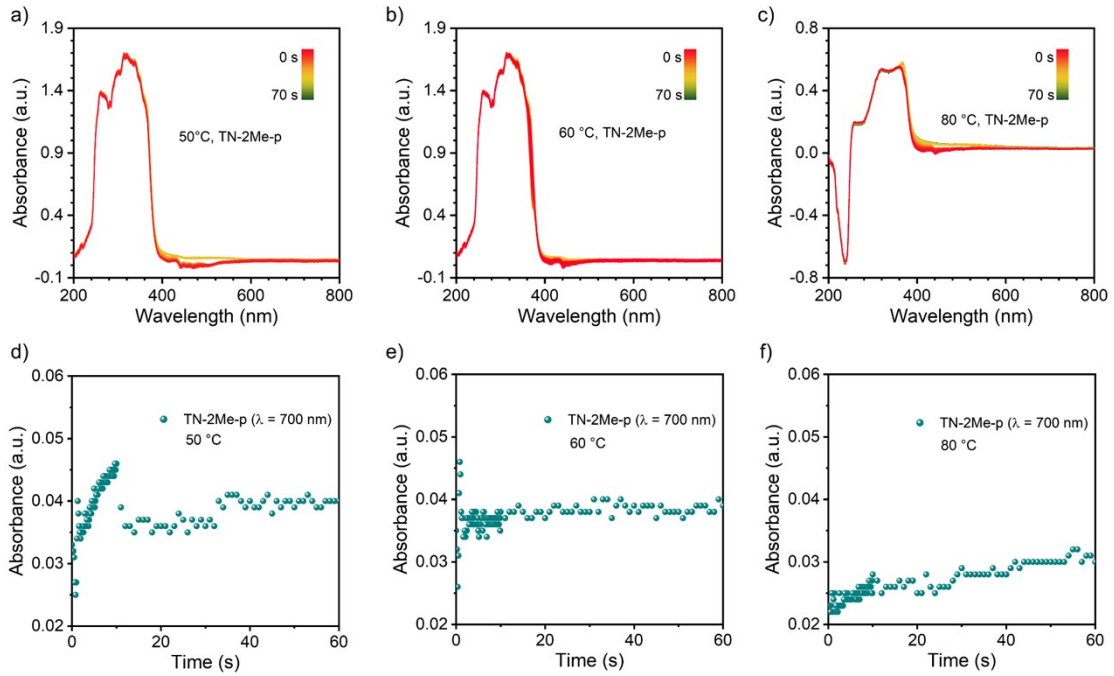


Fig. S17 In situ monitoring of absorption spectra and absorbance decay curves of TN-2Me-p during continuous exposure to 365 nm UV light (500 μW cm^{-2}) and subsequent recovery in air after the UV source is turned off, recorded at temperatures of 50 °C, 60 °C, and 80 °C.

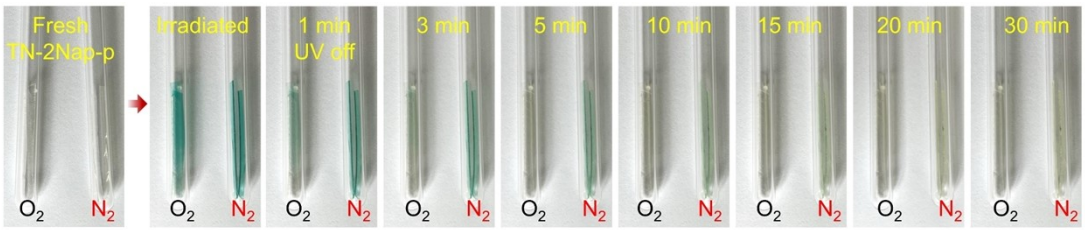


Fig. S18 Photographs of the photochromic recovery process of TN-2Nap-p films in nitrogen and oxygen atmospheres.

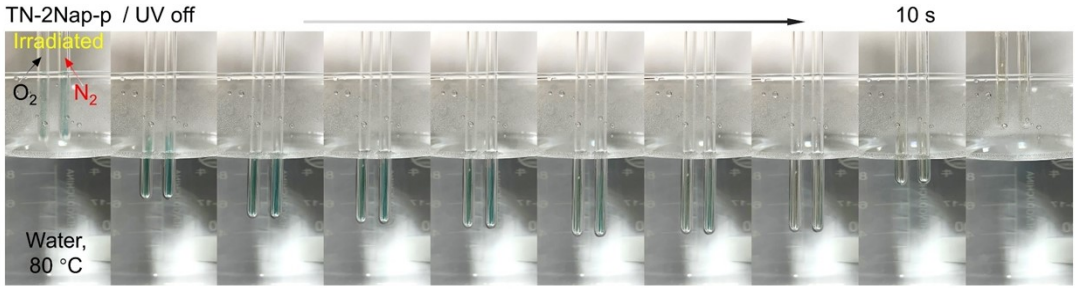


Fig. S19 Rapid fading process of the photochromic TN-2Nap-p films encapsulated in nitrogen and oxygen atmospheres after continuous UV irradiation. Samples were sealed in quartz tubes and immersed in 80°C water, resulting in complete fading within ~10 seconds.

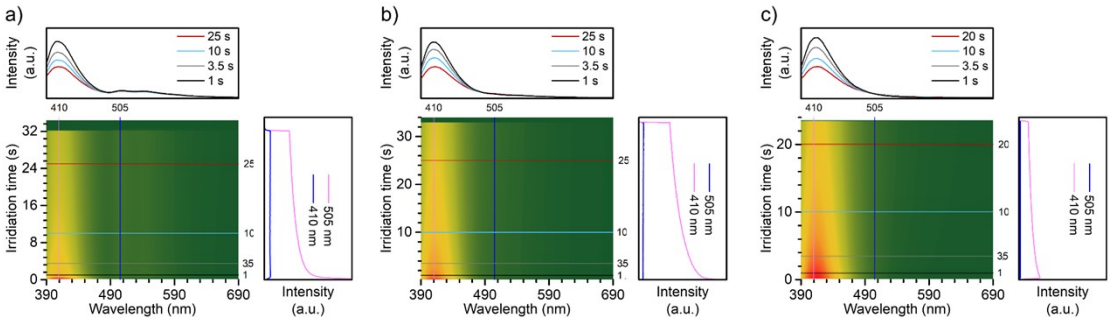


Fig. S20 The in-suit monitoring of changed steady-state PL spectra of TN-PhNap-p with different temperature (a) 25 °C, (b) 60 °C, (c) 100 °C. (PL spectra were collected by QE65 Pro. Mode: high-speed scanning).

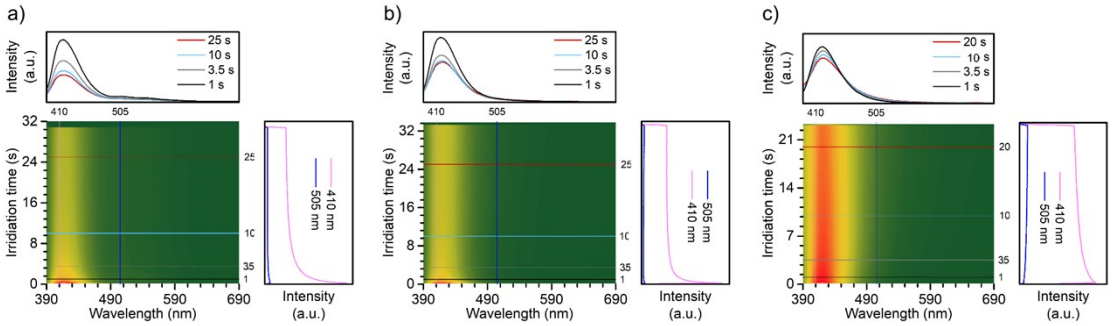


Fig. S21 The in-suit monitoring of changed steady-state PL spectra of TN-2Nap-p with different temperature (a) 25 °C, (b) 60 °C, (c) 100 °C. (PL spectra were collected by QE65 Pro. Mode: high-speed scanning).

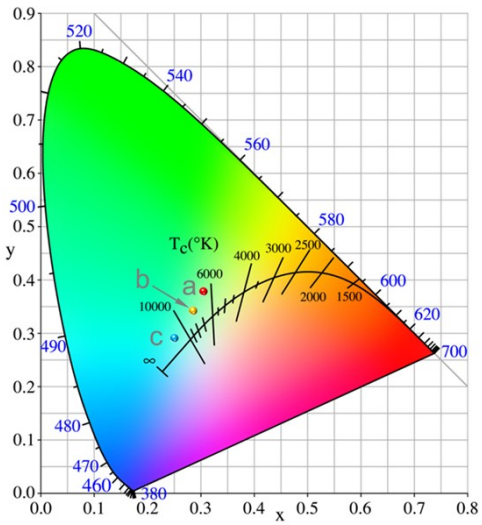


Fig. S22 The CIE 1931 coordinates of TN-2Me-doped PMMA film at various temperatures: 25 °C, a (0.30, 0.38); 60 °C, b (0.29, 0.34); 100 °C, c (0.25, 0.29).

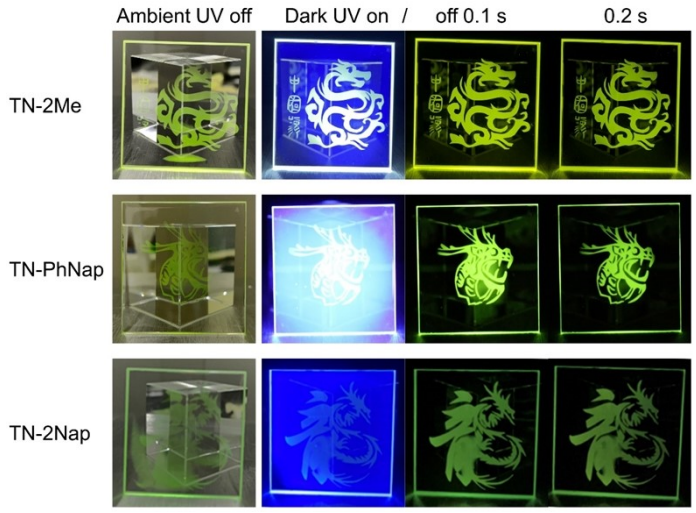


Fig. S23 Phosphorescent outputs of localized activation of the RTP patterns by UV light through masks (film size, 50 mm × 50 mm × 0.7 mm).

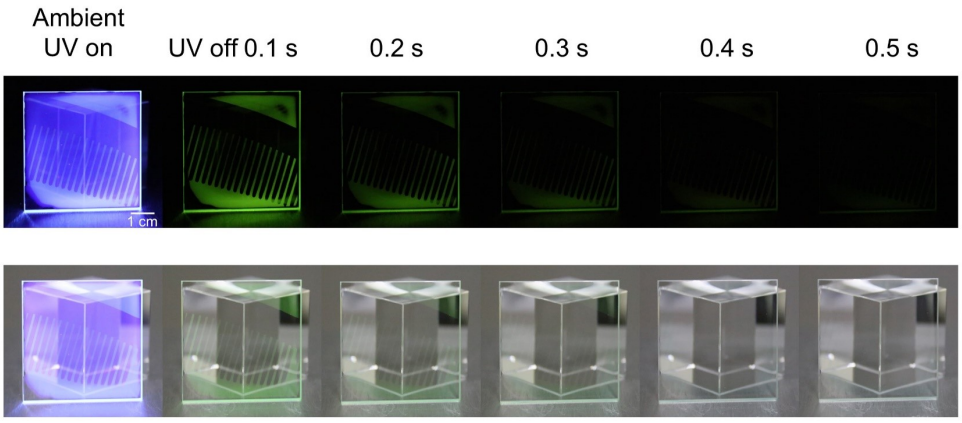


Fig. S24 High-resolution display of thin films (TN-2Me-p).

Table S1. The odd electron density distribution of TN-2Me.

Atomic space	Value	% of sum [a]	% of sum abs [b]	Isosurface graph (odd electron density) [c]
1(C)	0.001164	0.056046	0.056046	
2(C)	0.001827	0.087948	0.087948	
3(C)	0.003037	0.146167	0.146167	
4(C)	0.01114	0.536153	0.536153	
5(C)	0.003844	0.184991	0.184991	
6(C)	0.001175	0.056547	0.056547	
7(S)	0.084771	4.079965	4.079965	
8(C)	0.23509	11.31471	11.314707	
9(C)	0.078312	3.769114	3.769114	
10(S)	0.01917	0.922622	0.922622	
11(C)	0.080741	3.886017	3.886017	
12(C)	0.157698	7.58987	7.58987	
13(C)	0.200896	9.668993	9.668993	
14(C)	0.149674	7.203708	7.203708	
15(C)	0.2104	10.1264	10.126404	
16(C)	0.129132	6.215035	6.215035	
17(C)	0.083426	4.015228	4.015228	
18(C)	0.171122	8.235974	8.235974	
19(C)	0.083807	4.033548	4.033548	
20(C)	0.128407	6.180122	6.180122	
21(N)	0.16885	8.126614	8.126614	
22(C)	0.012108	0.582742	0.582742	
23(C)	0.012123	0.583456	0.583456	
24(H)	7.84E-05	0.003772	0.003772	
25(H)	0.000286	0.01376	0.01376	
26(H)	0.000272	0.013114	0.013114	
27(H)	6.04E-05	0.002909	0.002909	
28(H)	0.001636	0.078729	0.078729	
29(H)	0.003619	0.174181	0.174181	
30(H)	0.003422	0.164695	0.164695	
31(H)	0.002914	0.140228	0.140228	
32(H)	0.001546	0.074425	0.074425	
33(H)	0.001555	0.074844	0.074844	
34(H)	0.002882	0.138706	0.138706	
35(H)	0.007835	0.377081	0.377081	
36(H)	9.77E-05	0.0047	0.0047	
37(H)	0.007836	0.377148	0.377148	
38(H)	0.00784	0.377313	0.377313	
39(H)	9.8E-05	0.004719	0.004719	
40(H)	0.007848	0.377702	0.377702	

[a] Summing up above values: 2.07773952
[b] Summing up absolute value of above values: 2.07773952
[c] The contour value is 0.01 a.u.

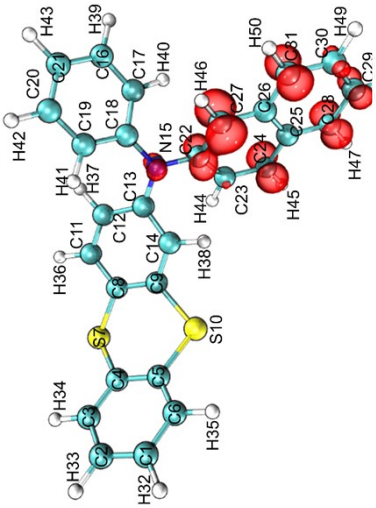
Table S2. The odd electron density distribution of TN-2Me$^{+\cdot}$.

Atomic space	Value	% of sum [a]	% of sum abs [b]	Isosurface graph (odd electron density) [c]
1(C)	0.023607	2.360732	2.268116	
2(C)	0.001806	0.180553	0.173469	
3(C)	0.010272	1.027211	0.986912	
4(C)	0.016959	1.695938	1.629403	
5(C)	0.026588	2.658788	2.554479	
6(C)	-0.0077	-0.77049	-0.74027	
7(S)	0.169452	16.94523	16.28044	
8(C)	0.107517	10.75173	10.32992	
9(C)	0.014422	1.442232	1.385651	
10(S)	0.066702	6.670218	6.408534	
11(C)	-0.01037	-1.03708	-0.99639	
12(C)	0.069963	6.996309	6.721832	
13(C)	0.028835	2.883475	2.770352	
14(C)	0.010493	1.049252	1.008088	
15(C)	0.105713	10.57132	10.15659	
16(C)	0.004982	0.49823	0.478684	
17(C)	0.05397	5.396992	5.185259	
18(C)	0.038255	3.825523	3.675441	
19(C)	0.059373	5.937275	5.704346	
20(C)	0.003956	0.395558	0.38004	
21(N)	0.171807	17.18077	16.50674	
22(C)	0.00099	0.099021	0.095136	
23(C)	0.001025	0.102538	0.098516	
24(H)	-6.3E-05	-0.0063	-0.00605	
25(H)	4.73E-05	0.004733	0.004547	
26(H)	-0.00022	-0.02239	-0.02152	
27(H)	-6.6E-05	-0.00656	-0.00631	
28(H)	-0.0003	-0.03036	-0.02917	
29(H)	-0.00055	-0.05471	-0.05256	
30(H)	-0.00024	-0.02425	-0.0233	
31(H)	-0.00033	-0.03257	-0.03129	
32(H)	-0.00014	-0.01352	-0.01299	
33(H)	-0.00012	-0.0122	-0.01172	
34(H)	-0.00031	-0.03125	-0.03003	
35(H)	0.008773	0.877272	0.842855	
36(H)	6.99E-05	0.00699	0.006716	
37(H)	0.007976	0.797561	0.766271	
38(H)	0.008837	0.883735	0.849065	
39(H)	7.22E-05	0.007222	0.006938	
40(H)	0.007953	0.795285	0.764084	

[a] Summing up above values: 0.99999900
[b] Summing up absolute value of above values: 1.04083260
[c] The contour value is 0.01 a.u.

Table S3. The odd electron density distribution of TN-PhNap.

Atomic space	Value	% of sum [a]	% of sum abs [b]	Isosurface graph (odd electron density) [c]
1(C)	7.79E-05	0.003629	0.003629	
2(C)	0.000112	0.005215	0.005215	
3(C)	0.000296	0.013814	0.013814	
4(C)	0.001113	0.051869	0.051869	
5(C)	0.000299	0.013931	0.013931	
6(C)	6.34E-05	0.002954	0.002954	
7(S)	0.00916	0.426793	0.426793	
8(C)	0.022528	1.049607	1.049607	
9(C)	0.006077	0.283151	0.283151	
10(S)	0.001552	0.072313	0.072313	
11(C)	0.004741	0.220911	0.220911	
12(C)	0.021479	1.000729	1.000729	
13(C)	0.016861	0.785591	0.785591	
14(C)	0.021854	1.018219	1.018219	
15(N)	0.086539	4.032011	4.032011	
16(C)	0.007048	0.328396	0.328396	
17(C)	0.039306	1.831332	1.831332	
18(C)	0.025558	1.190782	1.190782	
19(C)	0.02021	0.941615	0.941615	
20(C)	0.010698	0.498425	0.498425	
21(C)	0.030002	1.397866	1.397866	
22(C)	0.188575	8.786036	8.786036	
23(C)	0.089416	4.166051	4.166051	
24(C)	0.25031	11.6624	11.6624	
25(C)	0.063675	2.966744	2.966744	
26(C)	0.064262	2.994091	2.994091	
27(C)	0.37393	17.4221	17.4221	
28(C)	0.220653	10.28061	10.28061	
29(C)	0.161065	7.504312	7.504312	
30(C)	0.113866	5.305208	5.305208	
31(C)	0.257703	12.00685	12.00685	
32(H)	7.35E-06	0.000342	0.000342	
33(H)	3.01E-05	0.001402	0.001402	
34(H)	2.62E-05	0.001221	0.001221	
35(H)	3.02E-06	0.000141	0.000141	
36(H)	0.000165	0.007668	0.007668	
37(H)	0.000418	0.019464	0.019464	
38(H)	0.001179	0.054951	0.054951	
39(H)	0.000404	0.0188	0.0188	
40(H)	0.003237	0.150816	0.150816	
41(H)	0.000394	0.018341	0.018341	
42(H)	0.000336	0.015661	0.015661	
43(H)	0.00082	0.038194	0.038194	
44(H)	0.001726	0.080414	0.080414	
45(H)	0.005724	0.266683	0.266683	
46(H)	0.006875	0.320341	0.320341	
47(H)	0.004709	0.219382	0.219382	

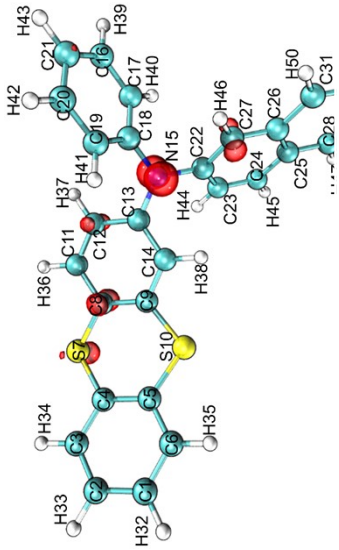


48(H)	0.003524	0.164196	0.164196
49(H)	0.002288	0.106585	0.106585
50(H)	0.005406	0.251857	0.251857

[a] Summing up above values: 2.14629889
[b] Summing up absolute value of above values: 2.14629889
[c] The contour value is 0.01 a.u.

Table S4. The odd electron density distribution of TN-PhNap$^{+\cdot}$.

Atomic space	Value	% of sum [a]	% of sum abs [b]	Isosurface graph (odd electron density) [c]
1(C)	0.016108	1.610834	1.334167	
2(C)	0.000142	0.014183	0.011747	
3(C)	0.008779	0.877857	0.727081	
4(C)	0.011543	1.154332	0.956071	
5(C)	0.016947	1.694727	1.403651	
6(C)	-0.00568	-0.56776	-0.47025	
7(S)	0.139489	13.94889	11.55311	
8(C)	0.11123	11.12296	9.212543	
9(C)	0.001101	0.110074	0.091168	
10(S)	0.037579	3.757891	3.112458	
11(C)	-0.0189	-1.88956	-1.56502	
12(C)	0.080879	8.087864	6.69874	
13(C)	0.015653	1.565282	1.296438	
14(C)	0.033246	3.324616	2.7536	
15(N)	0.219465	21.9465	18.1771	
16(C)	-0.01411	-1.41074	-1.16844	
17(C)	0.04425	4.424965	3.664959	
18(C)	0.002373	0.237258	0.196508	
19(C)	0.043887	4.388745	3.63496	
20(C)	-0.01364	-1.36359	-1.12939	
21(C)	0.056028	5.602834	4.640525	
22(C)	0.010603	1.060331	0.878214	
23(C)	0.018983	1.898301	1.57226	
24(C)	-0.00891	-0.89123	-0.73815	
25(C)	0.032417	3.241686	2.684913	
26(C)	-0.00832	-0.83219	-0.68926	
27(C)	0.101139	10.11393	8.376818	
28(C)	-0.0114	-1.13994	-0.94415	
29(C)	0.054172	5.417162	4.486742	
30(C)	-0.01794	-1.79426	-1.48609	
31(C)	0.046568	4.656847	3.857015	
32(H)	-7.6E-05	-0.00756	-0.00626	
33(H)	9.67E-05	0.009667	0.008006	
34(H)	-0.00015	-0.01543	-0.01278	
35(H)	-3.9E-05	-0.00387	-0.0032	
36(H)	-2.3E-05	-0.00233	-0.00193	
37(H)	-0.00086	-0.08576	-0.07103	
38(H)	-0.00046	-0.04554	-0.03772	
39(H)	0.0003	0.030037	0.024878	
40(H)	-0.00059	-0.05854	-0.04849	
41(H)	-0.00057	-0.0566	-0.04688	
42(H)	0.000339	0.033857	0.028042	
43(H)	-0.00013	-0.01317	-0.01091	
44(H)	-0.00031	-0.03074	-0.02546	
45(H)	0.000315	0.031481	0.026074	
46(H)	-0.00111	-0.11111	-0.09202	
47(H)	4.15E-05	0.004145	0.003433	

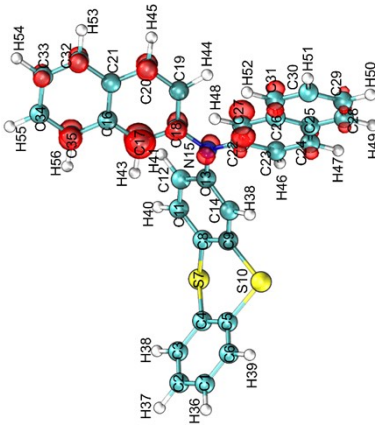


48(H)	-0.00013	-0.01289	-0.01068
49(H)	0.000013	0.0013	0.001077
50(H)	-0.00036	-0.03576	-0.02962

[a] Summing up above values: 1.00000011
[b] Summing up absolute value of above values: 1.20737105
[c] The contour value is 0.01 a.u.

Table S5. The odd electron density distribution of TN-2Nap.

Atomic space	Value	% of sum [a]	% of sum abs [b]	Isosurface graph (odd electron density) [c]
1(C)	6.77E-05	0.003117	0.003117	
2(C)	0.00015	0.006881	0.006881	
3(C)	0.000271	0.012462	0.012462	
4(C)	0.000991	0.045606	0.045606	
5(C)	0.000219	0.010066	0.010066	
6(C)	5.36E-05	0.002467	0.002467	
7(S)	0.007347	0.338026	0.338026	
8(C)	0.019587	0.901217	0.901217	
9(C)	0.005995	0.275858	0.275858	
10(S)	0.0015	0.069012	0.069012	
11(C)	0.004108	0.18901	0.18901	
12(C)	0.027485	1.264617	1.264617	
13(C)	0.017557	0.807834	0.807834	
14(C)	0.019028	0.87552	0.87552	
15(N)	0.091887	4.227801	4.227801	
16(C)	0.044727	2.057951	2.057951	
17(C)	0.253927	11.68344	11.68344	
18(C)	0.138847	6.388491	6.388491	
19(C)	0.062406	2.871372	2.871372	
20(C)	0.137442	6.323851	6.323851	
21(C)	0.046675	2.147563	2.147563	
22(C)	0.087255	4.014704	4.014704	
23(C)	0.041336	1.901912	1.901912	
24(C)	0.093047	4.28119	4.28119	
25(C)	0.032356	1.488714	1.488714	
26(C)	0.030244	1.391556	1.391556	
27(C)	0.178942	8.233328	8.233328	
28(C)	0.085261	3.922955	3.922955	
29(C)	0.078224	3.599154	3.599154	
30(C)	0.047225	2.172894	2.172894	
31(C)	0.110194	5.070139	5.070139	
32(C)	0.126577	5.823967	5.823967	
33(C)	0.114708	5.277847	5.277847	
34(C)	0.068522	3.152772	3.152772	
35(C)	0.162238	7.464731	7.464731	
36(H)	4.58E-06	0.000211	0.000211	
37(H)	2.72E-05	0.001252	0.001252	
38(H)	2.55E-05	0.001173	0.001173	
39(H)	2.63E-06	0.000121	0.000121	
40(H)	0.000278	0.012779	0.012779	
41(H)	0.001952	0.089823	0.089823	
42(H)	0.000677	0.031141	0.031141	
43(H)	0.004663	0.214531	0.214531	
44(H)	0.002262	0.104067	0.104067	
45(H)	0.00329	0.151382	0.151382	
46(H)	0.000837	0.038525	0.038525	
47(H)	0.002206	0.10148	0.10148	

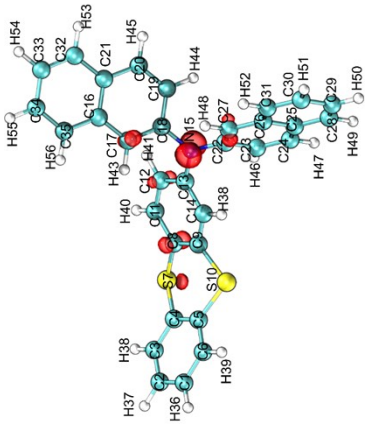


48(H)	0.003719	0.17111	0.17111
49(H)	0.001829	0.084141	0.084141
50(H)	0.001801	0.082883	0.082883
51(H)	0.000929	0.04276	0.04276
52(H)	0.00237	0.109052	0.109052
53(H)	0.00269	0.123792	0.123792
54(H)	0.00266	0.122369	0.122369
55(H)	0.001321	0.060785	0.060785
56(H)	0.003447	0.158596	0.158596

[a] Summing up above values: 2.17338907
[b] Summing up absolute value of above values: 2.17338907
[c] The contour value is 0.01 a.u.

Table S6. The odd electron density distribution of TN-2Nap$^{+\cdot}$.

Atomic space	Value	% of sum [a]	% of sum abs [b]	Isosurface graph (odd electron density) [c]
1(C)	0.011792	1.179191	0.939829	
2(C)	0.000301	0.03007	0.023967	
3(C)	0.006802	0.6802	0.542127	
4(C)	0.009433	0.943256	0.751786	
5(C)	0.012465	1.246495	0.993471	
6(C)	-0.00421	-0.42071	-0.33531	
7(S)	0.116157	11.61564	9.2578	
8(C)	0.100667	10.06665	8.023239	
9(C)	0.000145	0.014456	0.011521	
10(S)	0.029113	2.911248	2.320298	
11(C)	-0.0211	-2.11034	-1.68197	
12(C)	0.076987	7.698665	6.135925	
13(C)	0.012751	1.275111	1.016278	
14(C)	0.033954	3.395363	2.706144	
15(N)	0.222458	22.24577	17.73014	
16(C)	-0.00807	-0.80723	-0.64337	
17(C)	0.095346	9.534588	7.599177	
18(C)	0.010167	1.016683	0.810308	
19(C)	0.020204	2.020425	1.610302	
20(C)	-0.01129	-1.12925	-0.90002	
21(C)	0.03177	3.176947	2.532063	
22(C)	0.005867	0.586717	0.467621	
23(C)	0.020583	2.058329	1.640512	
24(C)	-0.01177	-1.17722	-0.93826	
25(C)	0.031683	3.168296	2.525169	
26(C)	-0.00747	-0.74685	-0.59525	
27(C)	0.094386	9.438538	7.522624	
28(C)	-0.01239	-1.23916	-0.98763	
29(C)	0.049945	4.994497	3.980672	
30(C)	-0.01667	-1.66707	-1.32868	
31(C)	0.041821	4.18213	3.333206	
32(C)	-0.0125	-1.25028	-0.99649	
33(C)	0.049753	4.975263	3.965342	
34(C)	-0.01668	-1.66818	-1.32956	
35(C)	0.041908	4.190812	3.340125	
36(H)	-0.00006	-0.006	-0.00478	
37(H)	0.000101	0.010055	0.008014	
38(H)	-0.00011	-0.01139	-0.00908	
39(H)	-3.5E-05	-0.00353	-0.00281	
40(H)	5.9E-05	0.005899	0.004701	
41(H)	-0.0009	-0.08973	-0.07151	
42(H)	-0.00048	-0.04773	-0.03804	
43(H)	-0.00111	-0.11099	-0.08846	
44(H)	-0.0003	-0.03021	-0.02408	
45(H)	0.000289	0.028926	0.023054	
46(H)	-0.00032	-0.03208	-0.02557	
47(H)	0.000307	0.030731	0.024493	



48(H)	-0.00099	-0.09923	-0.07909
49(H)	4.9E-05	0.004898	0.003904
50(H)	-0.00011	-0.01113	-0.00887
51(H)	1.67E-05	0.001669	0.00133
52(H)	-0.00033	-0.03334	-0.02657
53(H)	5.09E-05	0.005086	0.004054
54(H)	-0.00011	-0.01129	-0.009
55(H)	1.74E-05	0.001735	0.001383
56(H)	-0.00031	-0.03143	-0.02505

[a] Summing up above values: 1.00000120
[b] Summing up absolute value of above values: 1.25468843
[c] The contour value is 0.01 a.u.

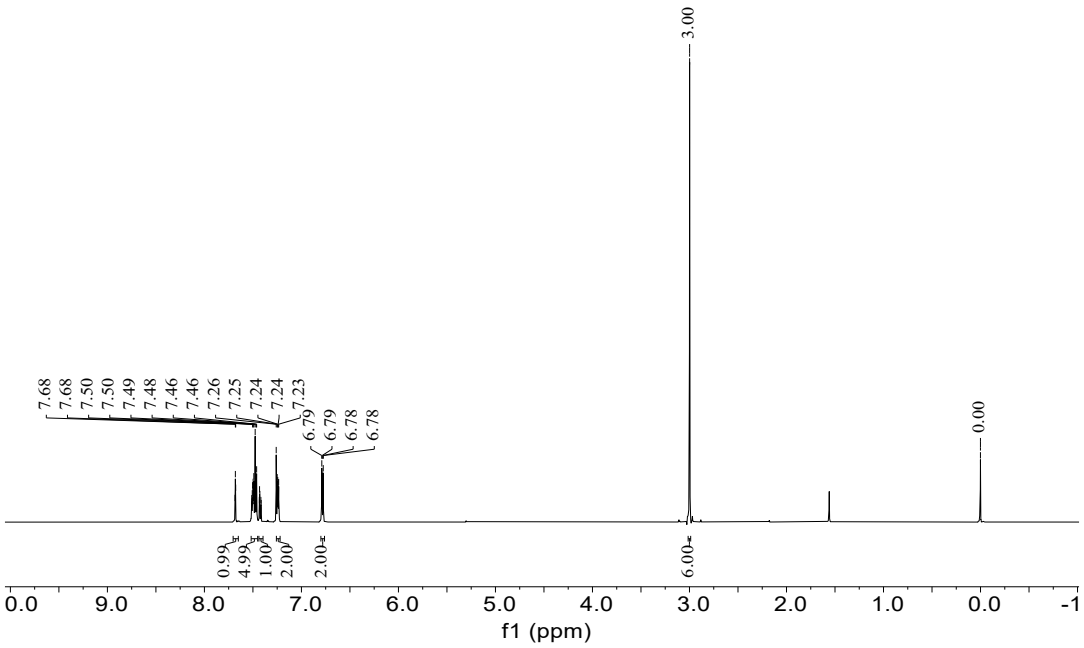


Fig. S25 The ^{1}H NMR spectrum of compound TN-2Me in $CDCl_3$

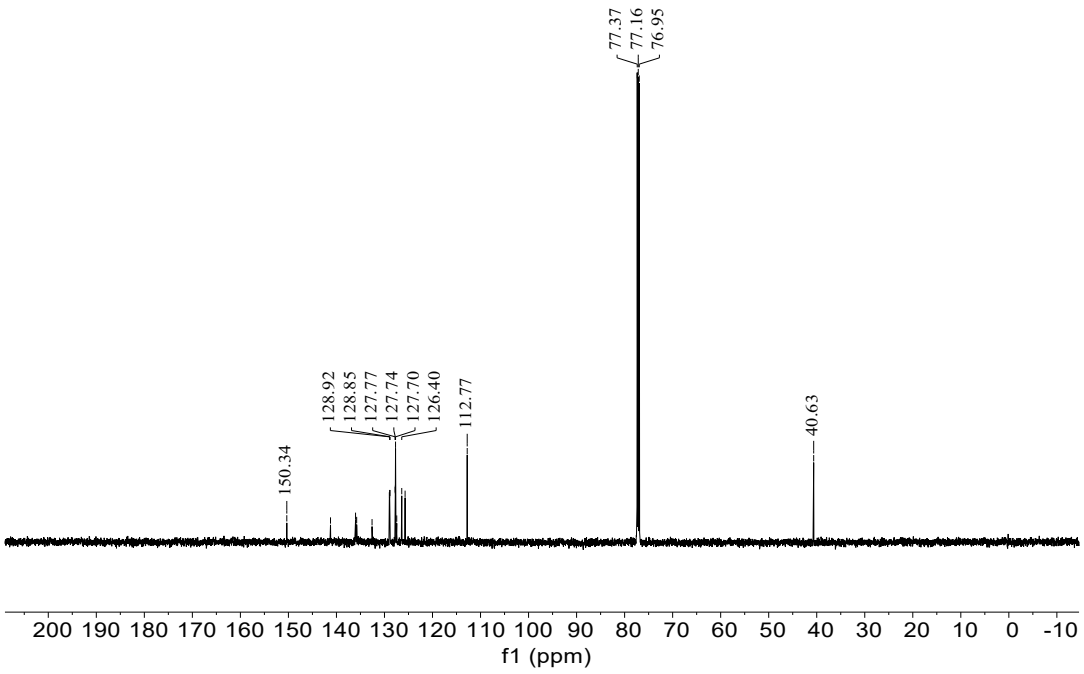


Fig. S26 The ^{13}C NMR spectrum of compound TN-2Me in $CDCl_3$

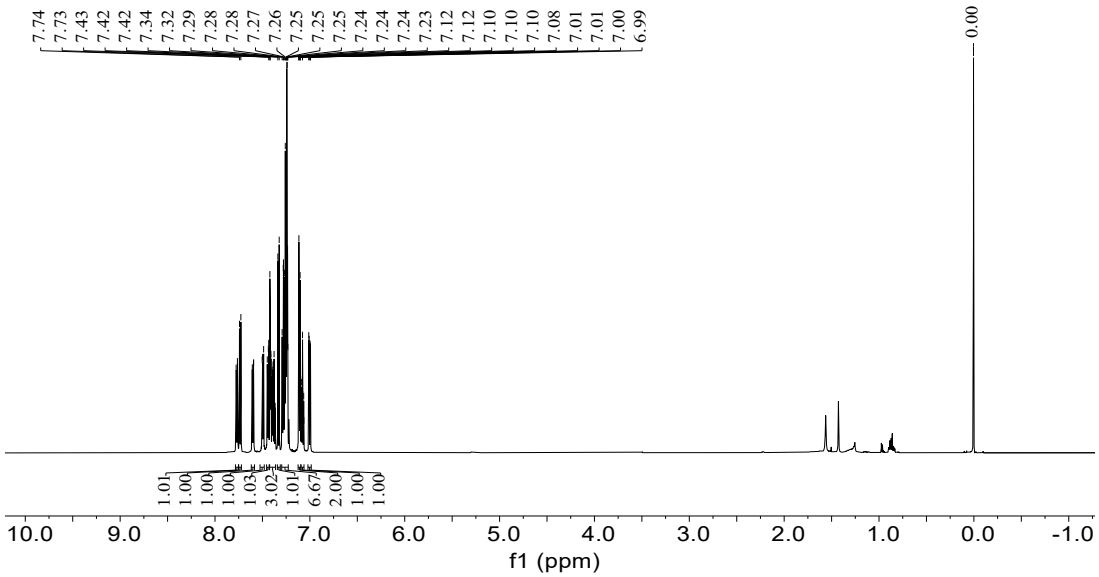


Fig. S27 The ^{1}H NMR spectrum of compound TN-PhNap in $CDCl_3$

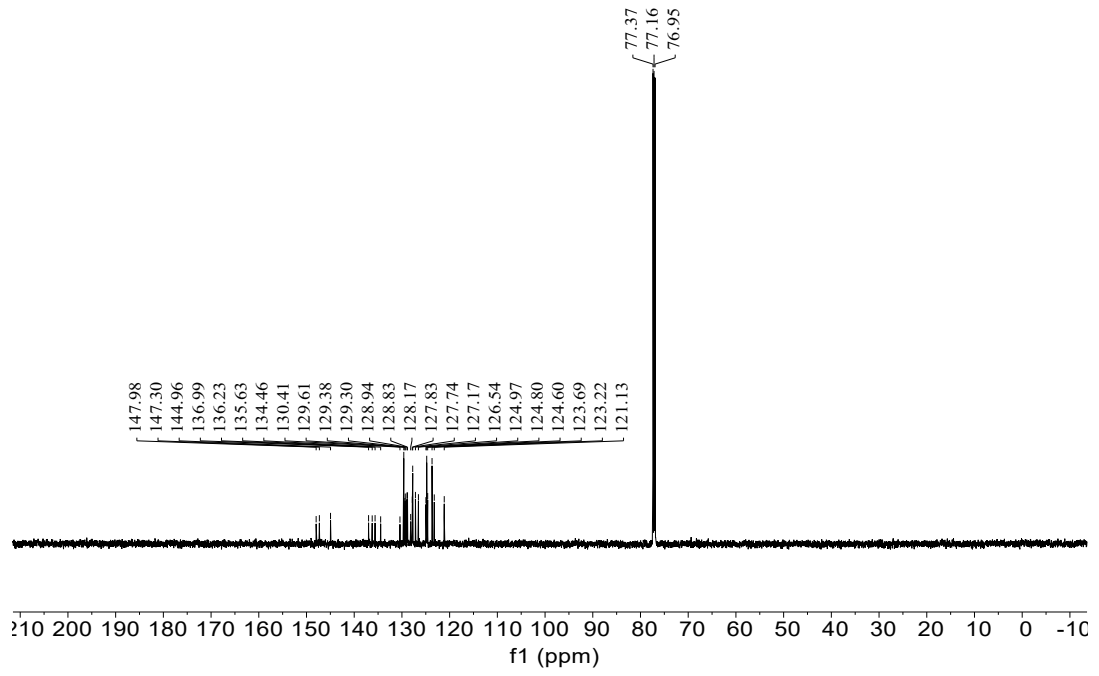


Fig. S28 The ^{13}C NMR spectrum of compound TN-PhNap in $CDCl_3$

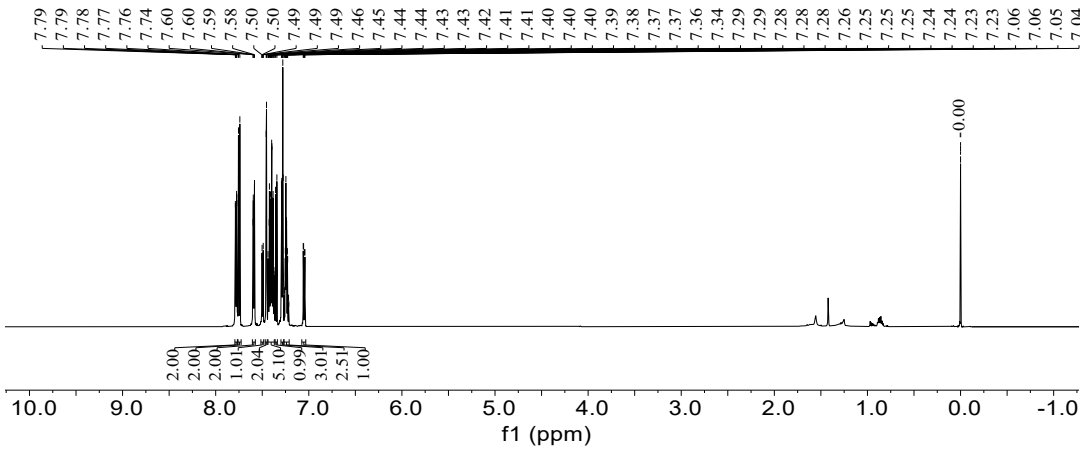


Fig. S29 The ^{1}H NMR spectrum of compound TN-2Nap in $CDCl_3$

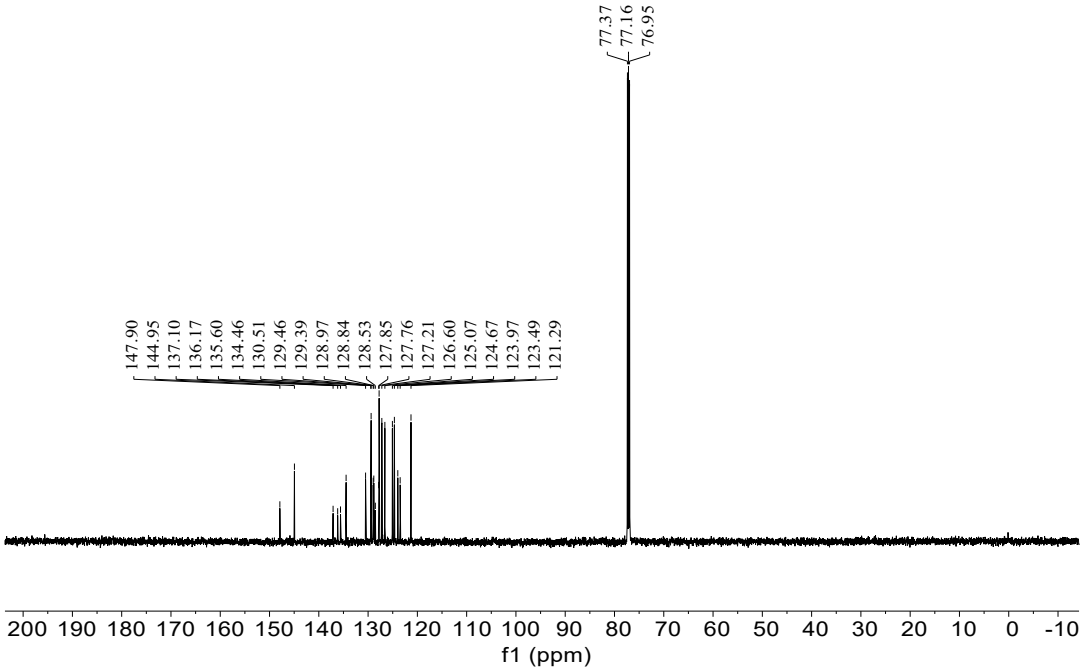


Fig. S30 The ^{13}C NMR spectrum of compound TN-2Nap in $CDCl_3$

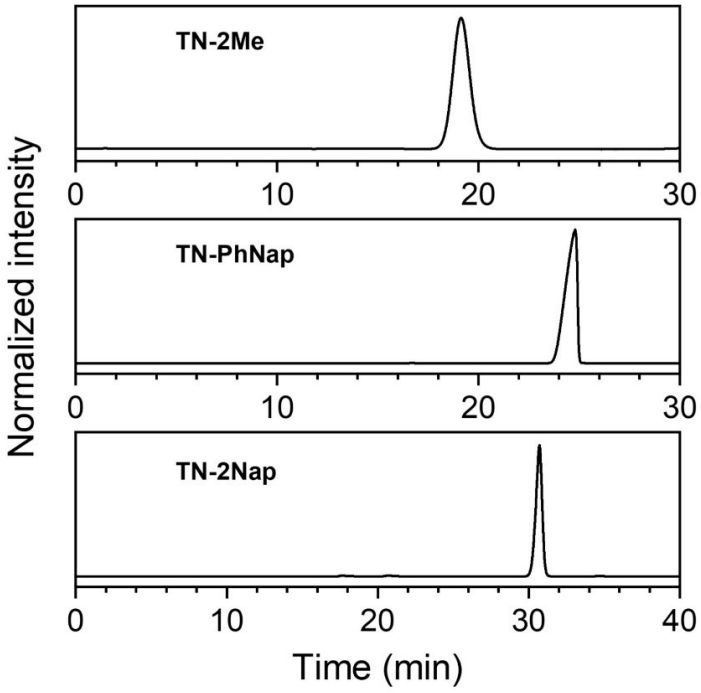


Fig. S31 High performance liquid chromatogram (HPLC) spectra of TN-2Me, TN-PhNap and TN-2Nap.

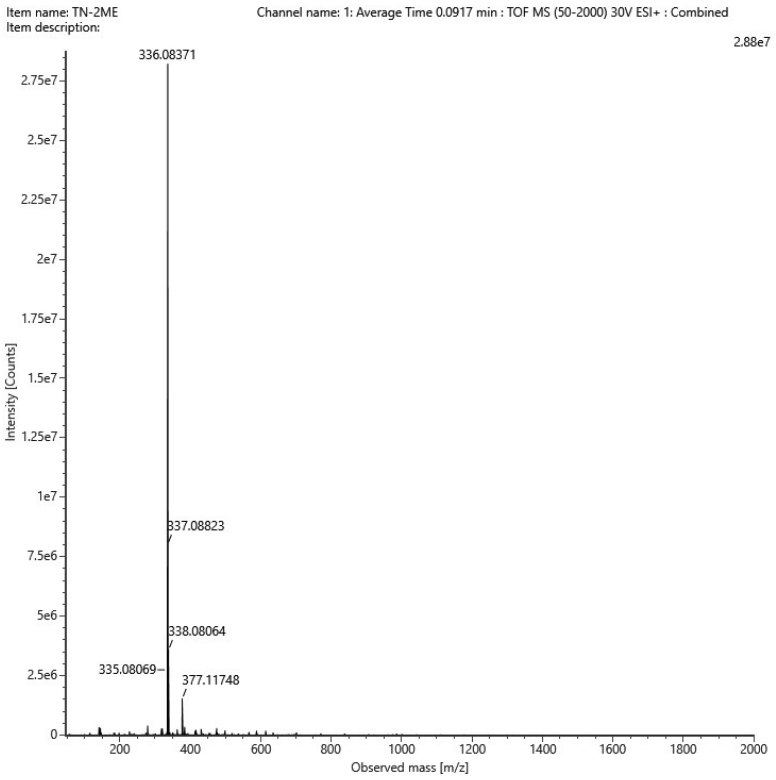


Fig. S32 The HRMS (FTMS-ESI) spectrum of TN-2Me.

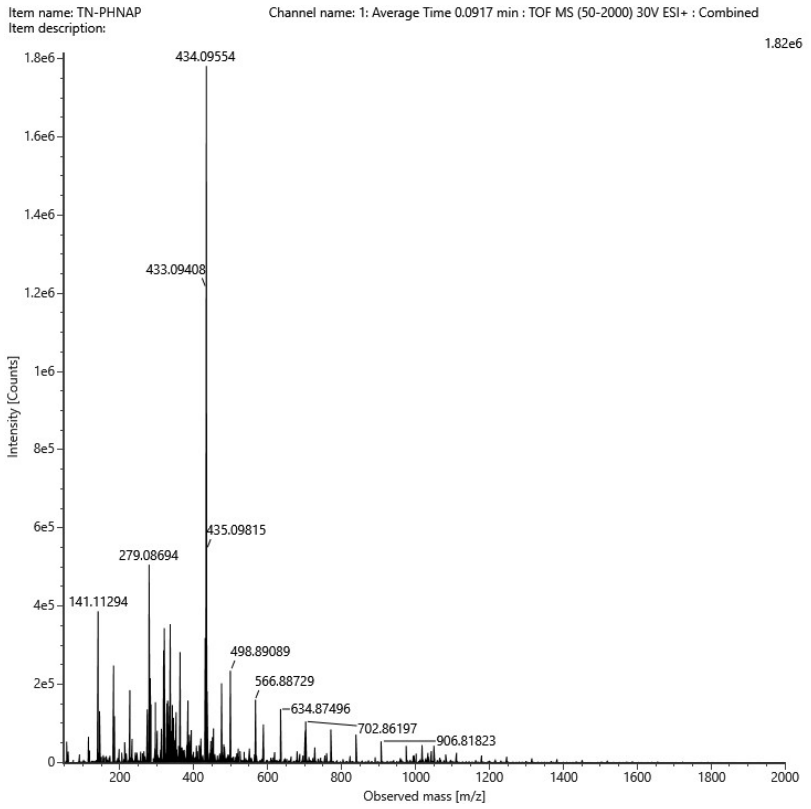


Fig. S33 The HRMS (FTMS-ESI) spectrum of TN-PhNap.

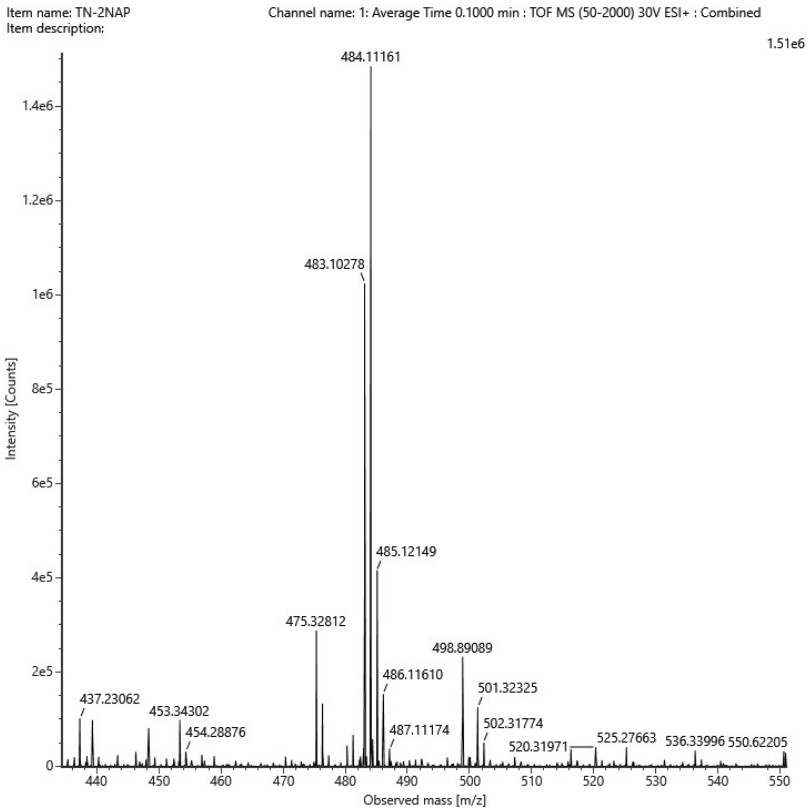


Fig. S34 The HRMS (FTMS-ESI) spectrum of TN-2Nap.

Supplementary Video 1.

60 °C hot water erases the photochromic pattern of the TN-2Nap-p film.

Supplementary Video 2.

80 °C hot water erases the photochromic pattern of the TN-2Nap-p film.

Supplementary Video 3.

TN-2Nap-p film immersed in liquid nitrogen, followed by UV irradiation, shows bright green long afterglow, but no photochromism is observed. Repeating the process, the film's color remains unchanged.

Supplementary Video 4.

TN-2Nap-p film immersed in ~25 °C water after continuous UV excitation shows that the blue color of the film does not fade immediately, in stark contrast to the rapid erasure of the photochromic pattern observed in 60 °C and 80 °C hot water.

Supplementary Video 5.

Afterglow pattern of TN-2Me-p film.

Supplementary Video 6.

Afterglow pattern of TN-PhNap-p film.

Supplementary Video 7.

Photo-induced RTP of the flexible TN-2Me-p.

Supplementary Video 8.

Photochromism and afterglow of TN-2Nap-p film in 60 °C water, with demonstration of repeatability. Repeatedly excited the sample 7 times, with 4 on/off cycles in ambient light and 3 in darkness. The afterglow and photochromic properties of the material showed no significant changes.

References

1. Y. Xiao, M. Shen, J. Li, H. Wang, H. Sun, Yunfei He, R. Huang, T. Yu and W. Huang. Thermally activated photochromism: realizing temperature-gated triphenylethylene photochromic materials. *Adv. Funct. Mater*., 2024, 2312930. DOI: 10.1002/adfm.202312930

2. Y. Sun, X. Yang, Z. Feng, B. Liu, D. Zhong, J. Zhang, G. Zhou and Z. Wu. Highly efficient deep-red organic light-emitting devices based on asymmetric iridium(III) complexes with the thianthrene 5,5,10,10-tetraoxide moiety. *ACS Appl. Mater. Interfaces*, 2019, **11**, 26152-26164.

3. W. Qiu, X. Cai, M. Li, L. Wang, Y. He, W. Xie, Z. Chen, M. Liu and S. Su. Dynamic adjustment of emission from both singlets and triplets: the role of excited state conformation relaxation and charge transfer in phenothiazine derivates. *J. Mater. Chem. C*., 2021, **9**, 1378-1386.

4. C. Burkhart and G. Haberhauer. A Light- and electricity-driven molecular pushing motor. *Eur. J. Org. Chem*. 2017, 1308-1317.