

Supplementary Information

Radical-Enhanced Photo-Activated Ultralong Organic Phosphorescence

Yuefei Wang,¹ Zaiyong Zhang,² Huanyu Yang,¹ Shunjie Li,¹ Xiaokang Yao,³ Huili Ma,³ Shengchen Yang,⁴ Suzhi Cai,^{1*} Zhongfu An,^{3, 5*} and Wei Huang^{1, 3, 5, 6*}

¹Strait Institute of Flexible Electronics (SIFE, Future Technologies), Fujian Key Laboratory of Flexible Electronics, Fujian Normal University and Strait Laboratory of Flexible Electronics (SLoFE), Fuzhou, Fujian 350117, China.

²Pharmaceutical Analytical & Solid-State Chemistry Research Center, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China.

³State Key Laboratory of Flexible Electronics (LoFE) and Institute of Advanced Materials (IAM), Nanjing Tech University (Nanjing Tech), Nanjing 211816, China.

⁴Department of Materials Chemistry, Huzhou University, Huzhou 313000, China

⁵Henan Institute of Flexible Electronics (HIFE) and School of Flexible Electronics (SoFE), Henan University, 379 Mingli Road, Zhengzhou 450046, China.

⁶State Key Laboratory of Flexible Electronics (LOFE) & Institute of Flexible Electronics (IFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xi'an 710072, China.

*Correspondence to: ifeszhcai@fjnu.edu.cn; iamzfan@njtech.edu.cn; vc@nwpu.edu.cn

Supplementary Methods

Electrochemical Analysis

Cyclic voltammetric (CV) studies were conducted using an Shanghai CH Instruments Co., Ltd. CHI760E potentiostat in a typical three-electrode cell with a glassy platinum-carbon working electrode, a platinum wire counter electrode, and a silver/silver chloride (Ag/AgCl) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in dichloromethane. The energy level of the HOMO was estimated according to the onset voltages of redox peaks in cyclic voltammetry analysis.

Spectroelectrochemistry (SEC) spectra

Spectroelectrochemistry measurements by recording the UV-vis absorbance spectral changes upon voltage changes were measured using N₂ bubbled samples in dry dichloromethane in a cuvette with an optical path length of 1 cm. To a sample solution containing a supporting electrolyte (0.05 M, Bu₄NPF₆), continuous voltage was applied using Pt-carbon, Pt wire, and silver/silver chloride (Ag/AgCl) electrodes as working, counter, and reference electrodes, respectively. The applied voltage was controlled by a CHI760E potentiostat from Shanghai CH Instruments Co., Ltd. The resulting UV-vis absorbance differences were recorded on a HITACHI UV5700.

Preparation of 1 wt.% r-MOP-1 in PVAc film and 1 wt.% r-MOP-1 in PLA film

297 mg PVAc or PLA was added into 3 mL glass bottle, and 1.0 mL chloroform was injected, then stirred at 40°C for 1 h. 3 mg r-MOP in 1.5 mL chloroform solution was photo-activated by 302 nm UV lamp (4.04 mW/cm²) for 4.5 minutes, then doped into PVAc or PLA solution. The resultant solution was subsequently poured onto a pristine glass plate, and the solvent slowly evaporated at room temperature overnight, then the resultant PVAc or PLA film was further dried at 50°C.

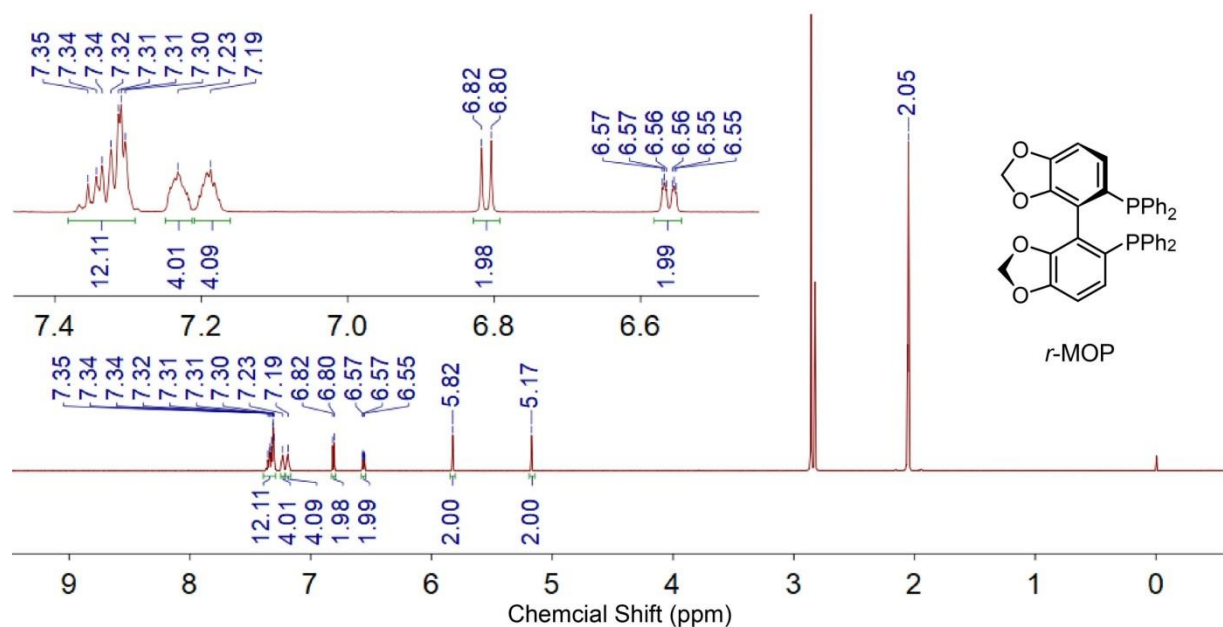
Preparation of 1 wt.% MOPY-1 in PMMA film

297 mg PMMA was added into 3 mL glass bottle, and 1.0 mL chloroform was injected, then stirred at 40°C for 1 h. 3 mg MOPY in 1.5 mL chloroform solution was photo-activated by 302 nm UV lamp (4.04 mW/cm²) for 2 minutes, then doped into PMMA solution. The resultant solution was subsequently poured onto a pristine glass plate, and the solvent slowly evaporated at room temperature overnight, then the PMMA film was further dried at 50°C.

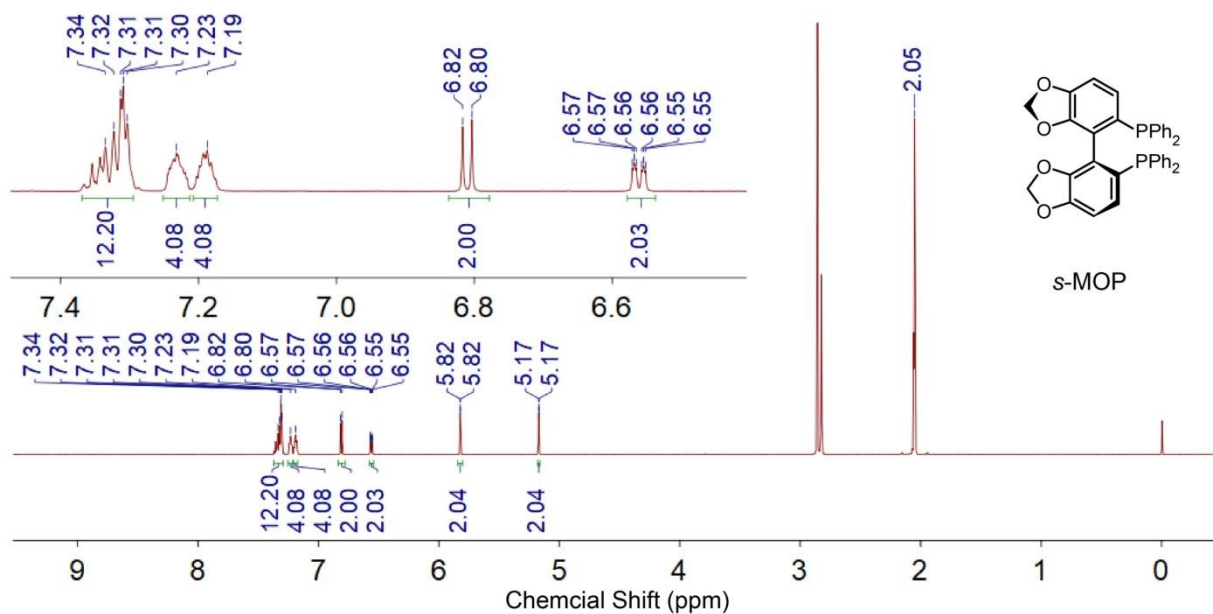
Preparation of 1 wt.% s-OBP-1 in PMMA film

297 mg PMMA was added into 3 mL glass bottle, and 1.0 mL chloroform was injected, then stirred at 40°C for 1 h. 3 mg s-OBP in 1.5 mL chloroform solution was photo-activated by 302 nm UV lamp (4.04

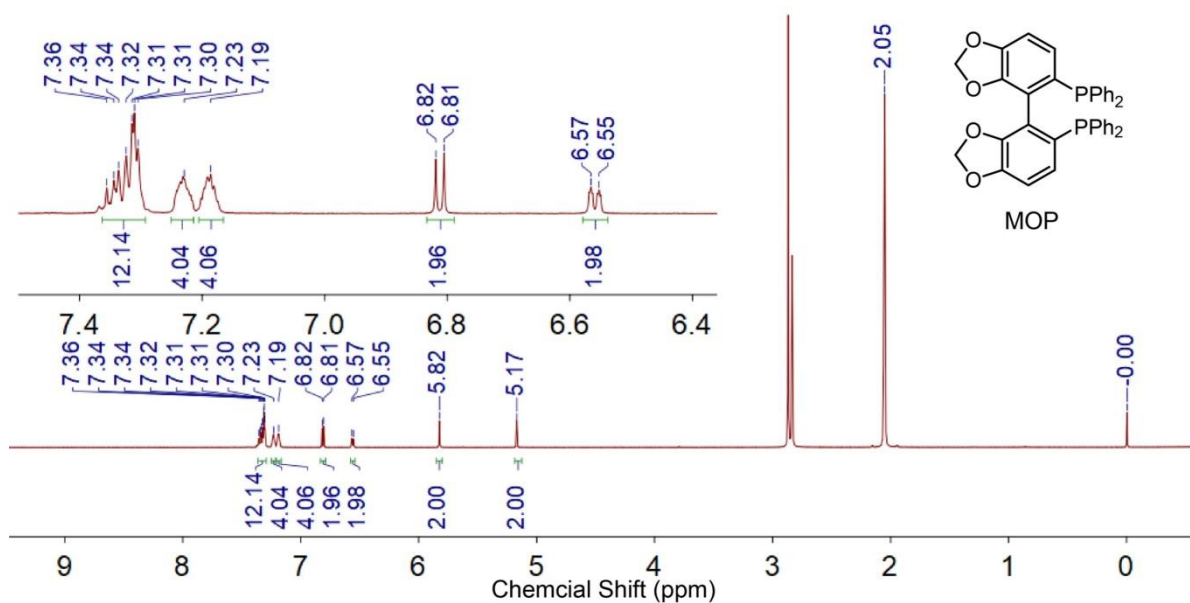
mW/cm²) for 5 minutes, then doped into PMMA solution. The resultant solution was subsequently poured onto a pristine glass plate, and the solvent slowly evaporated at room temperature overnight, then the PMMA film was further dried at 50°C.



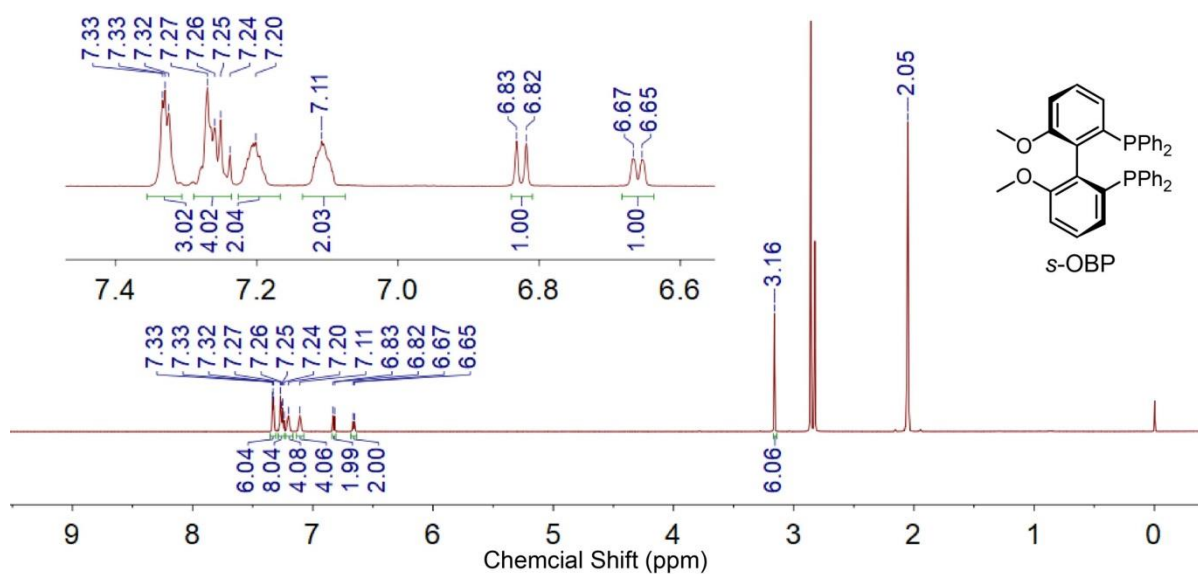
Supplementary Figure 1. ¹H NMR (600 MHz, acetone-d₆) spectrum of *r*-MOP molecule.



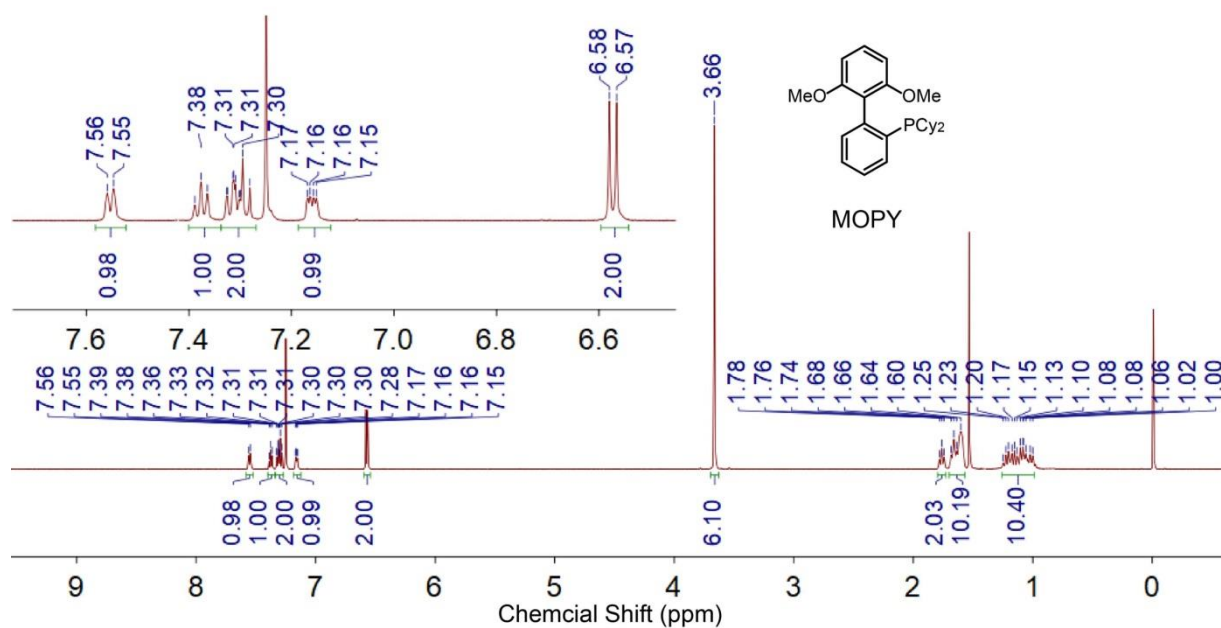
Supplementary Figure 2. ¹H NMR (600 MHz, acetone-d₆) spectrum of *s*-MOP molecule.



Supplementary Figure 3. ^1H NMR spectrum (600 MHz, acetone- d_6) of MOP molecule.



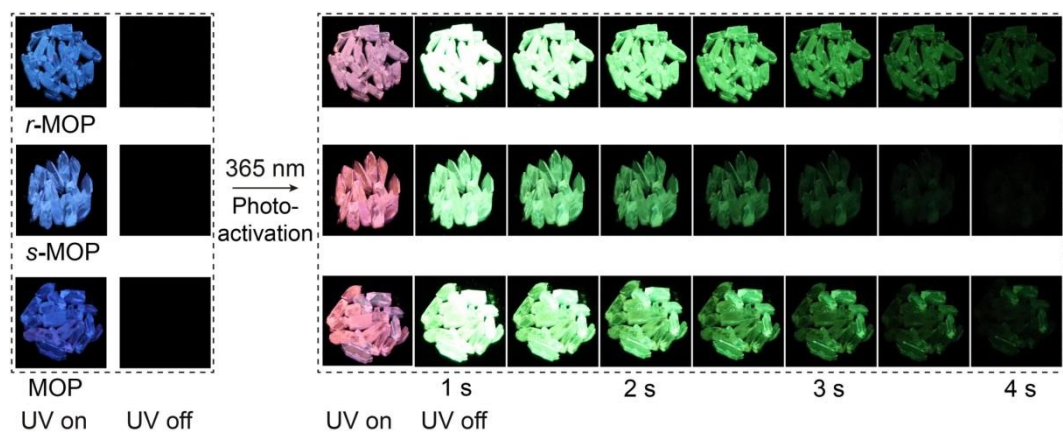
Supplementary Figure 4. ^1H NMR spectrum (600 MHz, acetone- d_6) of s-OBP molecule.



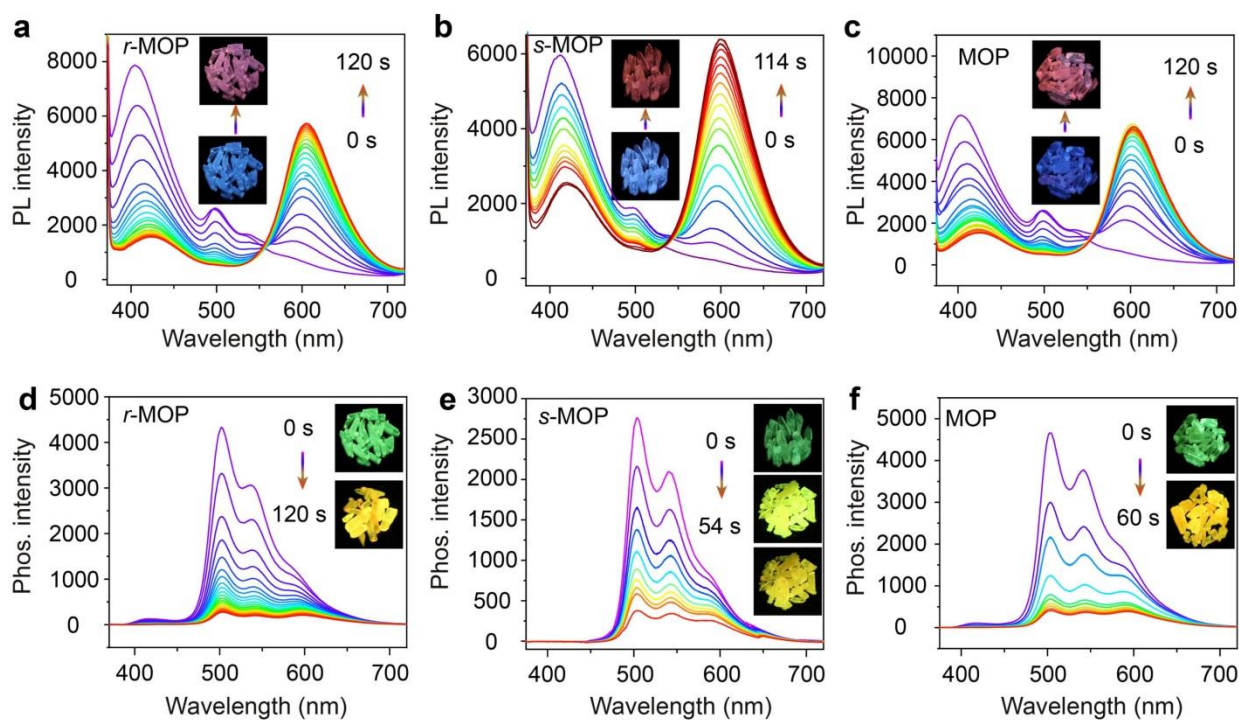
Supplementary Figure 5. ¹H NMR spectrum (600 MHz, CDCl₃) of MOPY molecule.

Supplementary Table 1. Crystal data for r-MOP, s-MOP, MOP, s-OBP, and MOPY.

Name	r-MOP	s-MOP	MOP	s-OBP	MOPY
Formula	C ₃₈ H ₂₈ O ₄ P ₂	C ₃₈ H ₂₈ O ₄ P ₂	C ₃₈ H ₂₈ O ₄ P ₂	C ₃₈ H ₃₂ O ₂ P ₂	C ₂₆ H ₃₅ O ₂ P
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space Group	P 21	P 21	P 21	P 1	Pbca
Cell Lengths (Å)	a 10.370(2) b 15.751(3) c 18.634(4)	a 10.397(4) b 15.741(6) c 18.594(6)	a 10.3431(3) b 15.6673(7) c 18.5549(9)	a 12.0712(4) b 8.387(2) c 15.5822(5)	a 16.2659(15) b 15.6008(13) c 18.0003(13)
Cell Angles (°)	α 90 β 90 γ 90	α 90 β 90 γ 90	α 90 β 90 γ 90	α 90 β 95.601 γ 90	α 90 β 90 γ 90
Cell Volume (Å ³)	3043.7(11)	3043.2(19)	3006.8(2)	1504.83(8)	4567.8(7)
Z	4	4	4	2	8
Density (g/cm ³)	1.335	1.333	1.349	1.286	1.194
F (000)	1272	1272	1272.0	612.0	1776.0
h _{max} , k _{max} , l _{max}	12, 17, 23	12, 19, 23	12, 19, 23	15, 10, 19	20, 19, 22
T _{min} , T _{max}	0.4908, 0.4290	0.6547, 0.7453	0.366, 0.491	0.370, 0.491	0.833, 0.928
Goof	1.053	1.1046	1.035	1.038	1.034
Refinement parameters	R1 = 0.0886, wR2 = 0.1024	R1 = 0.0983, wR2 = 0.1168	R1 = 0.0464, wR2 = 0.1060	R1 = 0.0407, wR2 = 0.0986	R1 = 0.0545, wR2 = 0.1423
CCDC	2401648	2401643	2401644	2401645	2401651



Supplementary Figure 6. Photographs of r-MOP, s-MOP, and MOP crystals before and after the photoactivation taken under 365 nm lamp on and off.

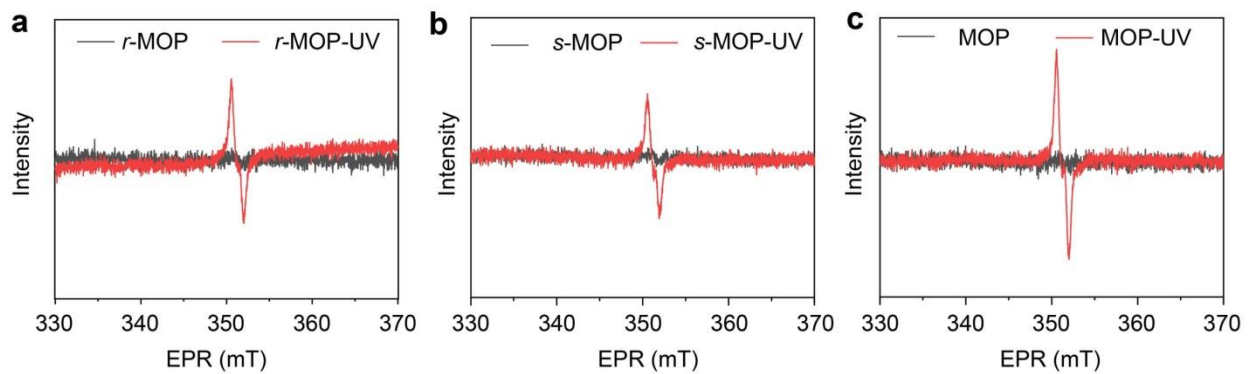


Supplementary Figure 7. (a-c) Steady-state photoluminescence and (d-f) phosphorescence spectra of r-MOP, s-MOP, and MOP crystals before and after photo-activated by 365 nm lamp (39.9 mW/cm^2) with the interval of 6 s. Inset: (a-c) Photographs of r-MOP, s-MOP, and MOP crystals before and after the photo-activation taken under a 365-nm lamp on. (d-f) Photographs of r-MOP, s-MOP, and MOP crystals after the photo-activation taken under a 365-nm lamp on.

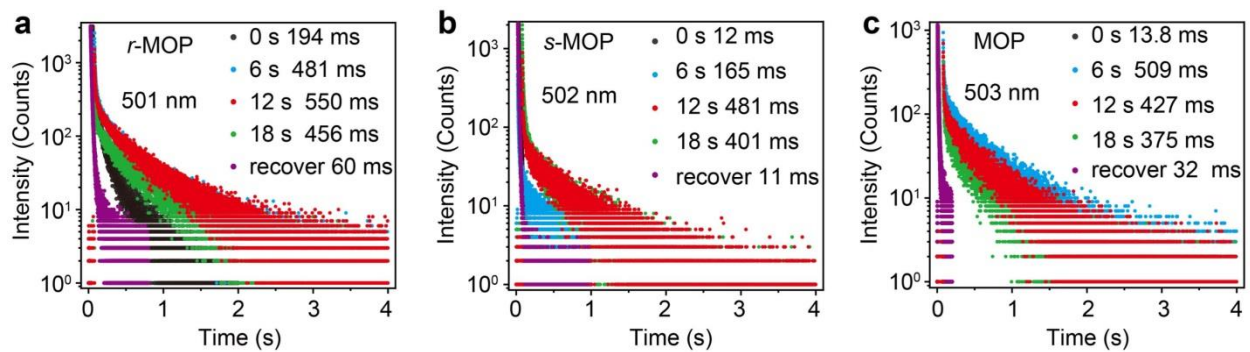
Supplementary Table 2. Fluorescence lifetimes (τ) of r-MOP, s-MOP and MOP in crystals before the photo-activation.^a

Compound	Wavelength (nm)	Photoluminescence			
		τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
r-MOP	409	1.1	66.42	2.5	33.58
	497	1.5	56.36	5.3	43.64
	598	6.5	100	-	-
MOP	414	1.2	77.7	2.7	22.3
	499	1.5	58.37	5.3	41.63
	599	6.8	100	-	-
s-MOP	409	1.0	59.99	2.2	40.01
	496	1.4	60.34	4.3	39.66
	601	6.3	100	-	-

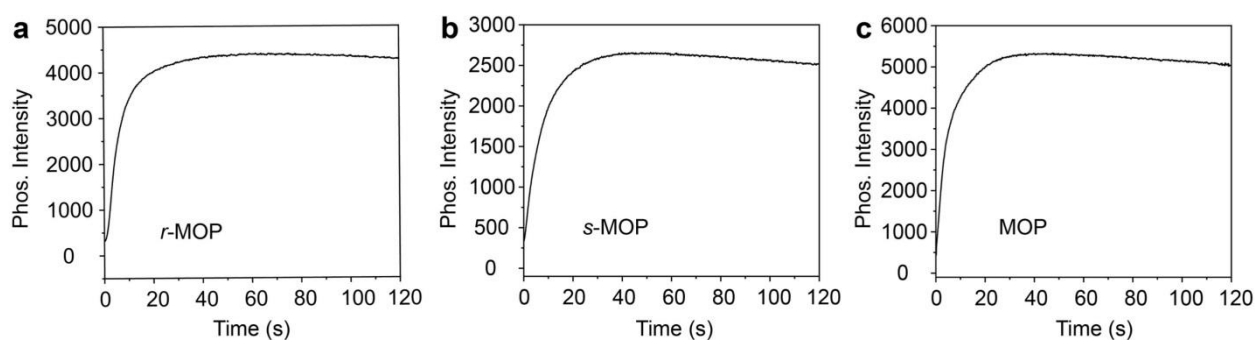
^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$ where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



Supplementary Figure 8. EPR spectra of r-MOP, s-MOP, MOP crystals before and after the photo-activation. (365 nm, 39.9 mW/cm²)



Supplementary Figure 9. Lifetime profiles of r-MOP, s-MOP and MOP crystals after photo-activated by 365 nm with different times, and after the photo-activated r-MOP, s-MOP and MOP crystals recovered in dark.

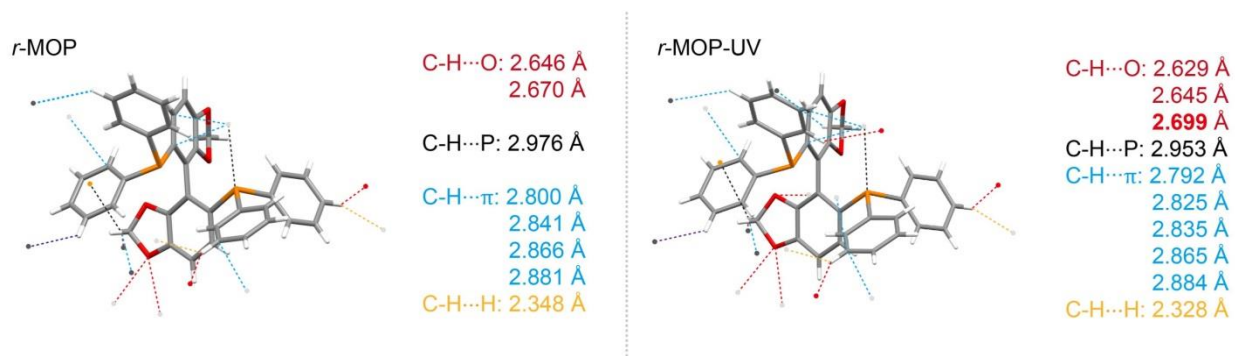


Supplementary Figure 10. The phosphorescence intensity of r-MOP, s-MOP and MOP crystals with the photo-activation time of a 365-nm Xe lamp (0.72 mW/cm²) monitoring 502 nm.

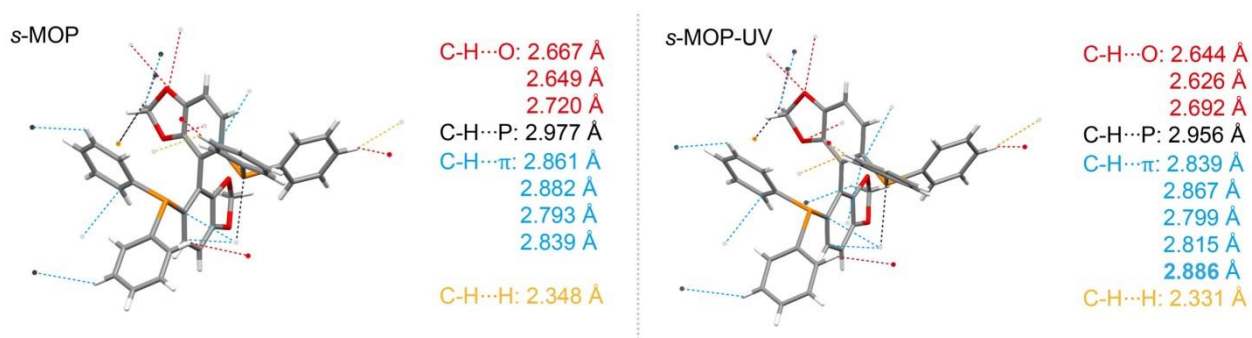
Supplementary Table 3. Phosphorescence lifetimes (τ) of r-MOP, s-MOP, MOP crystals.^a

Compound	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A ₁ (%)	τ_2 (ms)	A ₂ (%)	τ_3 (ms)	A ₃ (%)	τ_4 (ms)	A ₄ (%)
r-MOP 0s	501	1.96	16.73	8.22	50.48	33.07	19.17	194.17	13.00
r-MOP 6s	501	7.00	10.48	75.75	19.11	481.75	70.40	-	-
r-MOP 12s	501	6.88	6.06	95.04	18.13	550.26	75.81	-	-
r-MOP 18s	501	24.67	10.44	456.14	89.56	-	-	-	-
r-MOP-recover	501	1.20	10.35	5.18	44.09	12.54	42.12	60.59	3.44
s-MOP 0s	502	4.45	23.72	12.41	76.28	-	-	-	-
s-MOP 6s	502	2.14	16.60	15.36	37.95	165.79	45.45	-	-
s-MOP 12s	502	30.14	9.89	481.69	90.11	-	-	-	-
s-MOP 18s	502	3.32	19.27	24.78	27.73	401.25	53.00	-	-
s-MOP recover	502	8.57	50.63	2.02	10.16	11.30	39.21	-	-
MOP 0s	503	0.09	0.44	4.38	15.83	5.53	49.55	13.83	34.17
MOP 6s	503	5.61	5.01	78.04	12.74	509.15	82.26	-	-
MOP 12s	503	10.98	9.25	427.27	90.75	-	-	-	-
MOP 18s	503	9.70	11.01	375.63	88.99	-	-	-	-
MOP recover	503	86.96	0.90	1.64	22.32	7.83	52.80	32.26	23.98

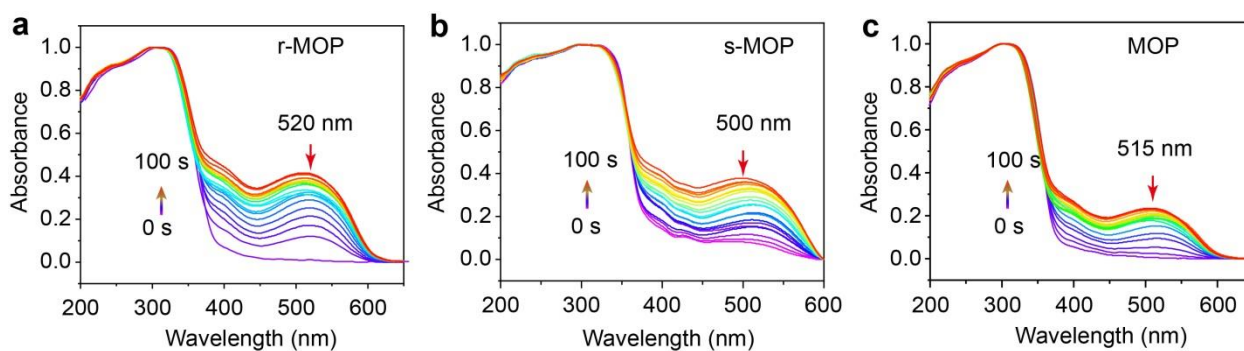
^aDetermined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



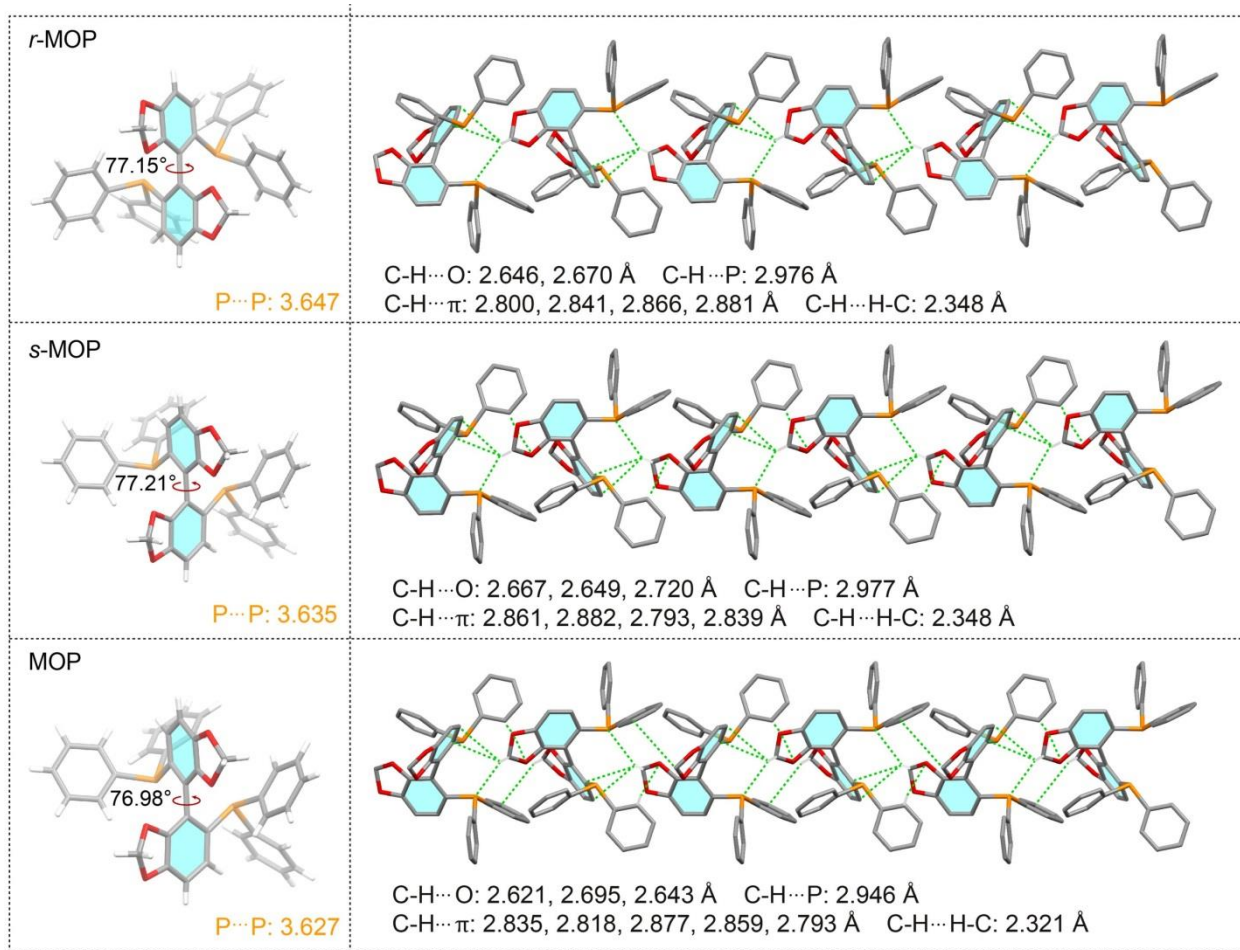
Supplementary Figure 11. The intermolecular interactions in *r*-MOP crystals before (left) and after the photo-activation (right).



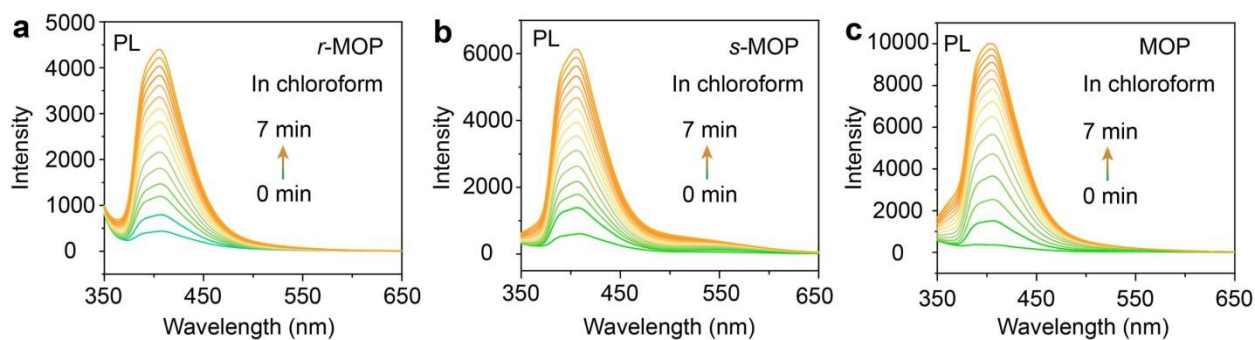
Supplementary Figure 12. The intermolecular interactions in *s*-MOP crystals before (left) and after the photo-activation (right).



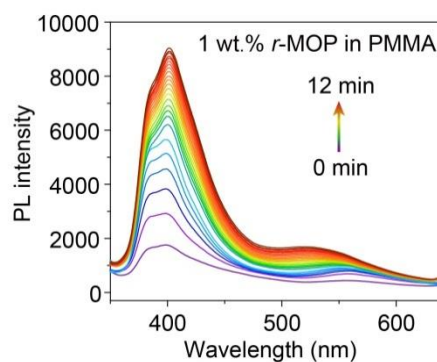
Supplementary Figure 13. The absorption spectra of *r*-MOP, *s*-MOP and MOP crystals after the photo-activated by 365 nm (39.9 mW/cm²) with an interval of 5 seconds.



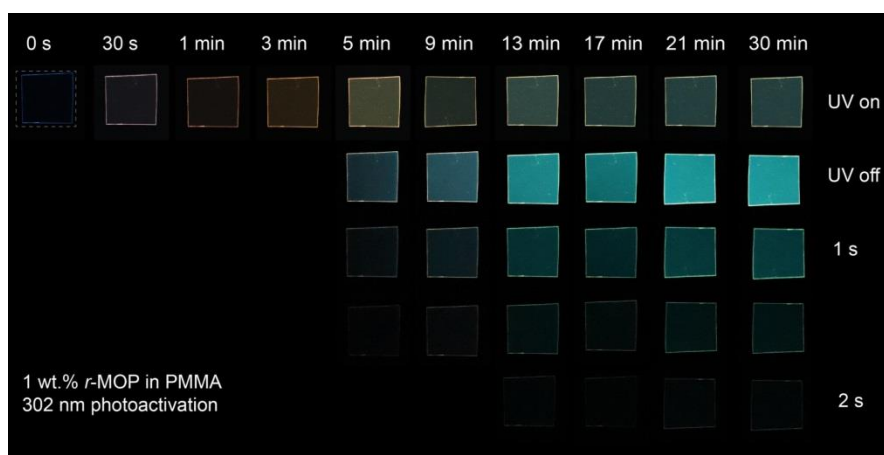
Supplementary Figure 14. Dihedral angle between biphenyls and molecular packing in *r*-MOP *s*-MOP and MOP crystals before the photo-activation.



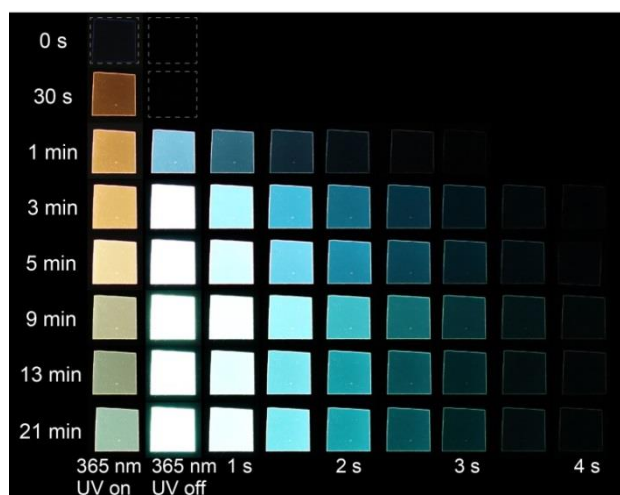
Supplementary Figure 15. Steady-state photoluminescence spectra of *r*-MOP ($\lambda_{\text{ex}} = 330$ nm, 5/5,700 V), *s*-MOP ($\lambda_{\text{ex}} = 330$ nm, 5/5, 700 V), MOP ($\lambda_{\text{ex}} = 330$ nm, 5/5,700 V) in the dilute chloroform at the concentration of 10^{-5} M. Note: each profile was collected after the solution was further photo-activated for 30 s.



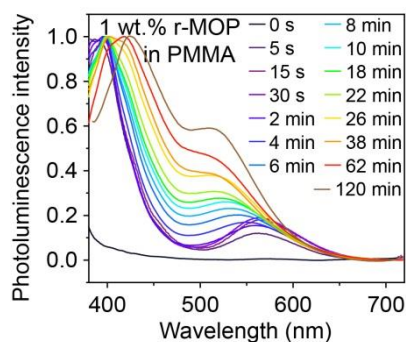
Supplementary Figure 16. Steady-state photoluminescence (PL) spectra of 1 wt.% r-MOP in PMMA films with a photo-activation interval of 30 s excited by 330 nm.



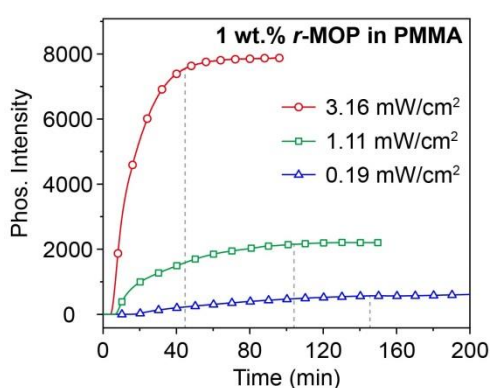
Supplementary Figure 17. Photographs of 1 wt.% r-MOP in PMMA film taken under 302 nm UV lamp (4.04 mW/cm^2) on and off after photo-activated by 302 nm UV lamp (4.04 mW/cm^2) with different irradiation time.



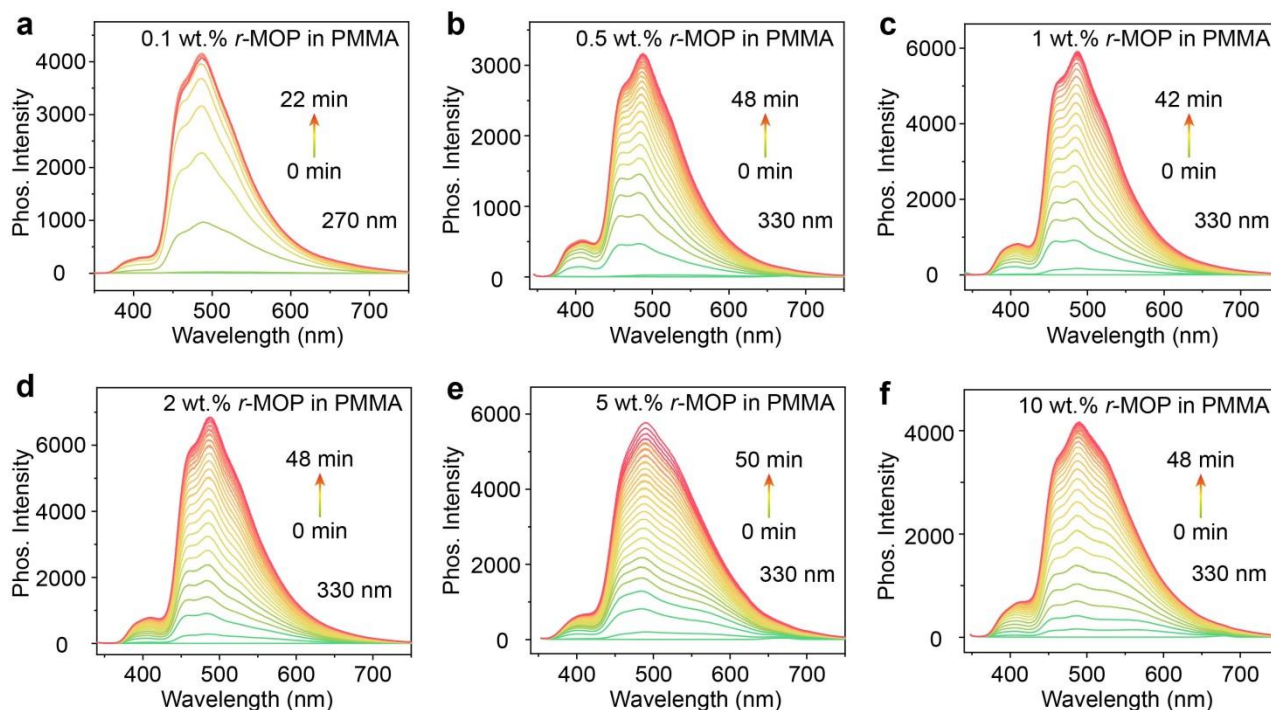
Supplementary Figure 18. Photographs of 1 wt.% r-MOP in PMMA film taken under 365 nm UV lamp (39.9 mW/cm^2) on and off after photo-activated by 302 nm UV lamp (4.04 mW/cm^2) with different irradiation time.



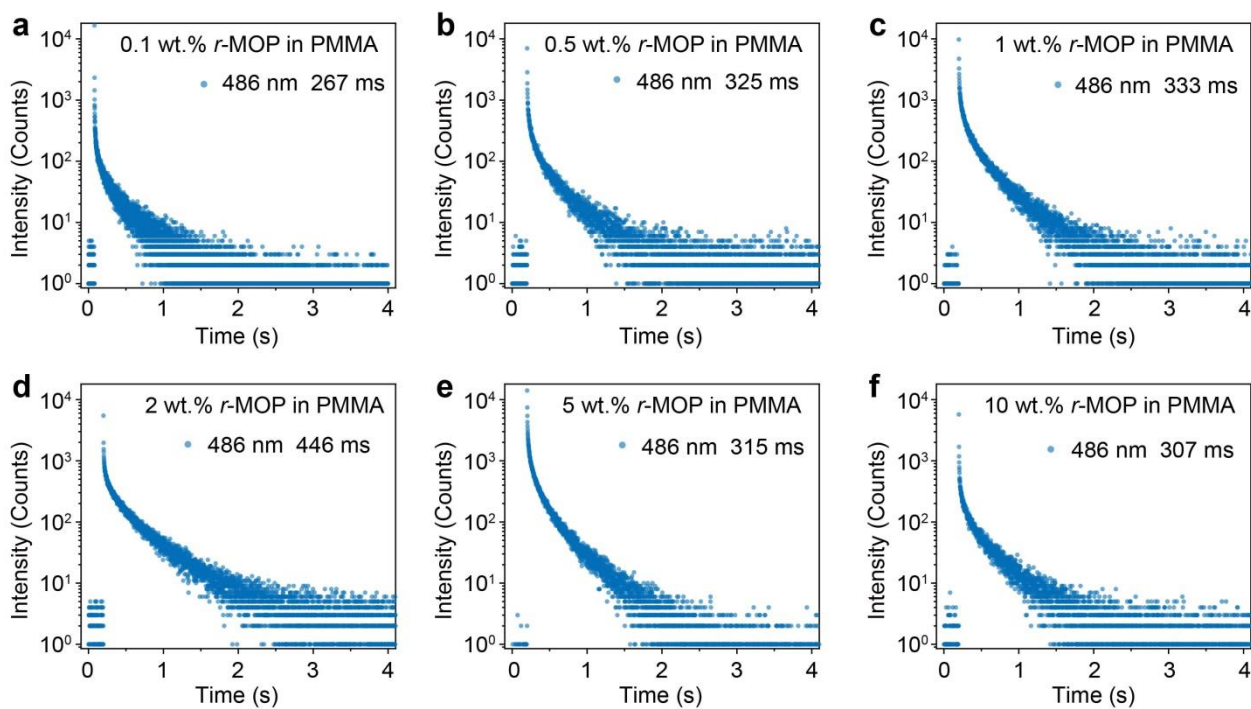
Supplementary Figure 19. Steady-state photoluminescence spectra of 1 wt.% r-MOP in PMMA films excited by 365 nm after photo-activated by 302 nm.



Supplementary Figure 20. Phosphorescence intensity of 1 wt.% r-MOP in PMMA film with the irradiation time monitoring 484 nm under different powers of 330 nm lamp.



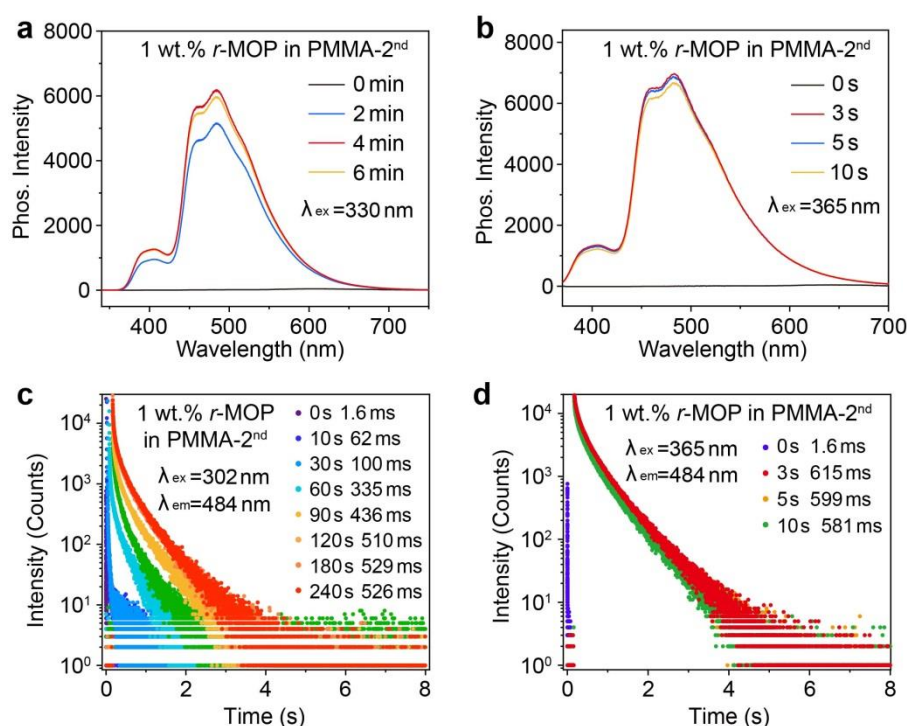
Supplementary Figure 21. Phosphorescence spectra of PMMA films with different doped concentration of r-MOP before and after photo-activated with an interval of 2 minutes. (a, $\lambda_{\text{ex}} = 270$ nm, $\text{ex} = 20$, $\text{em} = 10$, 700V; b-f, $\lambda_{\text{ex}} = 330$ nm, 3.16 mW/cm^2).



Supplementary Figure 22. Lifetime profiles of PMMA film with different doped concentration of r-MOP after the photo-activation.

Supplementary Table 4. Photoluminescence and phosphorescence efficiencies of PMMA films doped with r-MOP at different concentrations before and after the photo-activation.

Compounds	Different concentrations	Photo-activation	Φ_{PL} (%)	$\Phi_{Phos.}$ (%)
r-MOP in PMMA	0.1 wt. %	Pristine	3.0	0
		Photo-activated	10.3	3.12
	0.5 wt. %	Pristine	2.4	0
		Photo-activated	9.3	3.89
	1 wt. %	Pristine	2.7	0
		Photo-activated	16.8	9.17
	2 wt. %	Pristine	1.1	0
		Photo-activated	14.7	6.6
	5 wt. %	Pristine	1.8	0
		Photo-activated	14.3	5.57
	10 wt. %	Pristine	2.5	0
		Photo-activated	12.4	6.42

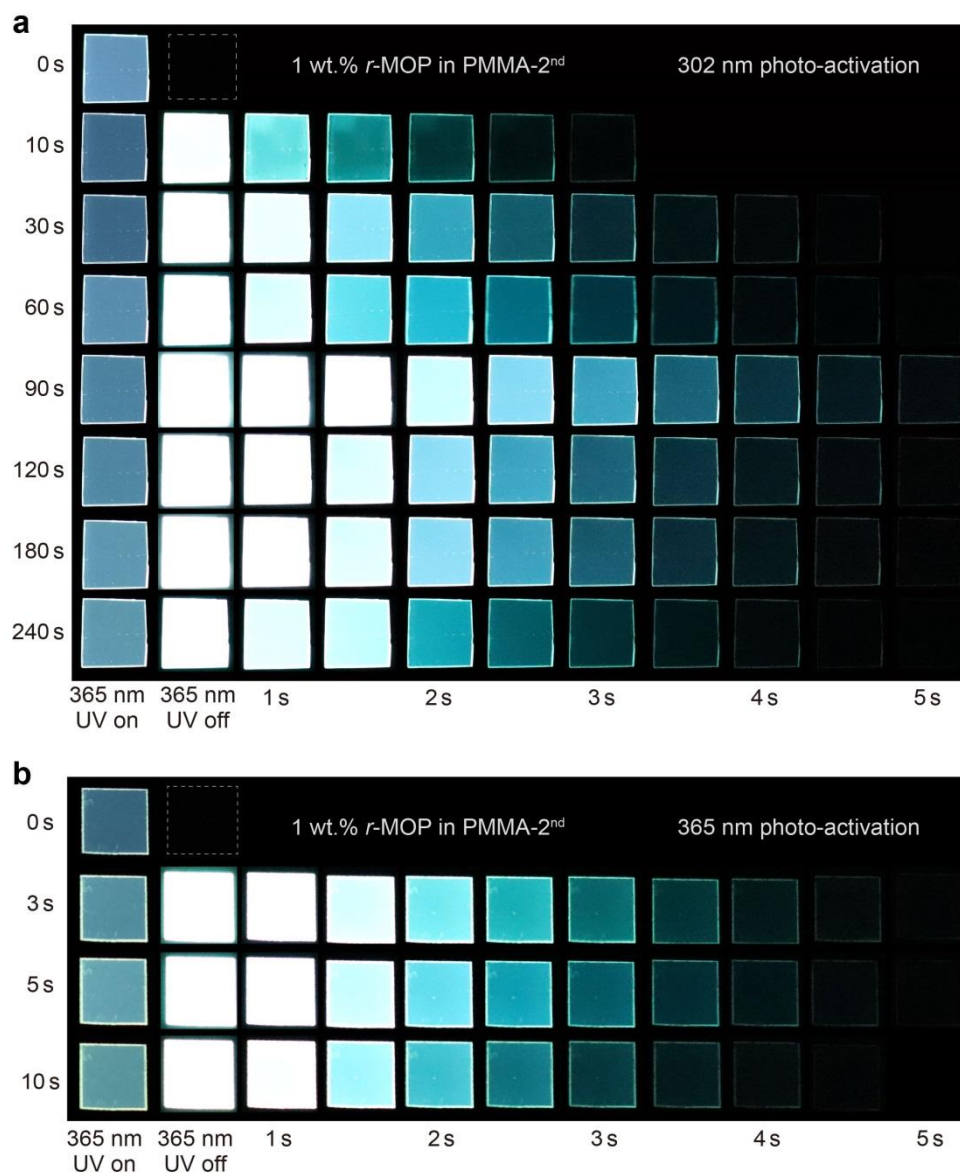


Supplementary Figure 23. **a**, Phosphorescence spectra of 1 wt.% r-MOP in PMMA films photo-activated by 330 nm (3.16 mW/cm²) for the second time. **b**, Phosphorescence spectra of 1 wt.% r-MOP in PMMA films photo-activated by 365 nm (39.9 mW/cm²) for the second time. **c**, Lifetime decay profiles of 1 wt.% r-MOP in PMMA film excited by 365 nm monitoring 484 nm before and after photo-activated by 302 nm for the second time. **d**, Lifetime decay profiles of 1 wt.% r-MOP in PMMA film excited by 365 nm monitoring 484 nm before and after photo-activated for by 365 nm for the second time.

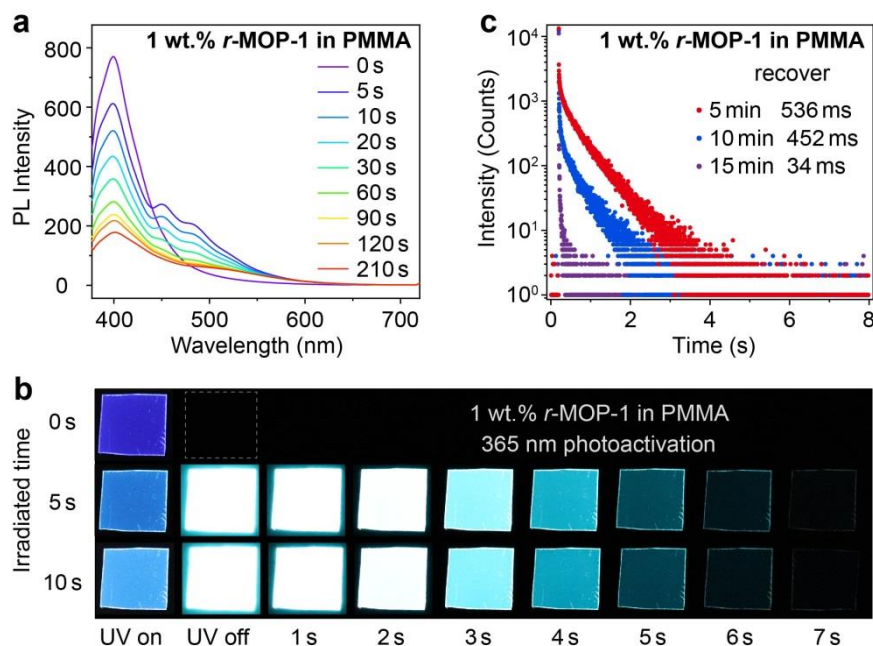
Supplementary Table 5. Phosphorescence lifetimes (τ) of 1 wt.% r-MOP in PMMA film excited by 365 nm monitoring 484 nm after photo-activated by 302 nm or 365 nm for the second time.

Compounds	Photo-activation Wavelength (nm)	Phosphorescence					
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)
1 wt.% r-MOP in PMMA-2 nd -0 s	302	0.028	51.43	1.610	48.57	-	-
1 wt.% r-MOP in PMMA-2 nd -10 s	302	1.93	18.20	18.03	36.31	61.92	45.49
1 wt.% r-MOP in PMMA-2 nd -30 s	302	4.22	19.03	25.36	58.38	100.01	22.60
1 wt.% r-MOP in PMMA-2 nd -60 s	302	13.01	11.46	80.01	37.69	335.77	50.85
1 wt.% r-MOP in PMMA-2 nd -90 s	302	51.03	13.73	164.53	44.67	436.79	41.60
1 wt.% r-MOP in PMMA-2 nd -120 s	302	27.17	12.16	145.90	39.90	510.01	47.94
1 wt.% r-MOP in PMMA-2 nd -180 s	302	28.35	11.80	160.85	41.46	529.74	46.74
1 wt.% r-MOP in PMMA-2 nd -240 s	302	25.57	12.60	157.22	41.58	526.79	45.82
1 wt.% r-MOP in PMMA-2 nd -0 s	365	0.028	51.43	1.610	48.57	-	-
1 wt.% r-MOP in PMMA-2 nd -3 s	365	62.68	8.80	250.39	41.80	614.81	49.40
1 wt.% r-MOP in PMMA-2 nd -5 s	365	49.43	7.86	229.50	40.93	599.61	51.21
1 wt.% r-MOP in PMMA-2 nd -10 s	365	29.35	7.56	196.36	39.57	581.39	52.87

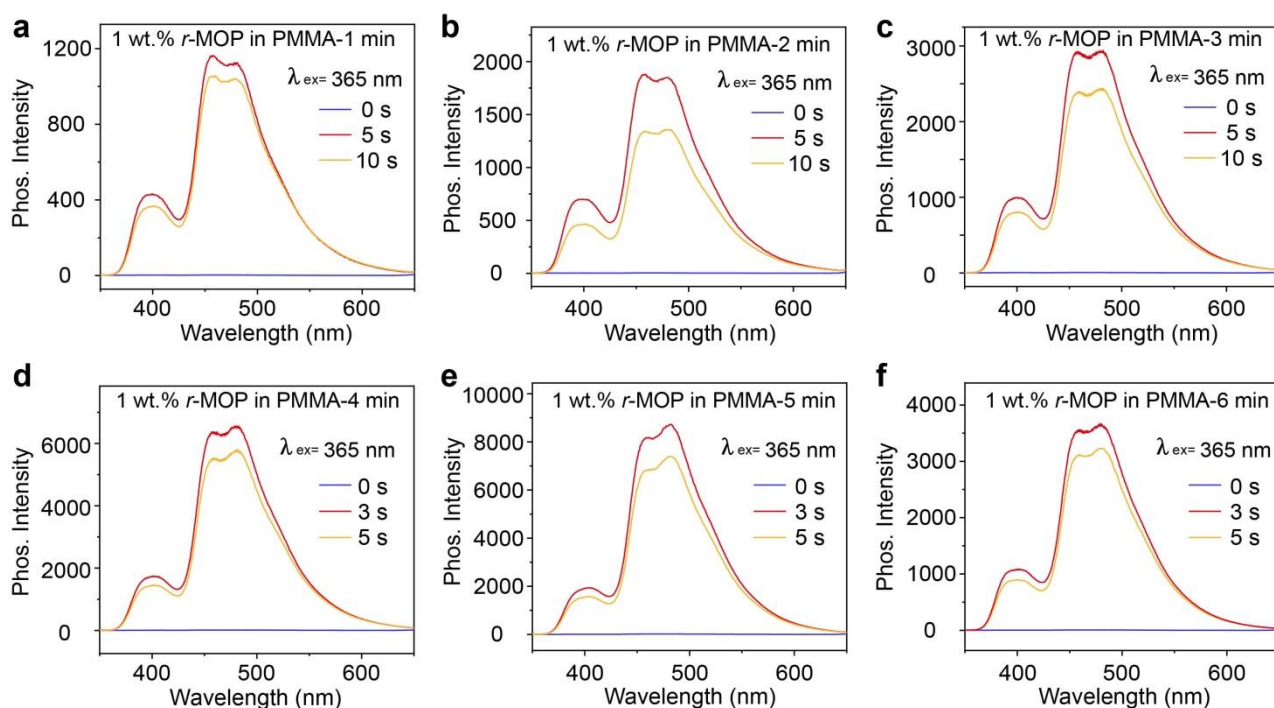
^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



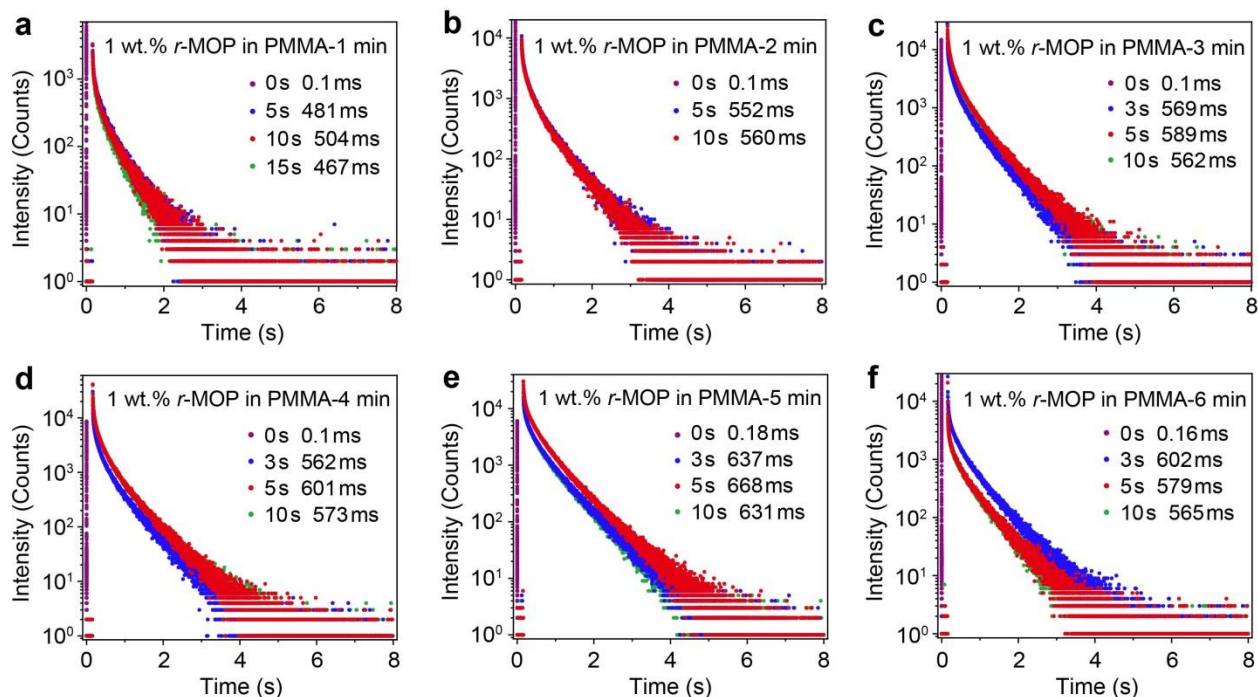
Supplementary Figure 24. **a**, Photographs of 1 wt.% *r*-MOP in PMMA film taken under 365 nm UV lamp (39.9 mW/cm²) on and off after photo-activated by 302 nm UV lamp (4.04 mW/cm²) for the second time. **b**, Photographs of 1 wt.% *r*-MOP in PMMA film taken under 365 nm UV lamp (39.9 mW/cm²) on and off before and after photo-activated by 365 nm UV lamp (39.9 mW/cm²) for the second time.



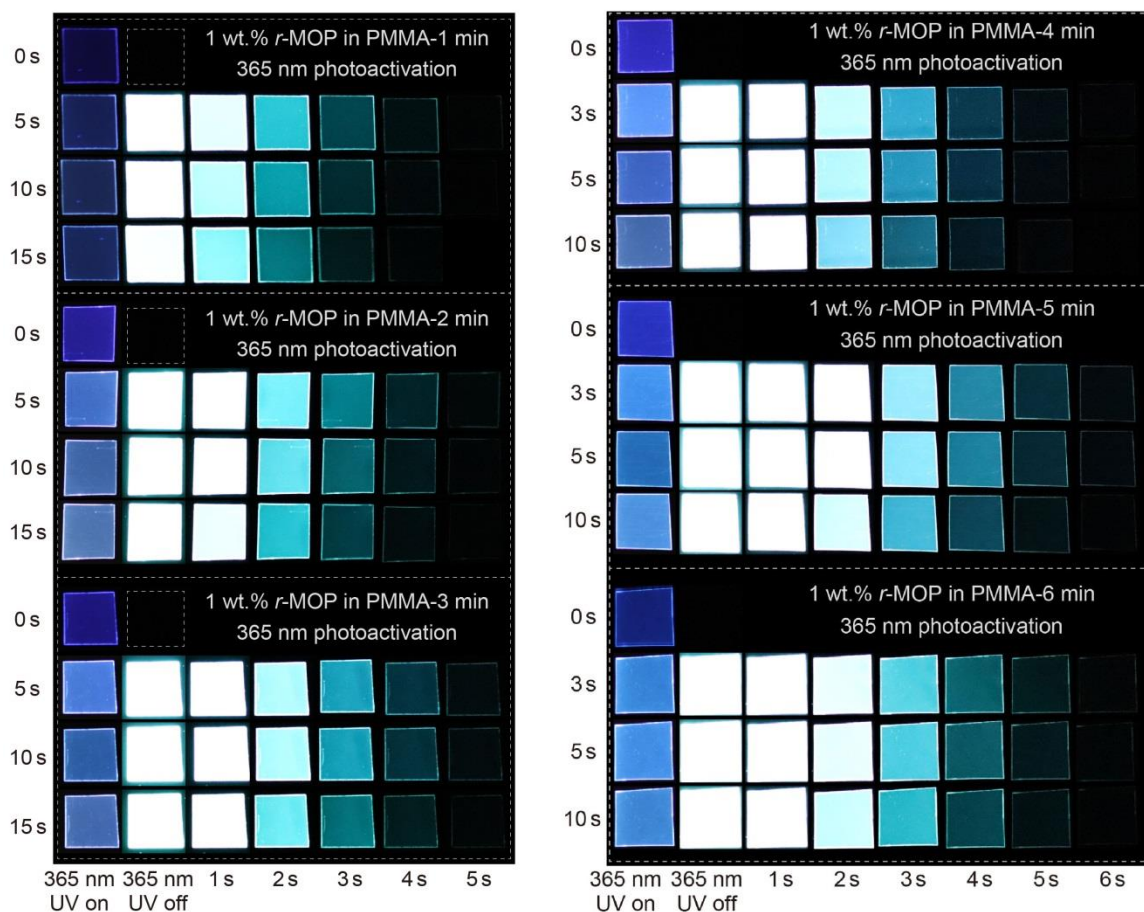
Supplementary Figure 25. a, Steady-state photoluminescence spectra of 1 wt.% r-MOP-1 in PMMA films photo-activated by 365 nm. b, Photographs of 1 wt.% r-MOP-1 in PMMA film taken under 365 nm UV lamp on and off after photo-activated by 365-nm UV lamp (39.9 mW/cm²) with different irradiation time. c, Lifetime decay profiles of 1 wt.% r-MOP-1 in PMMA film in dark after photo-activated for 10 s.



Supplementary Figure 26. a-f, Phosphorescence spectra of 1 wt.% r-MOP in PMMA-X min (X = 1, 2, 3, 4, 5, 6) films before and after photo-activated by 365 nm (39.9 mW/cm²).



Supplementary Figure 27. a-f, Lifetime decay profiles of 1 wt.% *r*-MOP-1 in PMMA-*X* min (*X* = 1, 2, 3, 4, 5, 6) films before and after photo-activated by 365 nm (39.9 mW/cm²) monitoring 484 nm.

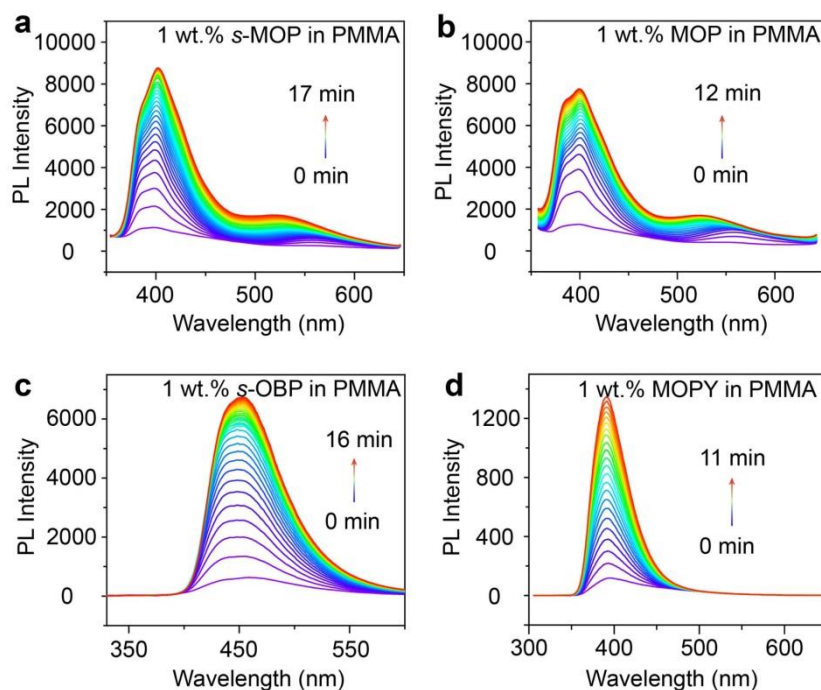


Supplementary Figure 28. Photographs of 1 wt.% *r*-MOP-1 in PMMA-*X* min (*X* = 1, 2, 3, 4, 5, 6) films before and after photo-activated by 365 nm (39.9 mW/cm²) taken under 365 nm UV lamp on and off.

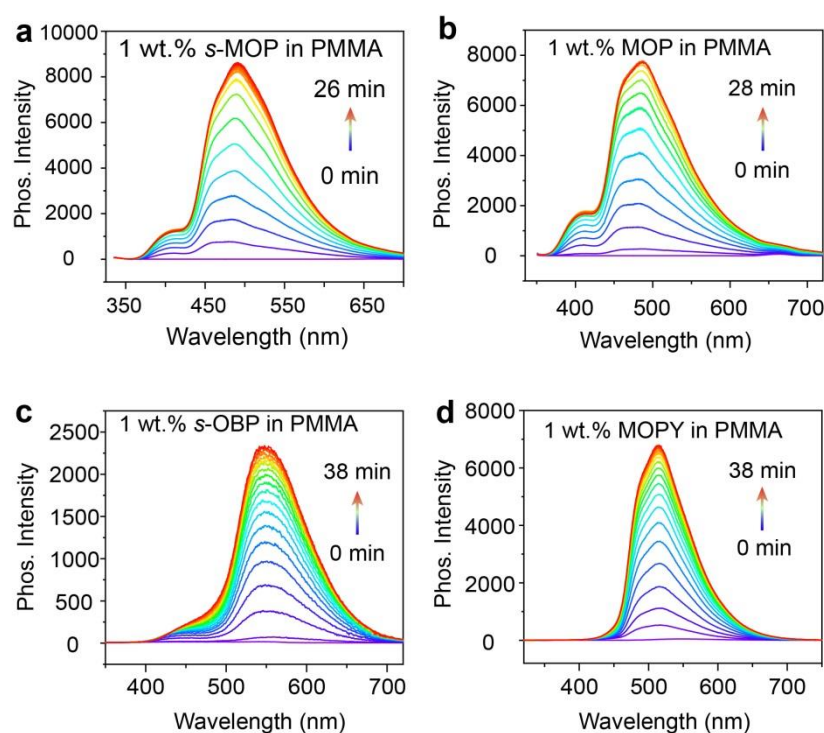
Supplementary Table 6. Phosphorescence lifetimes (τ) of 1 wt.% r-MOP-1 in PMMA-X min (X = 1, 2, 3, 4, 5, 6) films excited by 365 nm monitoring 484 nm after photo-activated by 365 nm.^a

Compounds	Wavelength (nm)	Phosphorescence					
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)
1 wt.% r-MOP in PMMA-1 min-0 s	484	0.006	53.71	100.45	46.29	-	-
1 wt.% r-MOP in PMMA-1 min-5 s	484	21.87	6.53	130.40	32.04	481.11	61.43
1 wt.% r-MOP in PMMA-1 min-10 s	484	33.82	6.49	158.45	33.43	504.73	60.08
1 wt.% r-MOP in PMMA1 min-15 s	484	18.10	7.47	123.44	32.83	466.92	59.70
1 wt.% r-MOP in PMMA-2 min-0 s	484	0.009	41.19	0.114	58.81	-	-
1 wt.% r-MOP in PMMA-2 min-5 s	484	35.09	8.17	175.92	38.11	552.37	53.71
1 wt.% r-MOP in PMMA-2 min-10 s	484	40.82	8.13	187.93	39.27	560.37	52.60
1 wt.% r-MOP in PMMA-3 min-0 s	484	0.008	44.39	140.11	55.61	-	-
1 wt.% r-MOP in PMMA-3 min-3 s	484	41.95	9.92	191.48	38.69	569.68	51.39
1 wt.% r-MOP in PMMA-3 min-5 s	484	42.03	10.42	199.76	41.82	589.02	47.76
1 wt.% r-MOP in PMMA-3 min-10 s	484	33.69	9.97	179.23	41.79	564.27	48.24
1 wt.% r-MOP in PMMA-4 min-0 s	484	0.007	51.15	0.108	48.85	-	-
1 wt.% r-MOP in PMMA-4 min-3 s	484	37.31	9.67	181.31	40.22	562.63	50.11
1 wt.% r-MOP in PMMA-4 min-5 s	484	68.44	10.11	235.13	40.51	601.37	49.38
1 wt.% r-MOP in PMMA-4 min-10 s	484	36.11	11.11	186.39	42.77	573.30	46.12
1 wt.% r-MOP in PMMA-5 min-0 s	484	0.008	69.89	0.188	30.11	-	-
1 wt.% r-MOP in PMMA-5 min-3 s	484	40.62	6.10	237.26	35.25	637.81	58.65
1 wt.% r-MOP in PMMA-5 min-5 s	484	72.01	6.02	288.35	38.50	668.46	55.47
1 wt.% r-MOP in PMMA-5 min-10 s	484	48.92	5.90	240.53	36.39	630.96	57.71
1 wt.% r-MOP in PMMA-6 min-0 s	484	0.008	70.20	0.166	29.80	-	-
1 wt.% r-MOP in PMMA-6 min-3 s	484	37.48	5.09	200.01	31.23	601.82	63.68
1 wt.% r-MOP in PMMA-6 min-5 s	484	41.67	5.62	197.16	28.24	579.24	66.14
1 wt.% r-MOP in PMMA-6 min-10 s	484	26.04	5.25	175.20	28.33	565.5	66.42

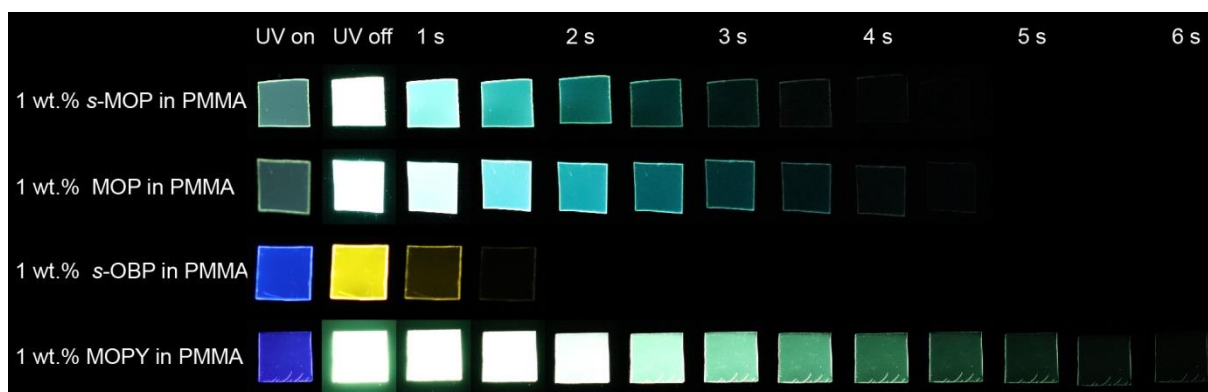
^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



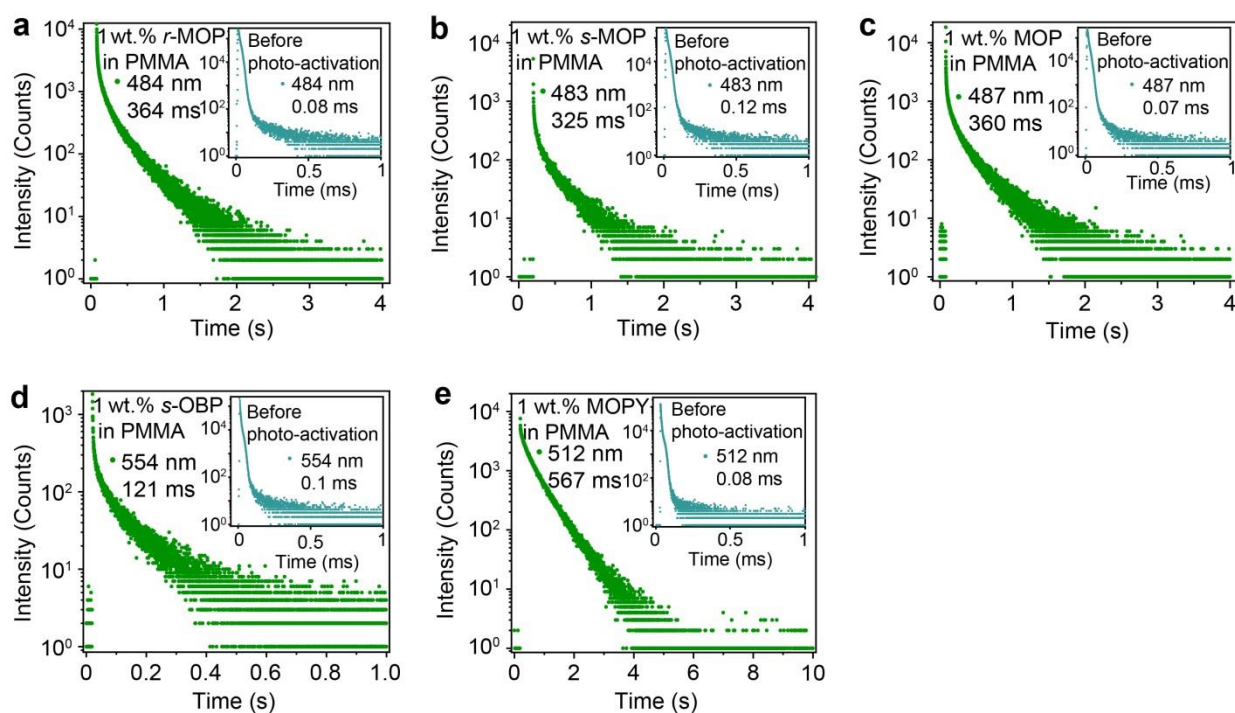
Supplementary Figure 29. Steady-state photoluminescence (PL) spectra of PMMA films doped with s-MOP, MOP, s-OBP, and MOPY at the concentration of 1 wt.% with a photo-activation interval of 30 s excited by 330, 330, 270, 297 nm, respectively.



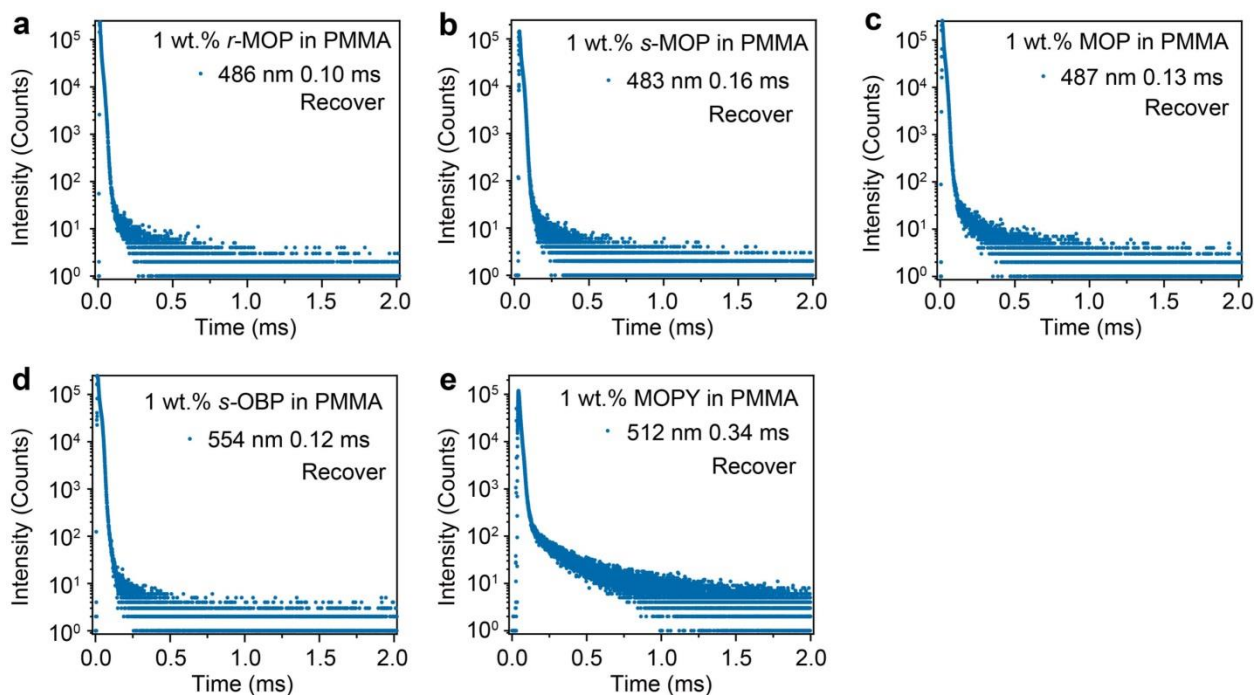
Supplementary Figure 30. Phosphorescence spectra of PMMA films doped with s-MOP ($\lambda_{\text{ex}} = 330$ nm, 3.16 mW/cm²), MOP ($\lambda_{\text{ex}} = 330$ nm, 3.16 mW/cm²), s-OBP ($\lambda_{\text{ex}} = 270$ nm, 20/20, 780 V) or MOPY ($\lambda_{\text{ex}} = 300$ nm, 0.18 mW/cm²) at the concentration of 1 wt.% with a photo-activation interval of 2 min.



Supplementary Figure 31. Photographs of photo-activated PMMA films doped with s-MOP, MOP, s-OBP or MOPY taken under 365 nm lamp on and off. Note: PMMA films doped with s-MOP, MOP were photo-activated by 330 nm (3.16 mW/cm^2), 1 wt.% s-OBP in PMMA ($\lambda_{\text{ex}}=270 \text{ nm}$, 20/20, 780 V) and 1 wt.% MOPY in PMMA ($\lambda_{\text{ex}}=300 \text{ nm}$, 0.18 mW/cm^2).



Supplementary Figure 32. Lifetime decay profiles of PMMA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% before and after the photo-activation.



Supplementary Figure 33. Lifetime decay profiles of the photo-activated PMMA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% after the recover in the dark.

Supplementary Table 7. Fluorescence lifetimes (τ) of PMMA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% after the photo-activation.

Compounds	Wavelength (nm)	Photoluminescence			
		τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)
r-MOP in PMMA	401	1.1	46.45	2.7	53.55
	516	2.1	25.01	9.6	74.99
MOP in PMMA	400	1.4	63.93	3.3	36.07
	520	1.4	26.26	8.6	73.74
s-MOP in PMMA	403	2.1	80.06	4.3	19.94
	516	3.6	42.76	9.6	57.24
s-OBP in PMMA	453	9.5	100	-	-
MOPY in PMMA	391	5.7	100	-	-

Supplementary Table 8. Phosphorescence lifetimes (τ) of PMMA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% before and after the photo-activation, and after the recover in dark.^a

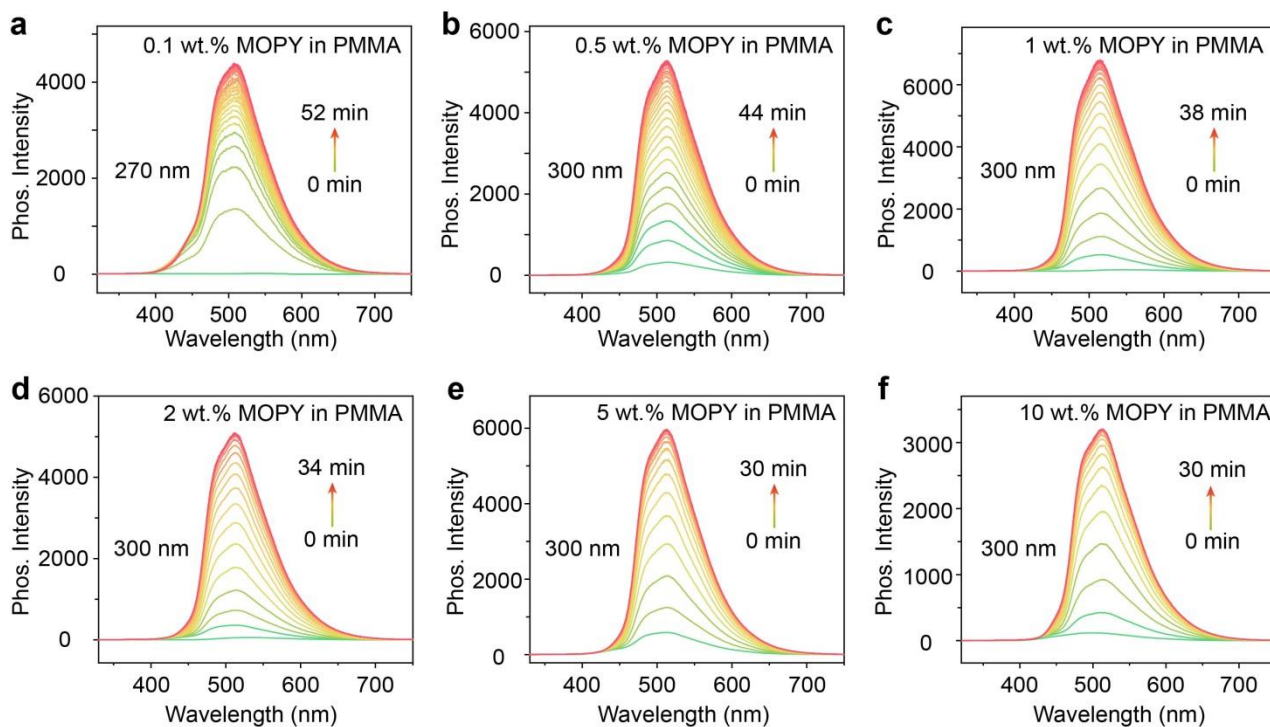
Compounds	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	τ_4 (ms)	A_4 (%)
r-MOP in PMMA-0 min	486	0.007	84.39	0.026	8.87	0.176	6.74	-	-
r-MOP in PMMA-42 min	486	63.7	30.86	361.71	69.14	-	-	-	-
r-MOP in PMMA-recover	486	0.01	48.25	0.10	51.75	-	-	-	-
MOP in PMMA-0 min	487	0.007	88.14	0.071	11.86	-	-	-	-
MOP in PMMA-28 min	487	1.31	5.87	13.61	12.53	94.12	35.72	360.45	45.88
MOP in PMMA-recover	487	0.13	100	-	-	-	-	-	-
s-MOP in PMMA-0 min	483	0.009	74.75	0.12	25.25	-	-	-	-
s-MOP in PMMA-26 min	483	56.35	27.38	325.29	72.62	-	-	-	-
s-MOP in PMMA-recover	483	0.006	58.52	0.017	25.55	0.16	15.93	-	-
s-OBP in PMMA-0 min	554	0.009	92.58	0.172	7.42	-	-	-	-
s-OBP in PMMA-26 min	554	0.95	12.48	15.79	20.33	111	67.19	-	-
s-OBP-PMMA-recover	554	0.007	79.24	0.17	18.23	0.12	2.53	-	-
MOPY in PMMA-0 min	512	0.007	88.97	0.060	11.03	-	-	-	-
MOPY in PMMA-40 min	512	138.57	31.35	513.13	68.65	-	-	-	-
MOPY in PMMA-recover	512	0.01	33.84	0.72	22.99	0.34	43.18	-	-

^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.

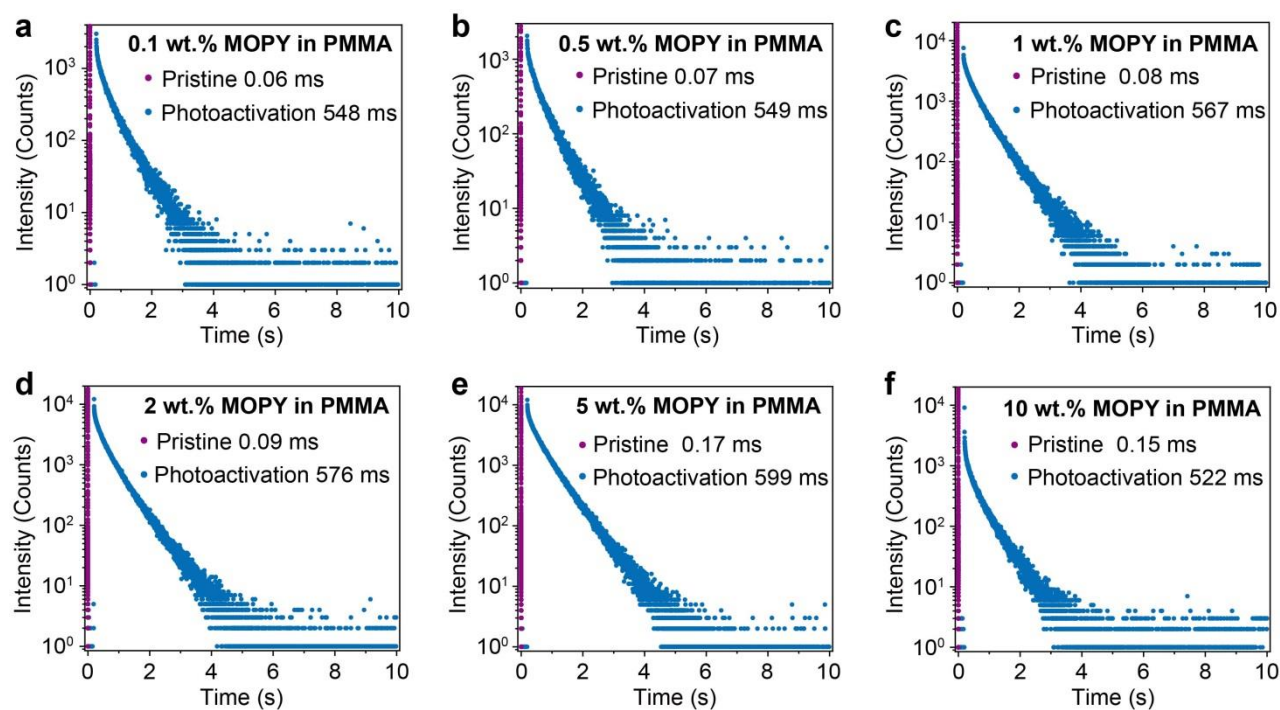
Supplementary Discussion

PMMA doped with MOPY or s-OBP at the different concentration of 0.1, 0.5, 1, 2, 5, and 10 wt.%. 5 wt.% MOPY in PMMA exhibited relatively short photo-activated time and longest photo-activated phosphorescence lifetime (Supplementary Figs. 34, 35, and Supplementary Table 9). Therefore, 5 wt.% is the best doped concentration for MOPY in PMMA. The photo-activation time of s-OBP in PMMA were longer at high doped concentration of 5, and 10 wt.%. The photo-activated phosphorescence lifetimes were increased with the doped concentration from 0.1 wt.% to 1 wt.%, and remained almost unchanged with the doped concentration from 2 wt.% to 5 wt.% (Supplementary Figs. 36, 37, and

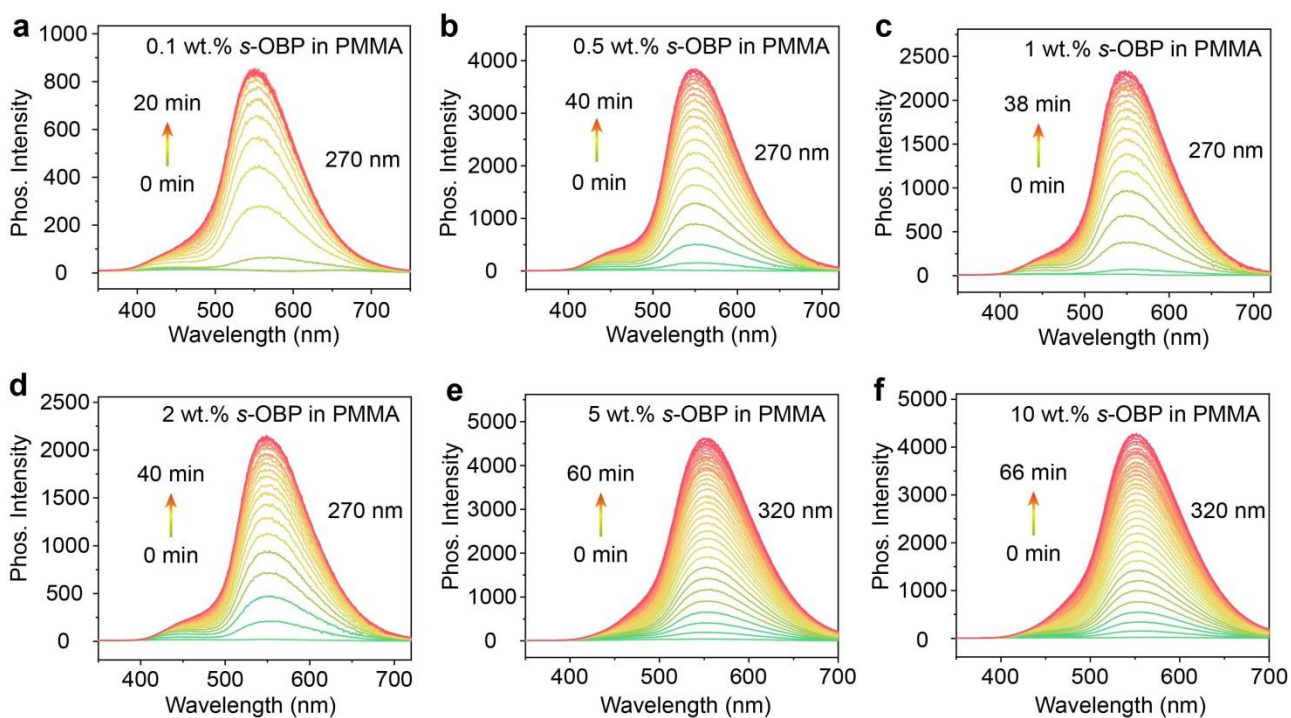
Supplementary Table 9). Considering the photo-activation time and phosphorescence lifetime of s-OBP in PMMA, both 1 wt.% and 2 wt.% are optimal doping concentration.



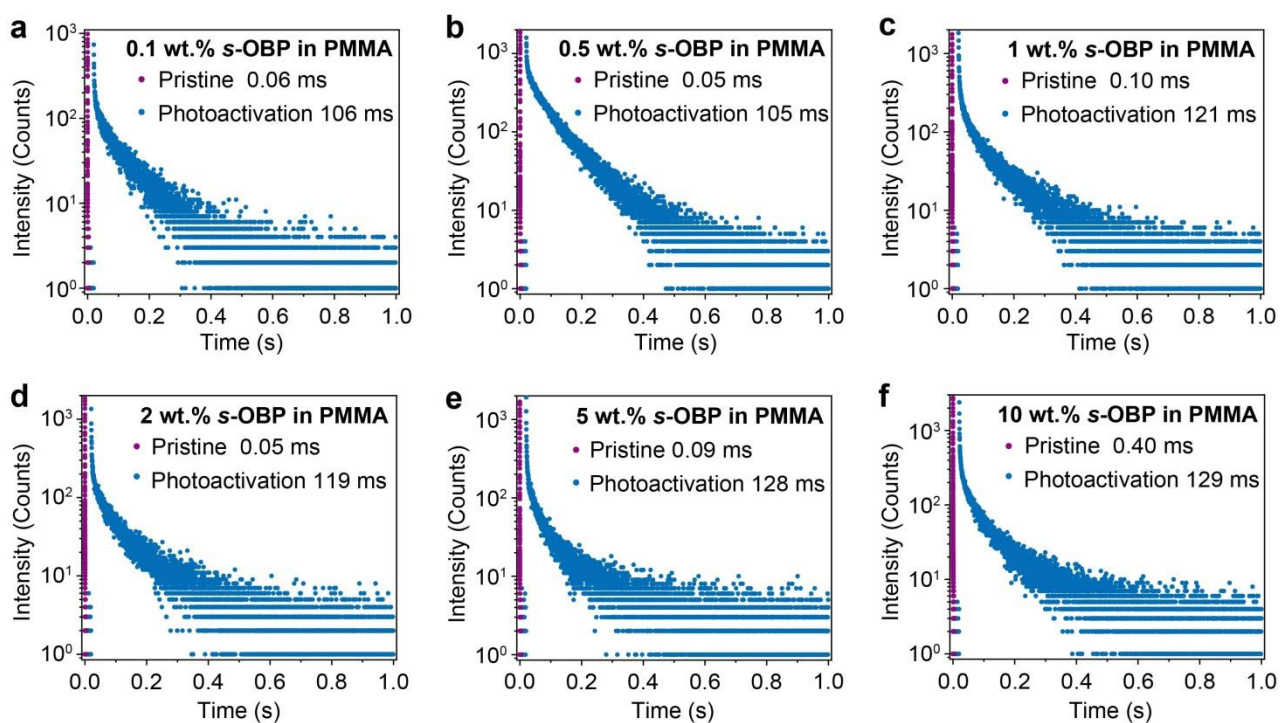
Supplementary Figure 34. Phosphorescence spectra of PMMA films with different doped concentration of MOPY before and after photo-activated with an interval of 2 minutes. (a, $\lambda_{\text{ex}} = 270$ nm, $\text{ex} = 20$, $\text{em} = 20$, 700V; b-f, $\lambda_{\text{ex}} = 300$ nm, 0.18 mW/cm^2).



Supplementary Figure 35. Lifetime profiles of PMMA films with different doped concentration of MOPY before and after the photo-activation.



Supplementary Figure 36. Phosphorescence spectra of PMMA films with different doped concentration of s-OBP before and after photo-activated with an interval of 2 minutes. (**a-d**, $\lambda_{\text{ex}} = 270 \text{ nm}$, $t_{\text{ex}} = 20$, $t_{\text{em}} = 20$, 800 V , **d-f**, $\lambda_{\text{ex}} = 320 \text{ nm}$, 2.06 mW/cm^2).

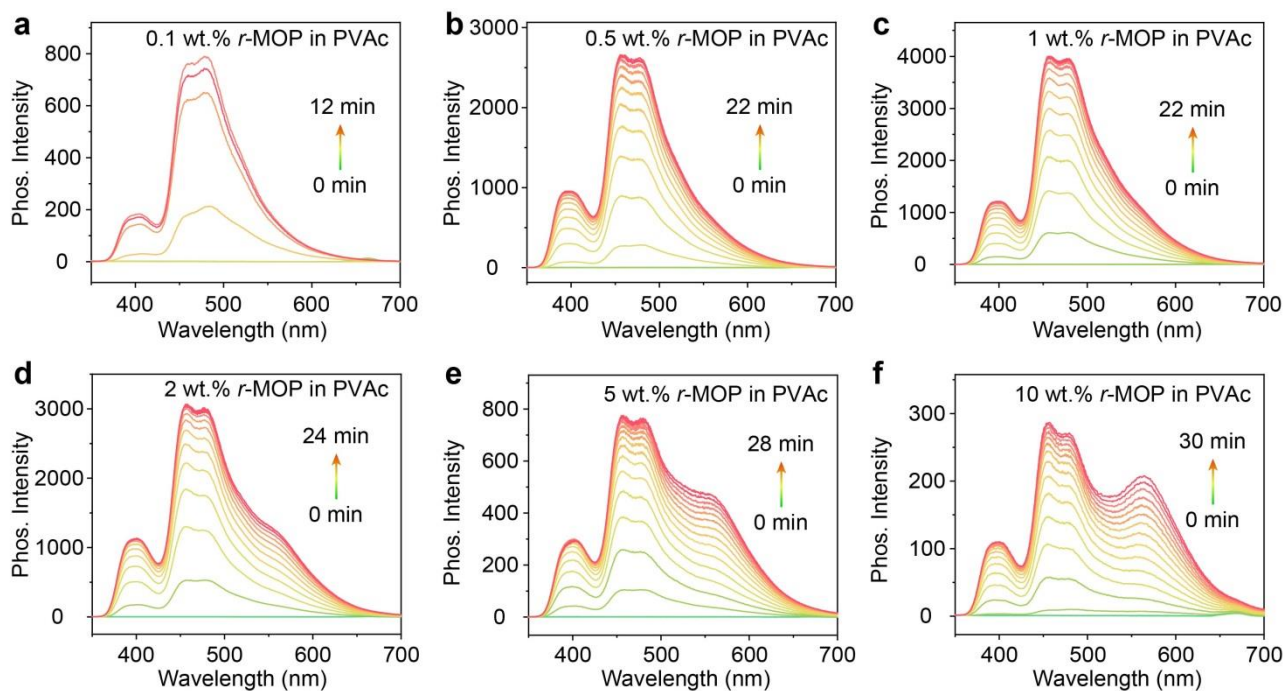


Supplementary Figure 37. Lifetime profiles of PMMA films with different doped concentration of s-OBP before and after the photo-activation.

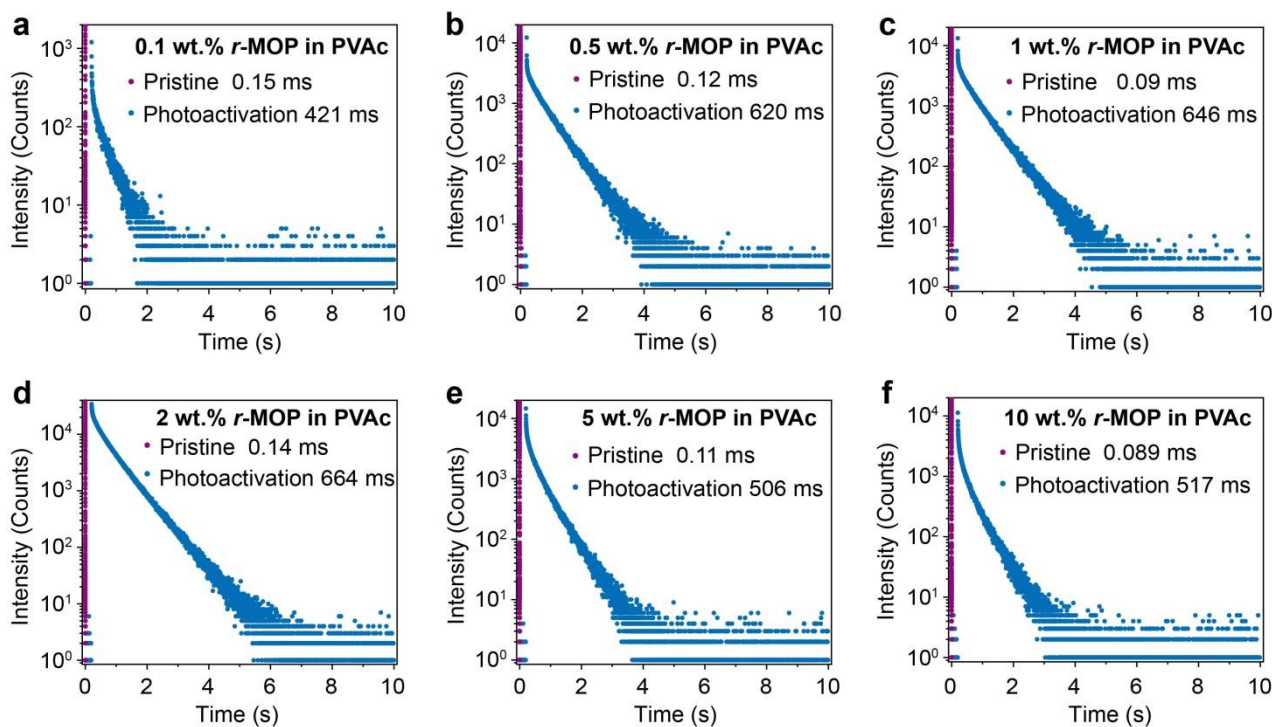
Supplementary Table 9. Phosphorescence lifetimes (τ) of PMMA films with different doped concentration of MOPY or s-OBP before and after the photo-activation. ^a

Compounds	Wavelength (nm)	Phosphorescence					
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)
0.1 wt.% MOPY in PMMA	509	0.005	13.33	0.059	86.67	-	-
0.1 wt.% MOPY in PMMA -UV	509	150.02	22.32	548.96	77.68	-	-
0.5 wt.% MOPY in PMMA	513	0.009	20.84	0.074	79.16	-	-
0.5 wt.% MOPY in PMMA -UV	513	151.90	23.53	549.35	76.48	-	-
1 wt.% MOPY in PMMA	513	0.012	15.32	0.085	84.68	-	-
1 wt.% MOPY in PMMA -UV	513	180.60	23.78	567.87	76.22	-	-
2 wt.% MOPY in PMMA	513	0.009	33.62	0.091	66.38	-	-
2 wt.% MOPY in PMMA -UV	513	163.30	23.89	576.10	76.11	-	-
5 wt.% MOPY in PMMA	513	0.040	37.81	0.171	62.19	-	-
5 wt.% MOPY in PMMA -UV	513	178.74	18.20	599.14	81.80	-	-
10 wt.% MOPY in PMMA	516	0.030	30.94	0.149	69.06	-	-
10 wt.% MOPY in PMMA -UV	516	126.01	23.51	522.487	76.49	-	-
0.1 wt.% s-OBP in PMMA	547	0.008	90.12	0.060	9.88	-	-
0.1 wt.% s-OBP in PMMA-UV	547	1.78	4.48	20.11	16.23	106.49	79.8
0.5 wt.% s-OBP in PMMA	547	0.007	57.04	0.054	42.96	-	-
0.5 wt.% s-OBP in PMMA-UV	547	3.25	2.58	34.95	24.07	104.74	73.35
1 wt.% s-OBP in PMMA	553	0.013	24.62	0.105	75.38	-	-
1 wt.% s-OBP in PMMA-UV	553	2.68	6.02	24.91	25.94	121.11	68.05
2 wt.% s-OBP in PMMA	548	0.009	45.71	0.094	54.29	-	-
2 wt.% s-OBP in PMMA-UV	548	3.71	3.06	29.25	24.31	119.50	72.62
5 wt.% s-OBP in PMMA	550	0.010	45.25	0.089	54.75	-	-
5 wt.% s-OBP in PMMA-UV	450	24.83	39.36	128.66	60.64	-	-
10 wt.% s-OBP in PMMA	549	0.039	17.28	0.419	82.72	-	-
10 wt.% s-OBP in PMMA-UV	549	3.84	5.04	32.51	36.09	129.29	58.87

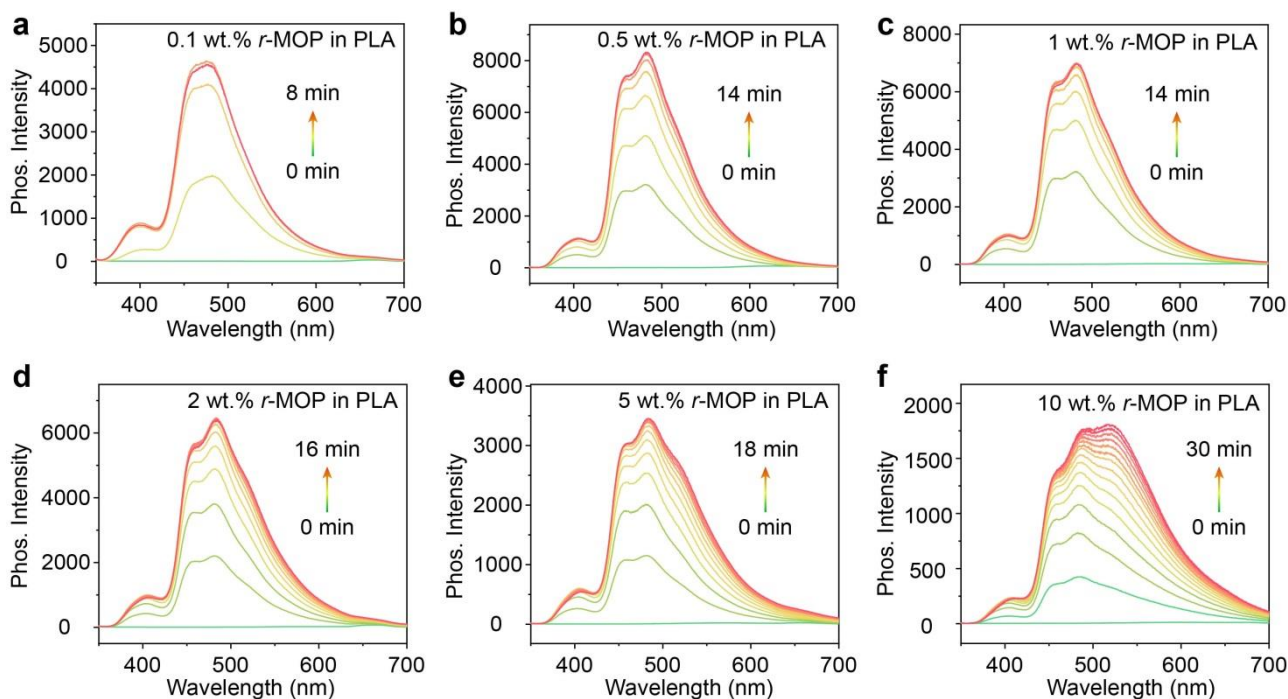
^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$ where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



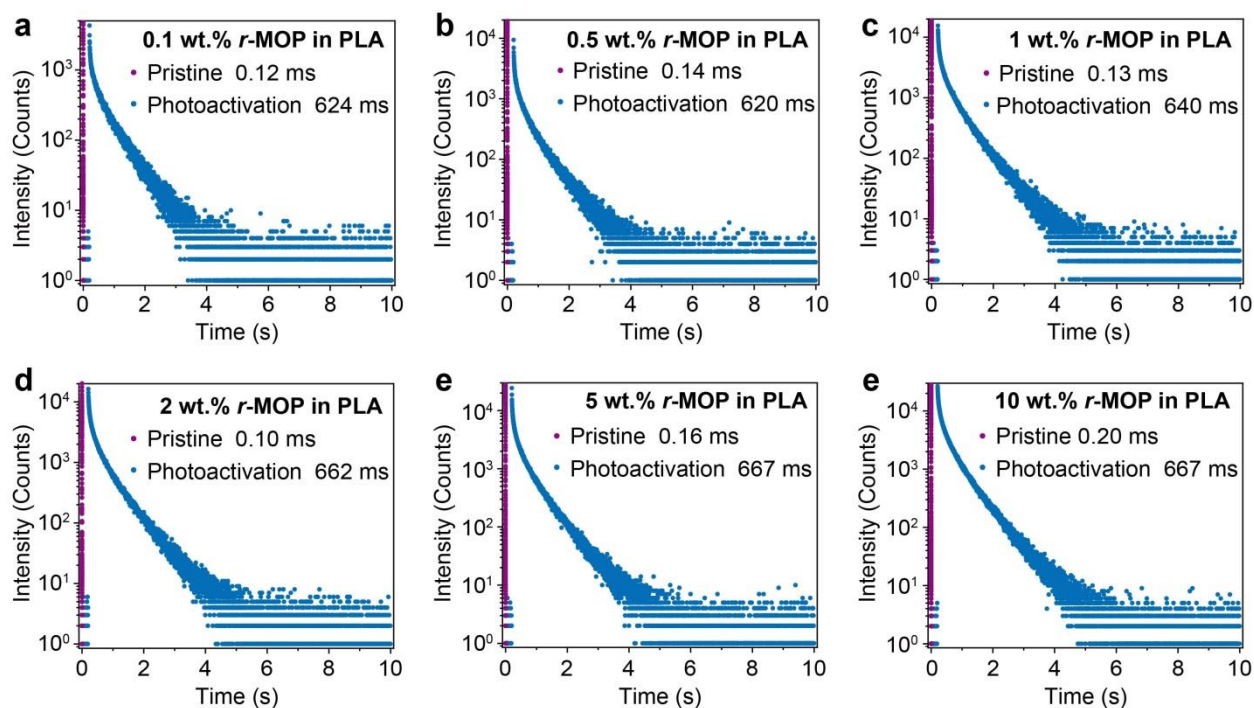
Supplementary Figure 38. Phosphorescence spectra of PVAc films with different doped concentration of r-MOP before and after photo-activated with an interval of 2 minutes (**a-f**, $\lambda_{\text{ex}} = 330 \text{ nm}$, 3.16 mW/cm^2).



Supplementary Figure 39. Lifetime profiles of PVAc films with different doped concentration of r-MOP before and after the photo-activation.



Supplementary Figure 40. Phosphorescence spectra of PLA films with different doped concentration of *r*-MOP before and after photo-activated with an interval of 2 minutes (a-f, $\lambda_{\text{ex}} = 330 \text{ nm}$, 3.16 mW/cm^2).



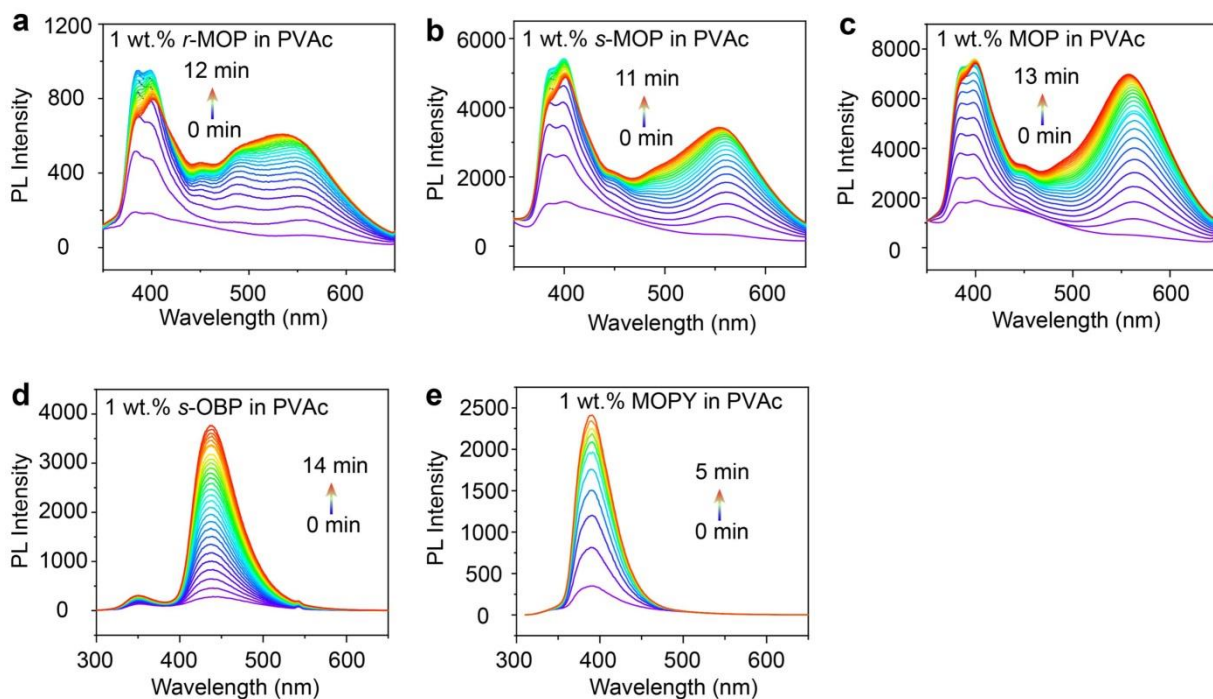
Supplementary Figure 41. Lifetime profiles of PLA films with different doped concentration of *r*-MOP before and after the photo-activation.

To explore the optimal doping concentration, r-MOP was doped into PMMA, PVAc or PLA films at the doped concentrations of 0.1, 0.5, 1, 2, 5, and 10 wt.%. As shown in Supplementary Figs. 21, 38, and 40, their photo-activation times were longer at high doped concentration of 2, 5, and 10 wt.%. In addition, photo-activated phosphorescence lifetimes were enhanced with the doped concentration from 0.1 wt.% to 2 wt.%, then shortened at the doping of 5 wt.% and 10 wt.% (Supplementary Figs. 22, 39, and 41 and Supplementary Table 10). Therefore, we chose the doping concentration of 1 wt.% after balancing the short photo-activation time and long photo-activated lifetime.

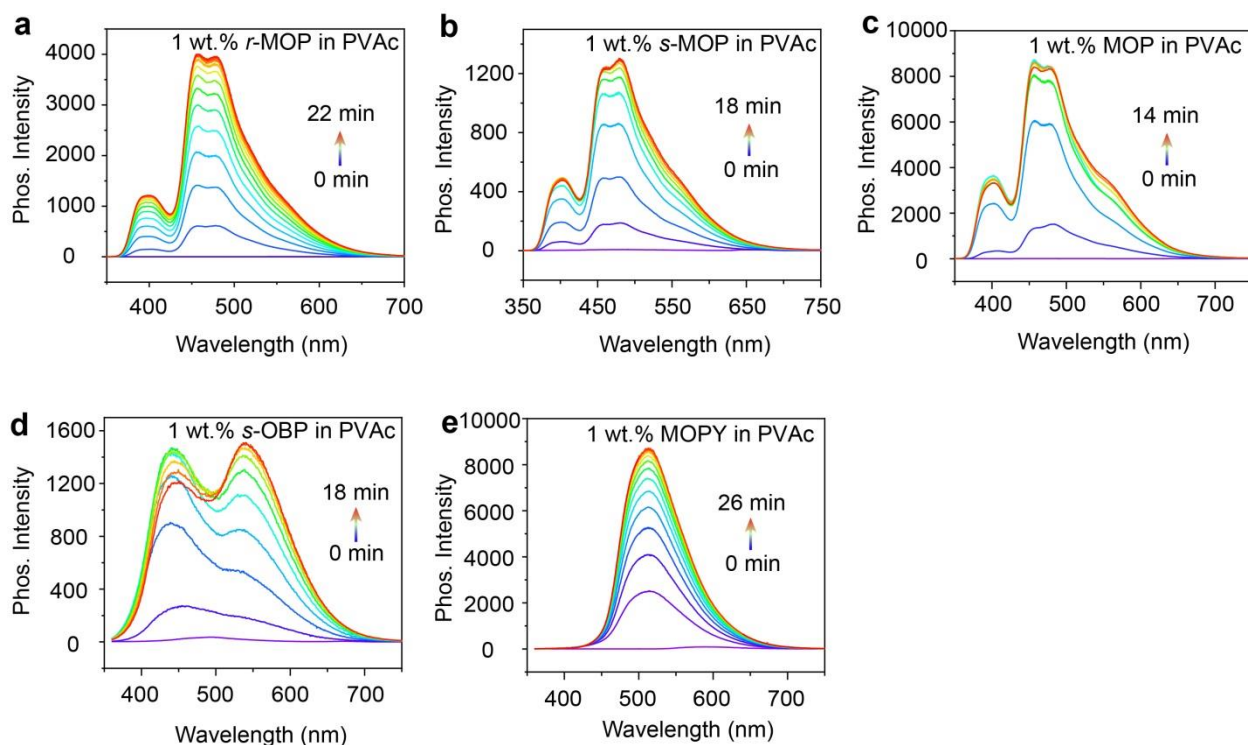
Supplementary Table 10. Phosphorescence lifetimes (τ) of PVAc or PLA films with different doped concentration of r-MOP before and after the photo-activation.^a

Compounds	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	τ_4 (ms)	A_4 (%)
0.1 wt.% r-MOP in PVAc	478	0.013	34.65	0.148	65.35	-	-	-	-
0.1 wt.% r-MOP in PVAc-UV	478	46.95	10.63	421.44	89.37	-	-	-	-
0.5 wt.% r-MOP in PVAc	477	0.012	29.72	0.123	70.28	-	-	-	-
0.5 wt.% r-MOP in PVAc-UV	477	42.28	1.22	261.17	16.31	620.55	82.47	-	-
1 wt.% r-MOP in PVAc	479	0.015	20.85	0.097	79.15	-	-	-	-
1 wt.% r-MOP in PVAc-UV	479	12.65	1.90	190.03	13.32	646.49	84.78	-	-
2 wt.% r-MOP in PVAc	477	0.018	31.73	139.96	68.27	-	-	-	-
2 wt.% r-MOP in PVAc-UV	477	47.01	2.75	304.05	23.11	664.00	74.14	-	-
5 wt.% r-MOP in PVAc	478	0.016	42.01	0.117	57.99	-	-	-	-
5 wt.% r-MOP in PVAc-UV	478	15.21	4.96	149.23	24.41	506.01	70.63	-	-
10 wt.% r-MOP in PVAc	481	0.012	33.21	0.089	66.79	-	-	-	-
10 wt.% r-MOP in PVAc-UV	481	49.10	5.16	202.31	34.98	517.72	59.86	-	-
0.1 wt.% r-MOP in PLA	476	0.013	23.02	0.118	76.98	-	-	-	-
0.1 wt.% r-MOP in PLA-UV	476	10.03	5.77	126.81	21.45	624.65	72.79	-	-
0.5 wt.% r-MOP in PLA	483	0.018	22.29	0.147	77.71	-	-	-	-
0.5 wt.% r-MOP in PLA-UV	483	25.26	9.04	175.88	32.98	619.93	57.98	-	-
1 wt.% r-MOP in PLA	483	0.011	20.74	0.131	79.26	-	-	-	-
1 wt.% r-MOP in PLA-UV	483	51.73	8.14	221.03	31.73	640.76	60.13	-	-
2 wt.% r-MOP in PLA	483	0.012	38.42	0.100	61.58	-	-	-	-
2 wt.% r-MOP in PLA-UV	483	29.22	9.55	195.73	33.83	661.98	56.62	-	-
5 wt.% r-MOP in PLA	484	0.025	27.14	0.167	72.86	-	-	-	-
5 wt.% r-MOP in PLA-UV	484	7.84	3.47	51.10	14.21	240.67	35.21	667.02	47.12
10 wt.% r-MOP in PLA	484	0.034	26.99	0.203	73.01	-	-	-	-
10 wt.% r-MOP in PLA-UV	484	45.54	10.24	236.23	37.79	667.07	51.97	-	-

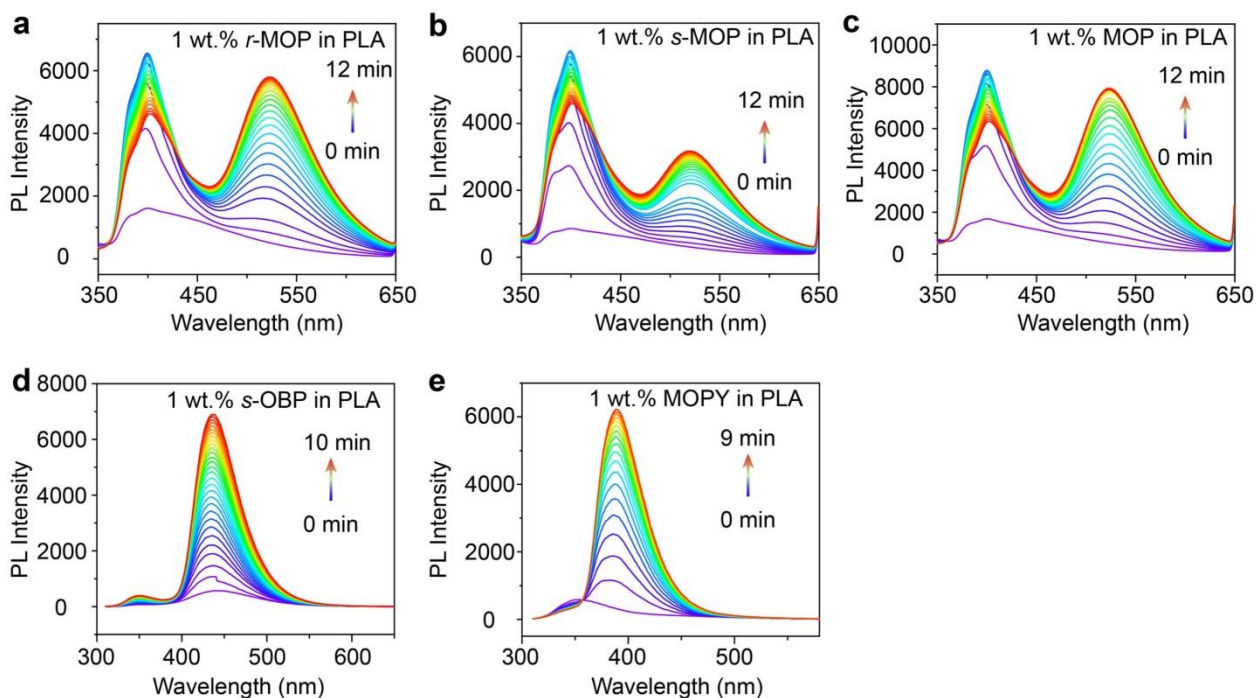
^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



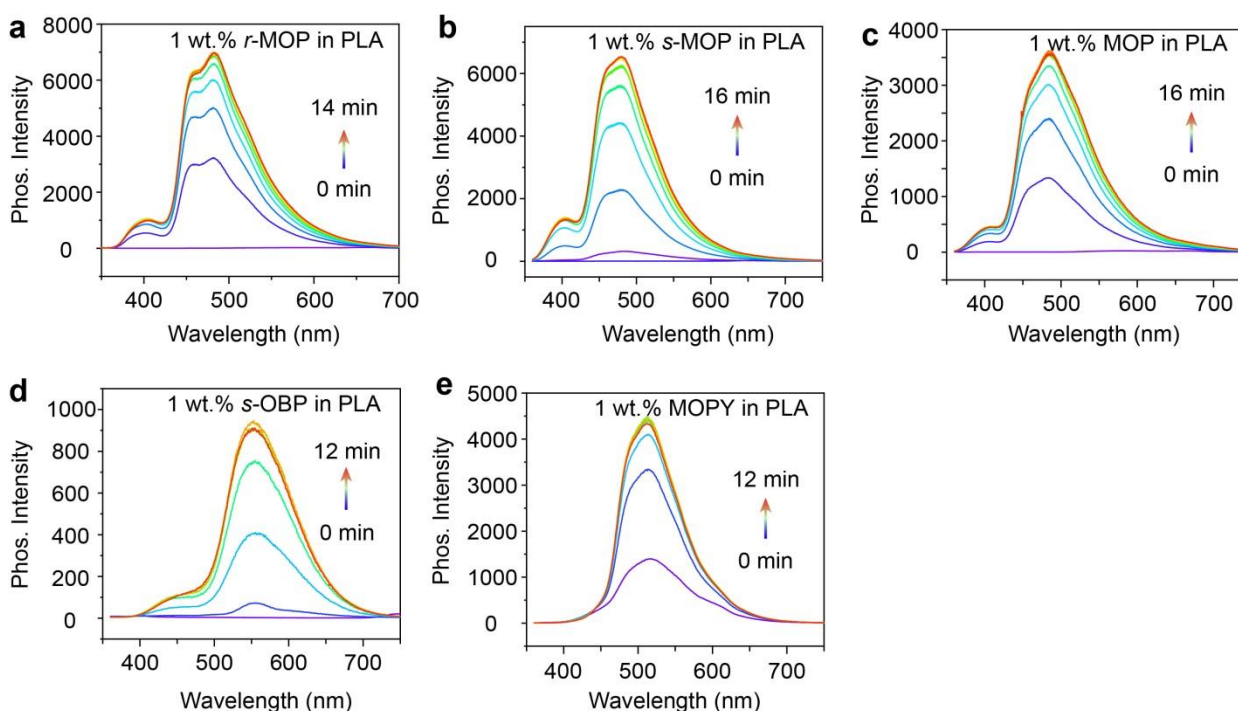
Supplementary Figure 42. Steady-state photoluminescence spectra of PVAc films doped with *r*-MOP ($\lambda_{\text{ex}} = 330$ nm), *s*-MOP ($\lambda_{\text{ex}} = 330$ nm), MOP ($\lambda_{\text{ex}} = 330$ nm), *s*-OBP ($\lambda_{\text{ex}} = 270$ nm) or MOPY ($\lambda_{\text{ex}} = 297$ nm) at the concentration of 1 wt.% with a photo-activation interval of 30 s.



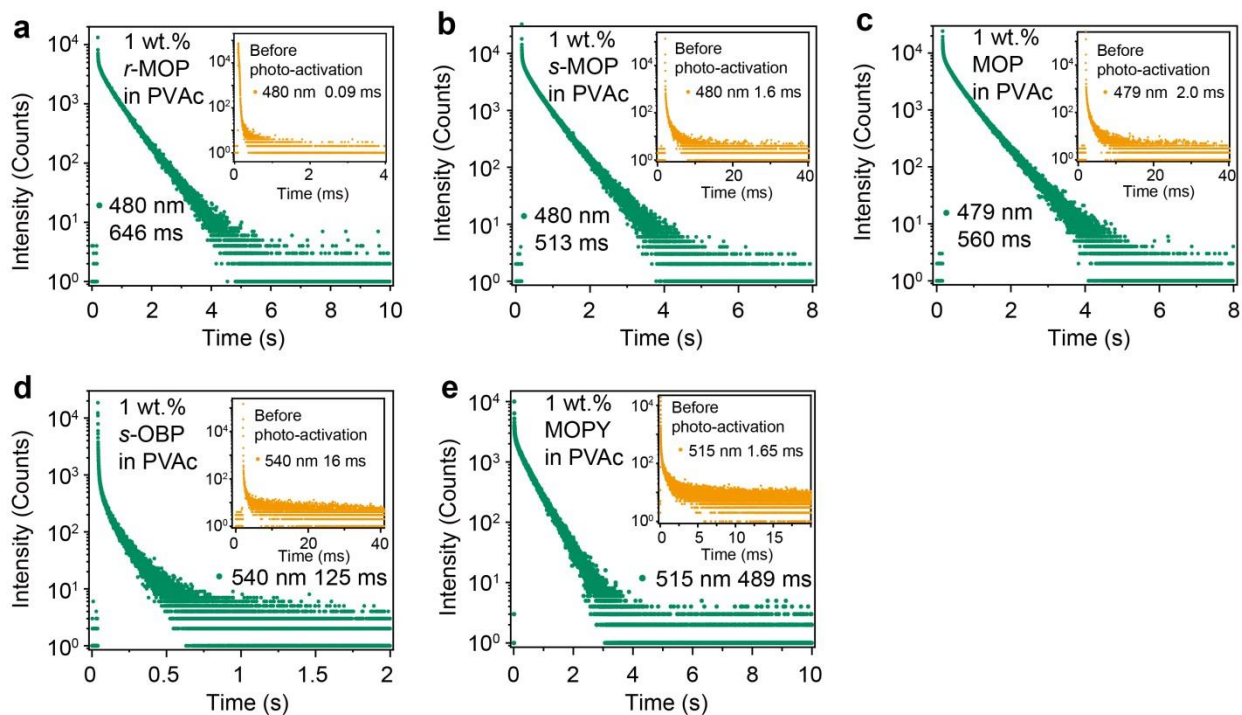
Supplementary Figure 43. Phosphorescence spectra of PVAc films doped with *r*-MOP ($\lambda_{\text{ex}} = 330$ nm, 3.15 mW/cm²), *s*-MOP ($\lambda_{\text{ex}} = 330$ nm, 3.15 mW/cm²), MOP ($\lambda_{\text{ex}} = 330$ nm, 3.15 mW/cm²), *s*-OBP ($\lambda_{\text{ex}} = 270$ nm, 20/20, 750 V) or MOPY ($\lambda_{\text{ex}} = 300$ nm, 0.18 mW/cm²) at the concentration of 1 wt.% with a photo-activation interval of 2 min.



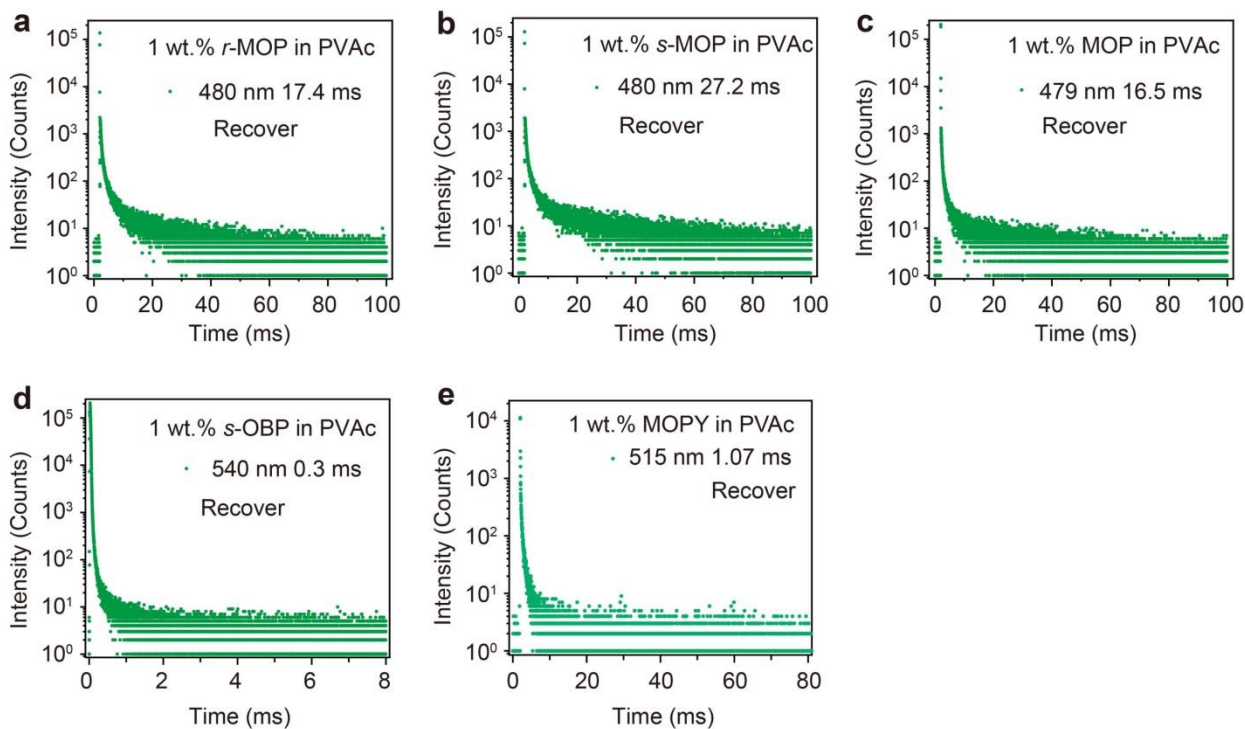
Supplementary Figure 44. Steady-state photoluminescence spectra of PLA films doped with *r*-MOP ($\lambda_{\text{ex}} = 330$ nm), *s*-MOP ($\lambda_{\text{ex}} = 330$ nm), MOP ($\lambda_{\text{ex}} = 330$ nm), *s*-OBP ($\lambda_{\text{ex}} = 270$ nm) and MOPY ($\lambda_{\text{ex}} = 297$ nm) at the concentration of 1 wt.% with a photo-activation interval of 30 s.



Supplementary Figure 45. Phosphorescence spectra of PLA films doped with *r*-MOP ($\lambda_{\text{ex}} = 330$ nm, 3.16 mW/cm²), *s*-MOP ($\lambda_{\text{ex}} = 330$ nm, 3.16 mW/cm²), MOP ($\lambda_{\text{ex}} = 330$ nm, 3.13 mW/cm²), *s*-OBP ($\lambda_{\text{ex}} = 275$ nm, 20/20, 750 V) and MOPY ($\lambda_{\text{ex}} = 300$ nm, 0.18 mW/cm²) at the concentration of 1 wt.% with a photo-activation interval of 2 min.



Supplementary Figure 46. Lifetime decay profiles of PVAc films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% before and after the photo-activation.

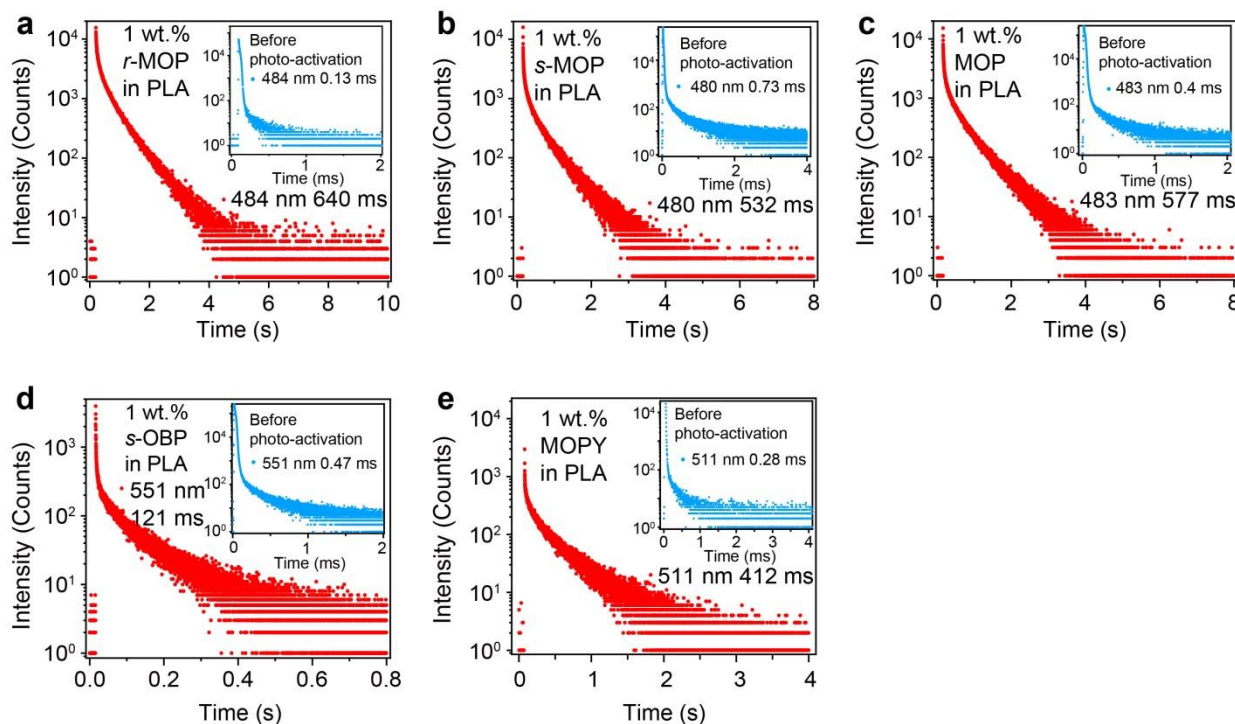


Supplementary Figure 47. Lifetime decay profiles of the photo-activated PVAc films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% after the recover in the dark.

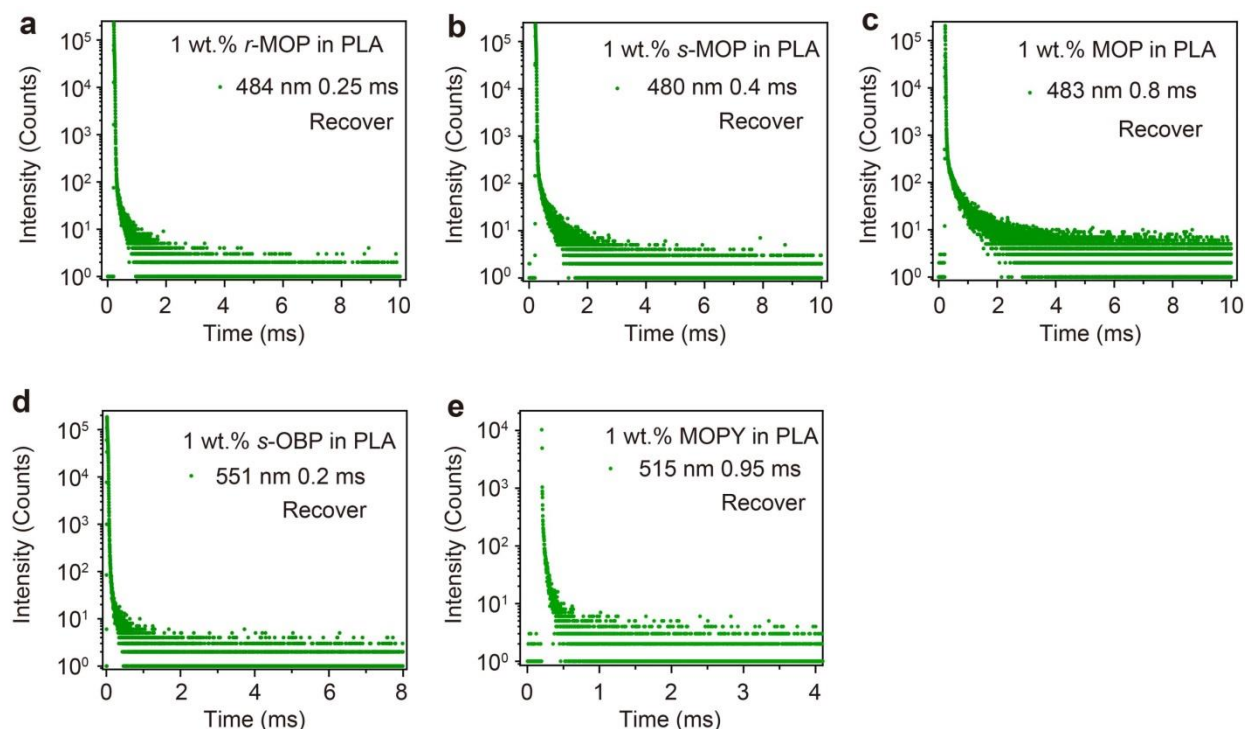
Supplementary Table 11. Phosphorescence lifetimes (τ) of PVAc films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% before and after the photo-activation, and after the recover in dark. ^a

Compound	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	τ_4 (ms)	A_4 (%)
r-MOP in PVAc-0 min	480	0.014	15.23	0.139	34.65	0.638	32.61	3.534	17.51
r-MOP in PVAc-14 min	480	123.3	10.60	618.6	89.40	-	-	-	-
r-MOP in PVAc-recover	480	0.373	29.27	2.035	36.65	17.40	34.08	-	-
s-MOP in PVAc-0 min	480	0.261	52.87	1.978	47.13	-	-	-	-
s-MOP in PVAc-18 min	480	168	15.82	560	84.18	-	-	-	-
s-MOP in PVAc-recover	480	0.27	15.45	1.0	23.96	3.658	18.42	27.23	42.18
MOP in PLA-0 min	479	0.206	53.23	1.605	46.77	-	-	-	-
MOP in PVAc-14 min	479	114.7	12.46	513.7	87.54	-	-	-	-
MOP in PVAc-recover	479	0.307	22.52	1.564	34.90	16.51	42.58	-	-
s-OBP in PVAc-0 min	540	0.515	27.28	16.21	72.72	-	-	-	-
s-OBP in PVAc-18 min	540	3.82	11.16	32.33	30.74	125.0	58.10	-	-
s-OBP in PVAc-recover	540	0.008	77.84	0.037	18.28	0.308	3.88	-	-
MOPY in PVAc-0 min	515	0.157	40.37	1.657	59.63	-	-	-	-
MOPY in PVAc-26 min	515	8.85	1.82	107.7	9.45	489.8	88.73	-	-
MOPY in PVAc-recover	515	0.18	50.80	1.07	49.20	-	-	-	-

^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



Supplementary Figure 48. Lifetime decay profiles of PLA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% before and after the photo-activation.

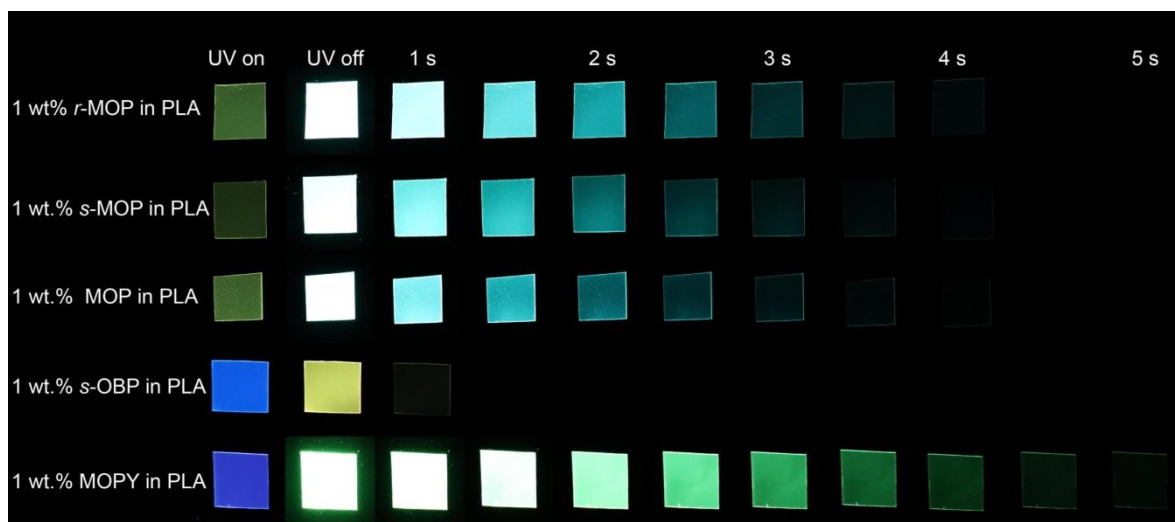


Supplementary Figure 49. Lifetime decay profiles of the photo-activated PLA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% after the recover in the dark.

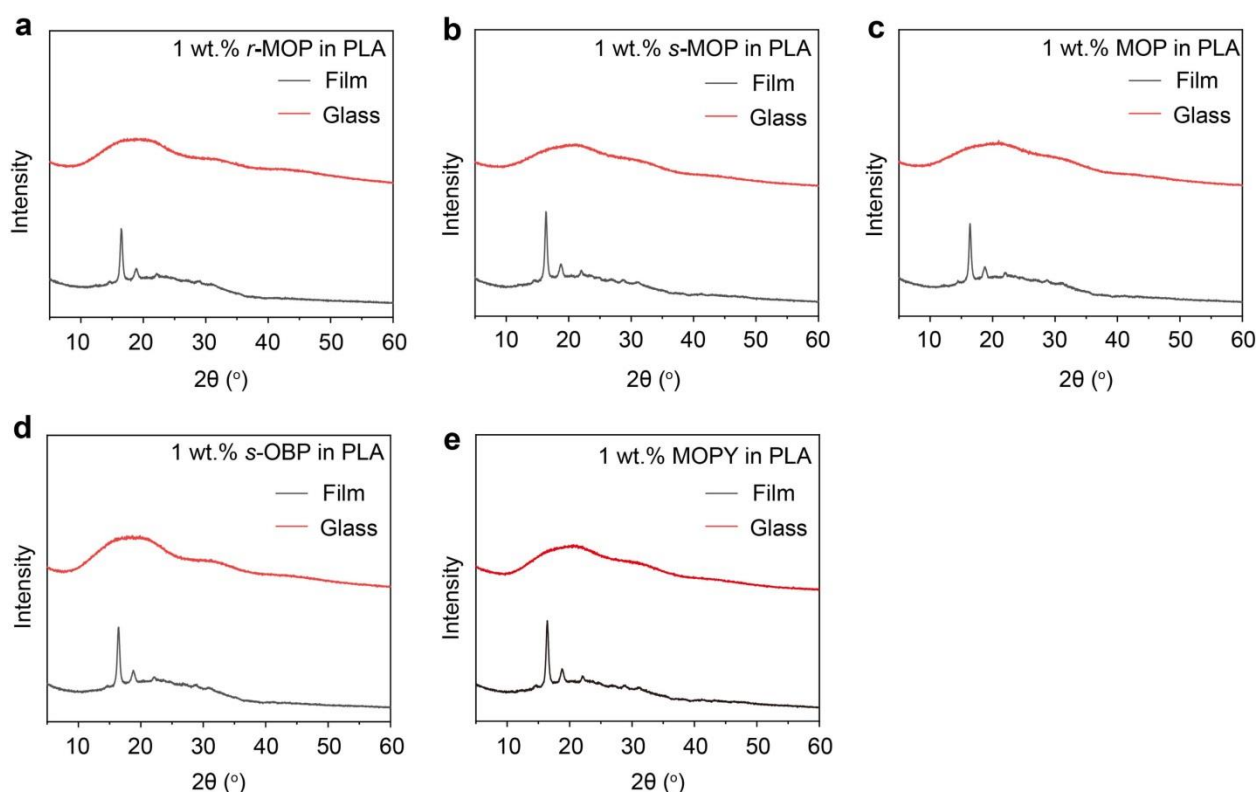
Supplementary Table 12. Phosphorescence lifetimes (τ) of PLA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% before and after the photo-activation, and after the recover in dark.^a

Compounds	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A ₁ (%)	τ_2 (ms)	A ₂ (%)	τ_3 (ms)	A ₃ (%)	τ_4 (ms)	A ₄ (%)
r-MOP in PLA-0 min	484	0.017	15.89	0.111	38.70	0.472	45.41	-	-
r-MOP in PLA-24 min	484	63	25.01	497.1	69.14	-	-	-	-
r-MOP in PLA-recover	484	0.007	86.26	0.043	6.11	0.246	7.63	-	-
s-MOP in PLA-0 min	480	0.017	24.43	0.145	37.43	0.726	38.23	-	-
s-MOP in PLA-16 min	480	94.1	27.40	532	71.60	-	-	-	-
s-MOP in PLA-recover	480	0.007	83.40	0.064	7.67	0.403	8.93	-	-
MOP in PLA-0 min	483	0.015	33.24	0.1	30.54	0.440	36.22	-	-
MOP in PLA-16 min	483	97.5	25.73	577.0	74.27	-	-	-	-
MOP in PLA-recover	483	0.006	29.39	0.025	20.73	177.7	26.75	0.797	23.13
s-OBP in PLA-0 min	551	0.012	33.87	0.08	29.87	0.40	36.26	-	-
s-OBP in PLA-12 min	551	2.48	6.5	27.85	25.95	122.7	67.55	-	-
s-OBP in PLA-recover	551	0.006	82.71	0.026	13.04	0.182	4.26	-	-
MOPY in PLA-0 min	511	0.007	74.5	30.75	13.71	287.5	11.79	-	-
MOPY in PLA-12 min	511	4.65	3.35	83.36	23.66	412.0	72.99	-	-
MOPY in PLA-recover	511	0.17	51.23	0.958	48.77	-	-	-	-

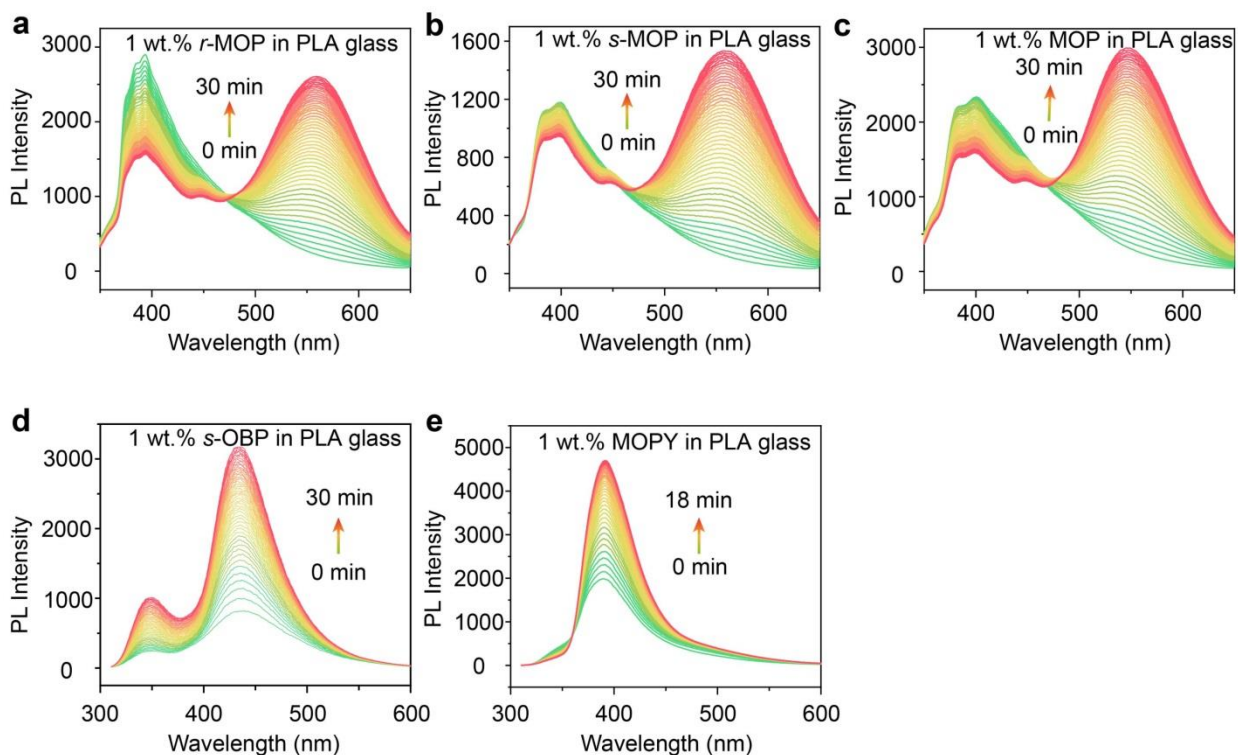
^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



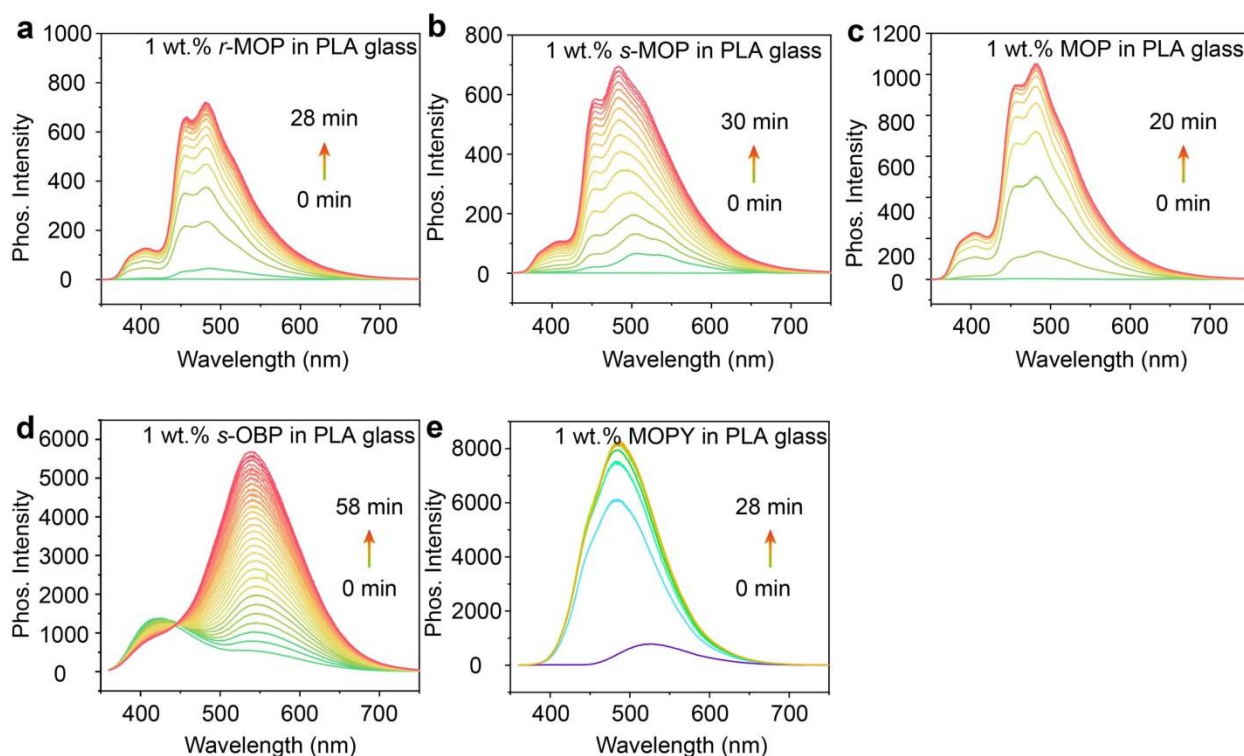
Supplementary Figure 50. Photographs of the photo-activated PLA films doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% taken under 365 nm lamp on and off. Note: All PLA films were photo-activated by 302 nm.



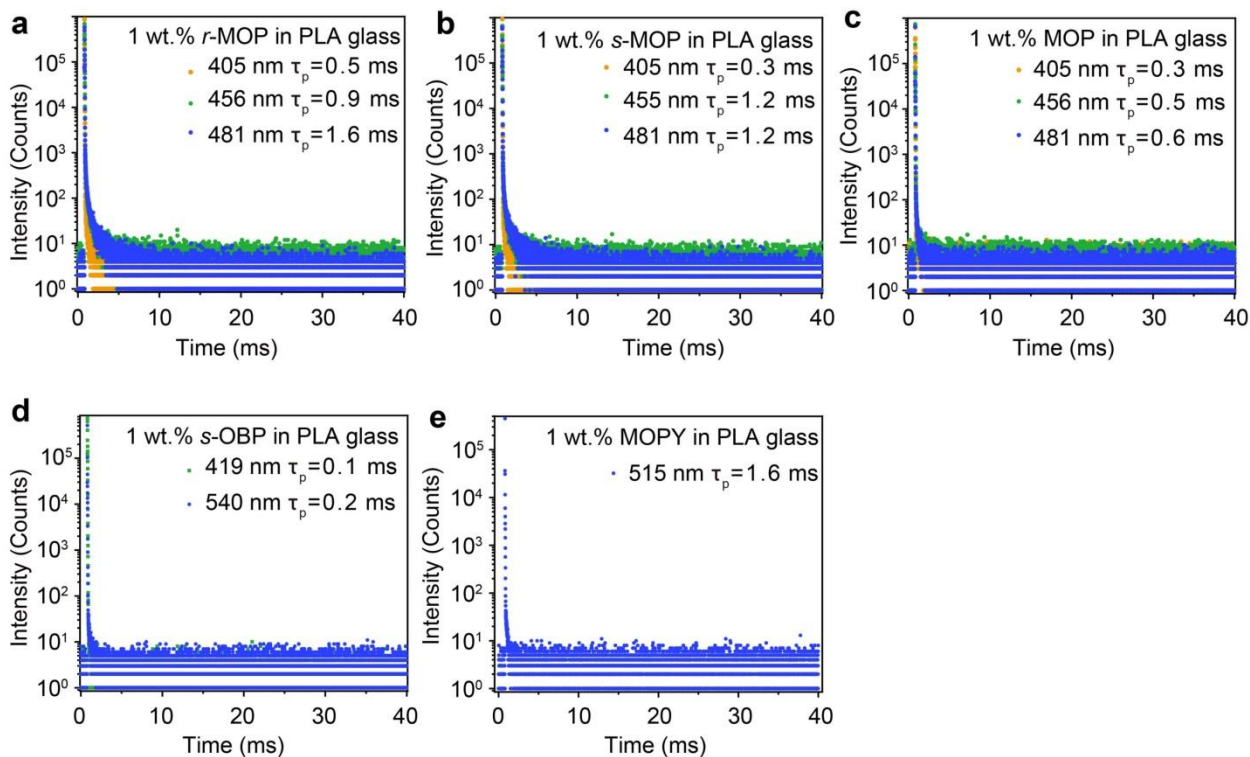
Supplementary Figure 51. PXRD patterns of PLA films (black lines) and glass (red lines) doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.%.



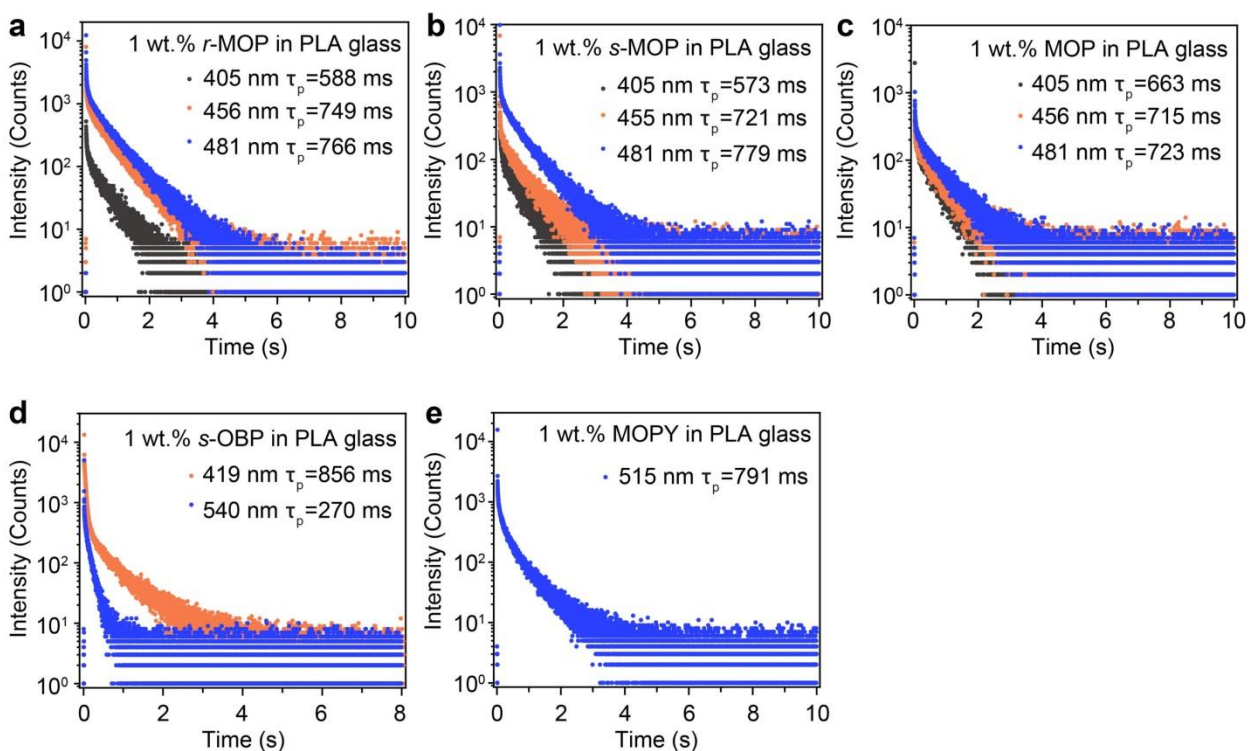
Supplementary Figure 52. Steady-state photoluminescence spectra of PLA glass doped with r-MOP ($\lambda_{\text{ex}} = 330 \text{ nm}$), s-MOP ($\lambda_{\text{ex}} = 330 \text{ nm}$), MOP ($\lambda_{\text{ex}} = 330 \text{ nm}$), s-OBP ($\lambda_{\text{ex}} = 270 \text{ nm}$) or MOPY ($\lambda_{\text{ex}} = 300 \text{ nm}$) at the concentration of 1 wt.% with a photo-activation interval of 30 s.



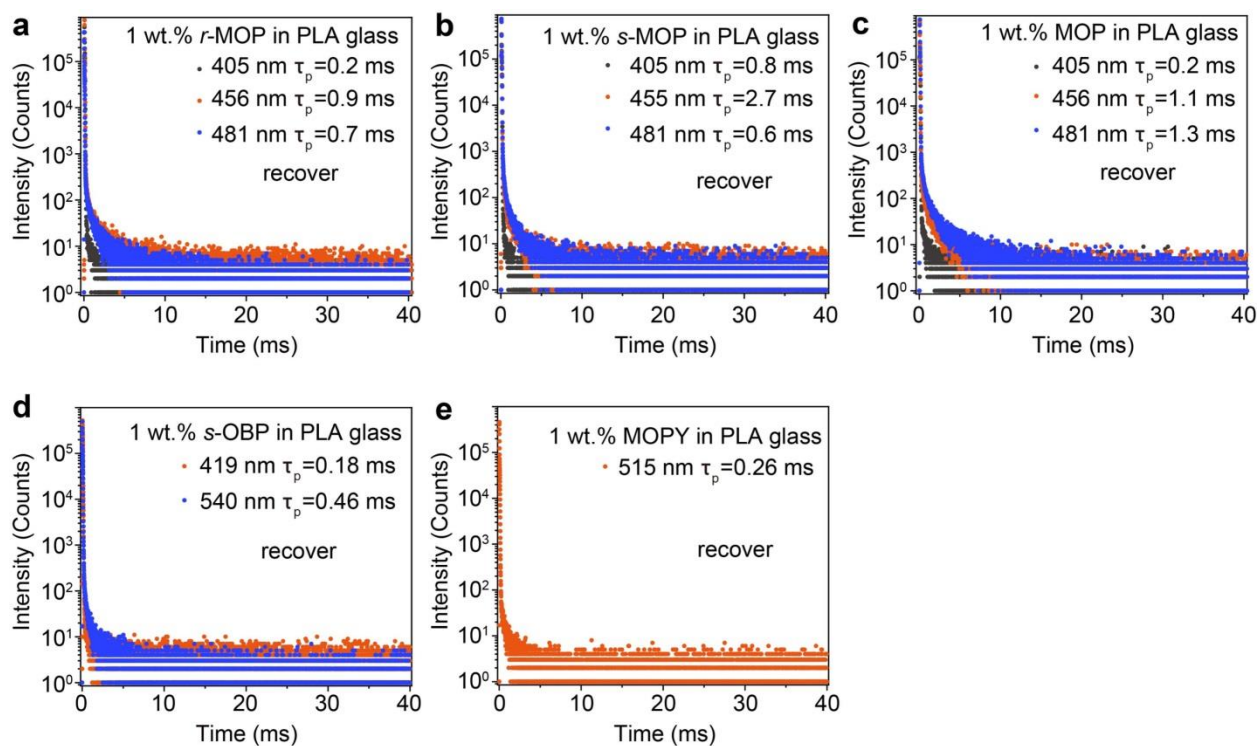
Supplementary Figure 53. Phosphorescence spectra of PLA glass doped with r-MOP ($\lambda_{\text{ex}} = 330 \text{ nm}$, 1.10 mW/cm^2), s-MOP ($\lambda_{\text{ex}} = 330 \text{ nm}$, 1.10 mW/cm^2), MOP ($\lambda_{\text{ex}} = 330 \text{ nm}$, 1.10 mW/cm^2), s-OBP ($\lambda_{\text{ex}} = 270 \text{ nm}$, 20/20, 750 V) or MOPY ($\lambda_{\text{ex}} = 300 \text{ nm}$, 10/10, 700 V) at the concentration of 1 wt.% with a photo-activation interval of 2 min.



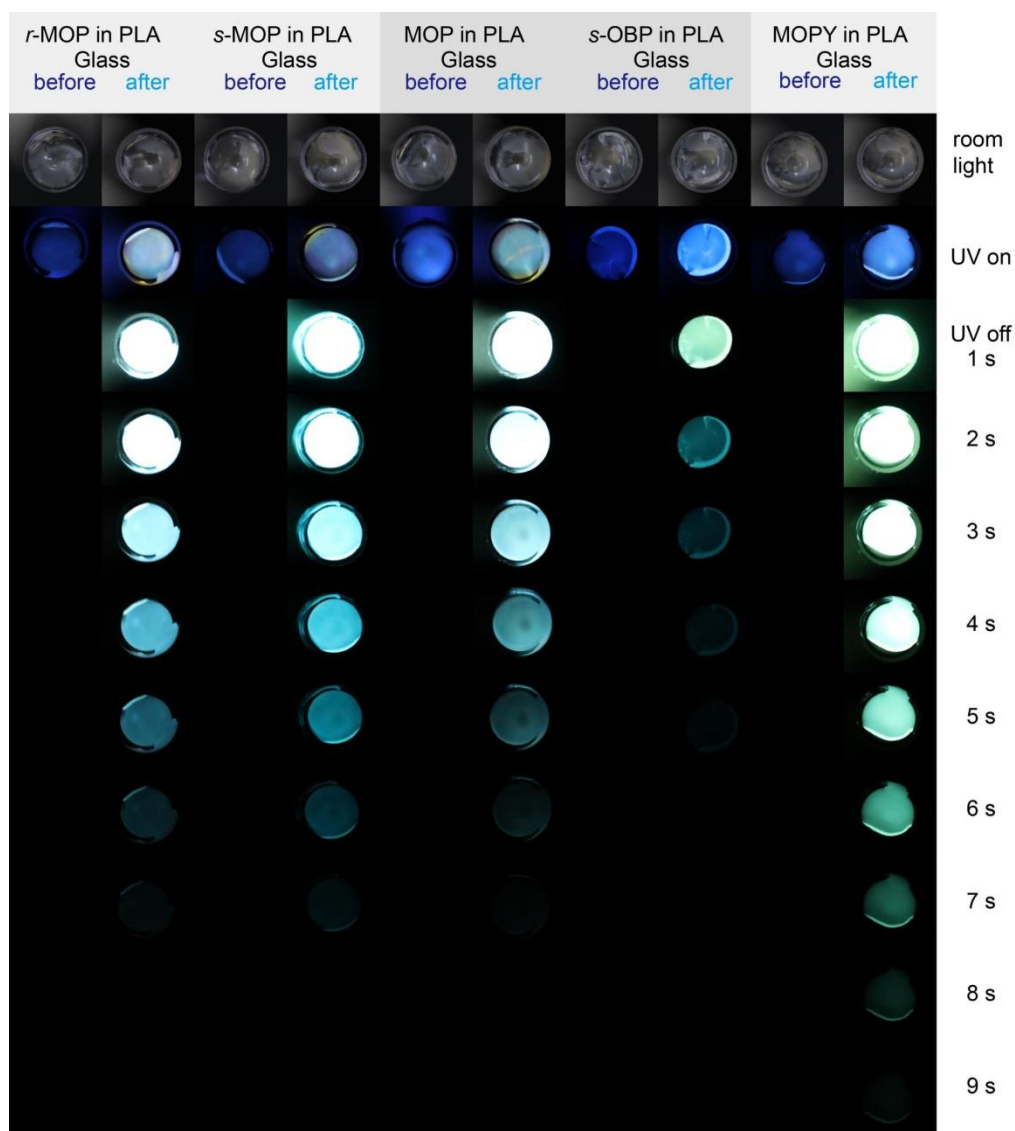
Supplementary Figure 54. Lifetime decay profiles of PLA glass doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% before the photo-activation.



Supplementary Figure 55. Lifetime decay profiles of PLA glass doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt.% after the photo-activation.



Supplementary Figure 56. Lifetime decay profiles of PLA glass doped with *r*-MOP, *s*-MOP, MOP, *s*-OBP or MOPY at the concentration of 1 wt.% after the recover in the dark.



Supplementary Figure 57. Photographs of the photo-activated PLA glass doped with *r*-MOP, *s*-MOP, MOP, *s*-OBP or MOPY at the concentration of 1 wt.% taken under 365 nm lamp on and off. Note: All PLA films were photo-activated by 302 nm.

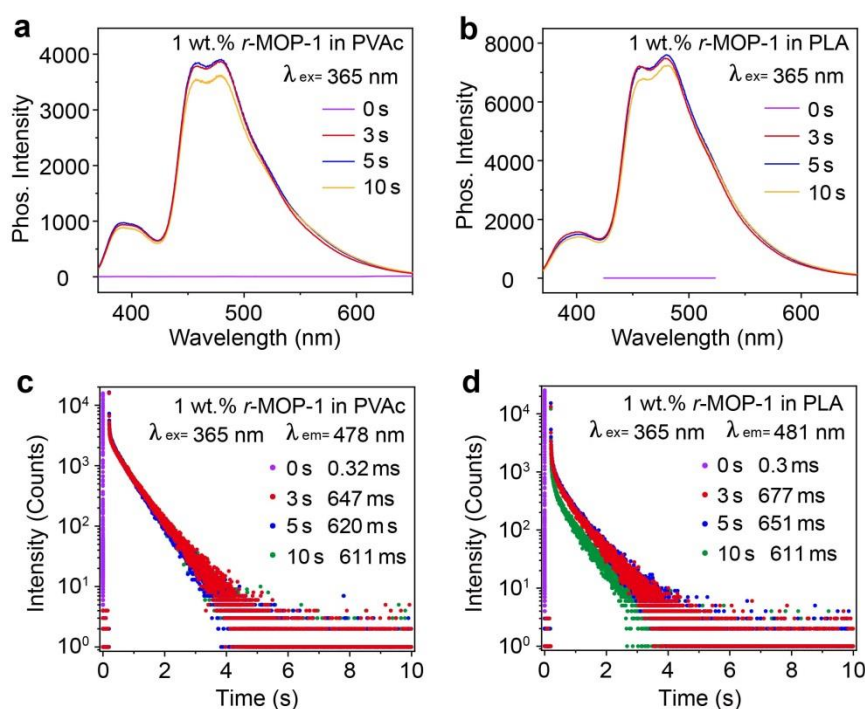
Supplementary Table13. Phosphorescence lifetimes of PLA glass doped with r-MOP, s-MOP, MOP, s-OBP or MOPY at the concentration of 1 wt. % before and after the photo-activation, and after the recover in dark.^a

Compounds	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	τ_4 (ms)	A_4 (%)
r-MOP in PLA-0 min	405	0.008	83.20	0.062	9.27	0.518	7.54	-	-
	456	0.030	25.59	0.208	41.47	1.611	32.94	-	-
	481	0.009	57.00	102.7	25.96	0.966	17.04	-	-
r-MOP in PLA-28 min	405	39.80	10.54	588.58	89.46	-	-	-	-
	455	11.25	3.42	202.8	18.12	766.28	78.46	-	-
	481	7.08	3.23	138.9	14.42	749.61	82.35	-	-
r-MOP in PLA-recover	405	0.007	50.27	0.011	43.26	0.258	6.47	-	-
	456	0.012	22.33	0.126	30.64	0.909	47.03	-	-
	481	0.008	70.20	0.102	13.04	0.704	16.76	-	-
MOP in PLA-0 min	405	0.001	14.75	0.011	74.51	0.299	10.74	-	-
	456	0.011	34.14	67.48	32.88	0.583	32.97	-	-
	481	0.012	29.93	0.096	38.12	0.680	31.95	-	-
MOP in PLA-30 min	405	40.54	7.84	633.6	92.16	-	-	-	-
	455	42.67	6.42	714.9	93.58	-	-	-	-
	481	33.82	7.00	723.2	93.00	-	-	-	-
MOP in PLA-recover	405	0.004	28.88	0.011	61.06	215.7	10.05	-	-
	456	0.007	64.94	0.033	10.17	0.210	11.98	1.103	12.92
	481	0.007	54.38	0.040	12.09	0.259	18.89	1.308	14.65
s-MOP in PLA-0 min	405	0.007	81.43	0.021	14.13	0.354	1.13	-	-
	455	0.014	37.94	0.123	32.05	1.233	30.01	-	-
	481	0.019	28.27	0.161	36.43	1.204	35.30	-	-
s-MOP in PLA-20 min	406	33.35	11.83	573.3	88.17	-	-	-	-
	455	7.154	2.93	114.8	11.34	721.2	85.73	-	-
	481	2.77	1.64	28.71	4.25	242.7	15.99	779.3	78.12
s-MOP in PLA-recover	405	0.014	32.87	0.101	58.2	0.824	8.93	-	-
	456	0.012	22.27	0.069	32.99	0.439	27.93	2.736	16.80
	481	0.008	77.84	0.037	18.28	0.632	3.88	-	-
s-OBP in PLA-0 min	419	0.009	93.86	0.098	6.14	-	-	-	-
	540	12.4	41.97	0.200	58.03	-	-	-	-
s-OBP in PLA-58 min	419	0.034	37.33	252.0	21.23	856.8	41.43	-	-
	540	1.68	3.06	17.14	9.68	107.8	62.18	270.8	25.07
s-OBP in PLA-recover	419	0.006	48.82	0.011	50.00	0.188	1.19	-	-
	540	0.006	45.60	0.014	29.71	0.085	13.29	0.466	11.39
MOPY in PLA-0 min	515	0.009	74.43	0.169	25.57	-	-	-	-
MOPY in PLA-28 min	515	4.759	2.35	47.85	9.62	234.1	33.74	791.0	54.28

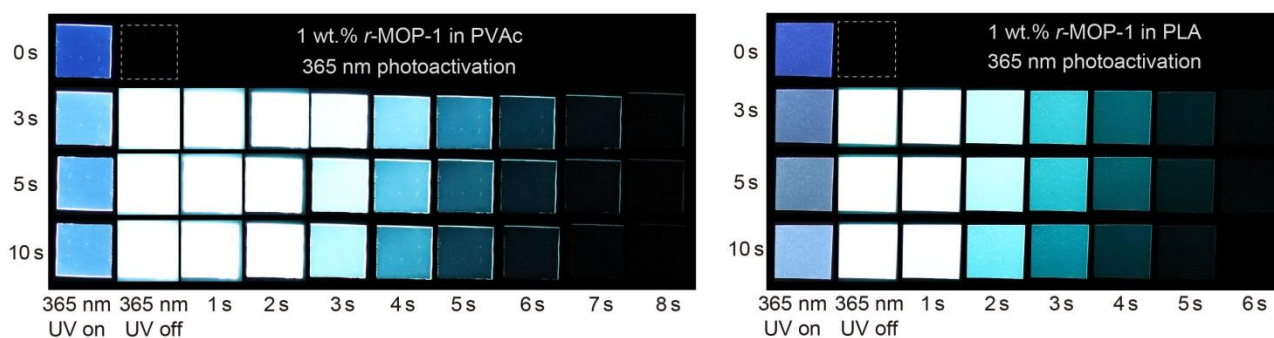
MOPY in PLA-recover	515	0.008	90.56	0.042	2.98	0.264	6.46	-	-
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^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.

3 mg r-MOP in 1.5 mL chloroform solution was photo-activated by 302 nm UV lamp (4.04 mW/cm²) for 4.5 minutes, then doped into PVAc or PLA solution to prepare 1 wt.% r-MOP-1 in PVAc film and 1 wt.% r-MOP-1 in PLA film. As anticipated, 1 wt.% r-MOP-1 in PVAc film and 1 wt.% r-MOP-1 in PLA film can be photo-activated by 365 nm for only 3 s, their phosphorescence lifetimes are longer than that of 1 wt.% r-MOP in PVAc film and 1 wt.% r-MOP in PLA film (Supplementary Figs. 58 and 59, Supplementary Table 14). In a word, Route 2 is applicable to PMMA, PVAc, and PLA polymers.



Supplementary Figure 58. Phosphorescence spectra of (a) 1 wt.% r-MOP-1 in PLA film and (b) 1 wt.% r-MOP-1 in PVAc film after photo-activated by 365 nm (39.9 mW/cm²). Lifetime decay profiles of (c) 1 wt.% r-MOP-1 in PLA film and (d) 1 wt.% r-MOP-1 in PVAc film before and after photo-activated by 365 nm (39.9 mW/cm²).



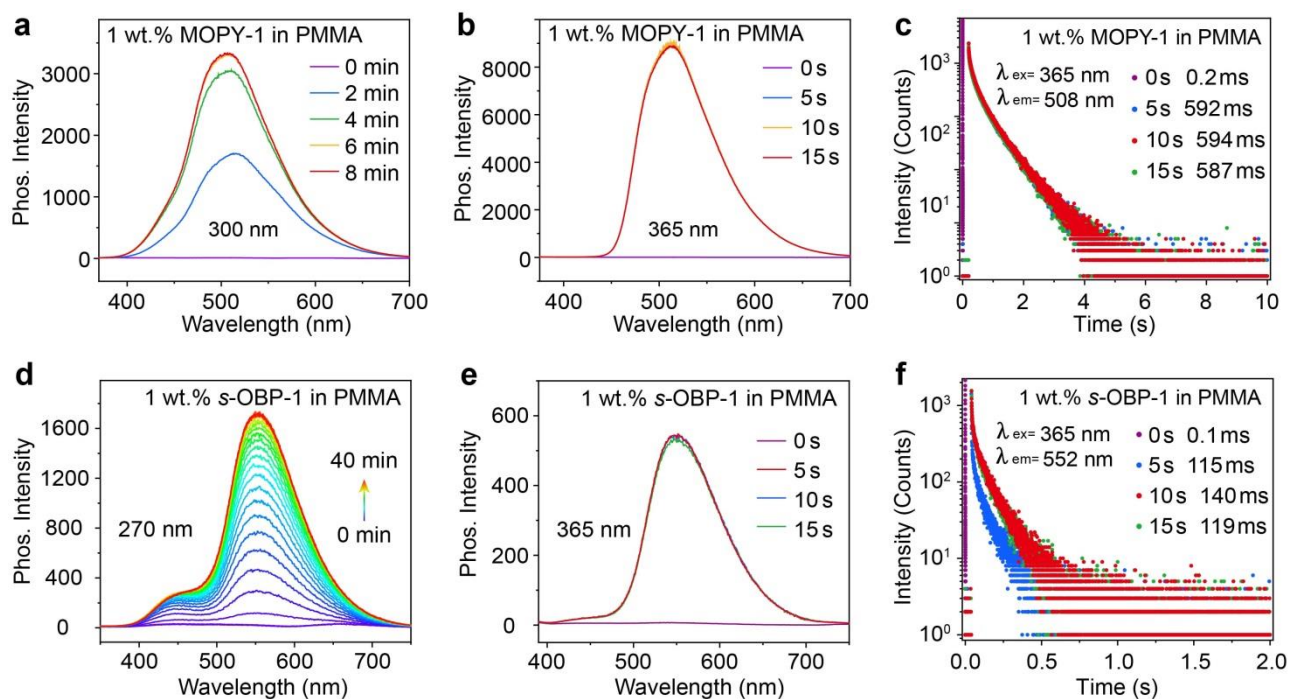
Supplementary Figure 59. Photographs of 1 wt.% r-MOP-1 in PLA film and 1 wt.% r-MOP-1 in PVAc film before and after photo-activated by 365 nm UV lamp (39.9 mW/cm²) taken under 365 nm UV lamp (39.9 mW/cm²) on and off.

Supplementary Table 14. Phosphorescence lifetimes (τ) of 1 wt.% r-MOP-1 in PVAc and 1 wt.% r-MOP-1 in PLA film before and after the photo-activation. ^a

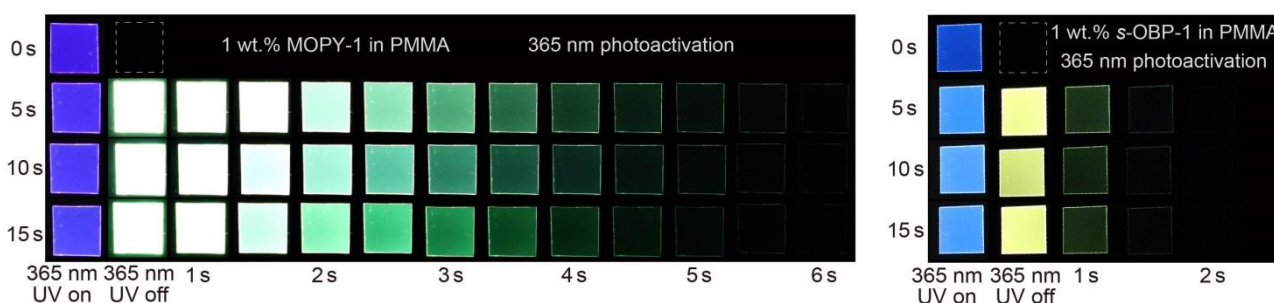
Compounds	Wavelength (nm)	Phosphorescence					
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)
1 wt.% r-MOP-1 in PVAc-0 s	478	0.008	4.76	0.062	17.69	0.319	77.55
1 wt.% r-MOP-1 in PVAc-5 s	478	25.92	1.96	239.12	14.32	647.11	83.72
1 wt.% r-MOP-1 in PVAc-10 s	478	32.27	2.02	262.46	18.03	620.09	79.96
1 wt.% r-MOP-1 in PVAc-15 s	478	176.25	13.50	611.03	86.50	-	-
1 wt.% r-MOP-1 in PLA-0 s	481	0.008	6.81	0.084	35.98	0.300	57.21
1 wt.% r-MOP-1 in PLA-3 s	481	27.34	5.12	192.22	22.50	677.56	72.38
1 wt.% r-MOP-1 in PLA-5 s	481	9.80	5.78	130.43	20.20	651.60	74.02
1 wt.% r-MOP-1 in PLA-10 s	481	12.75	6.10	115.22	21.63	611.09	72.27

^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.

MOPY and s-OBP in chloroform were photo-activated by 302 nm, then were doped into PMMA to prepare PMMA films doped with 1 wt.% MOPY-1 and 1 wt.% s-OBP-1, respectively. As shown in Supplementary Fig. 60, the photo-activation time of 1 wt.% MOPY-1 in PMMA films photo-activated by 300 nm is shorter compared with that of 1 wt.% MOPY in PMMA films. The photo-activation time of 1 wt.% s-OBP-1 in PMMA films photo-activated by 270 nm remains almost unchanged compared with that of 1 wt.% s-OBP in PMMA films. Notably, both 1 wt.% MOPY-1 in PMMA films and 1 wt.% s-OBP-1 in PMMA film can be quickly photo-activated by a 365-nm UV lamp (Supplementary Figs. 60 and 61). Their phosphorescence lifetimes are slightly longer than that of 1 wt.% MOPY in PMMA films and 1 wt.% s-OBP in PMMA film, respectively (Fig. 3 and Supplementary Fig. 60, Supplementary Table 15). These results confirm the universality of this strategy.



Supplementary Figure 60. Phosphorescence spectra of 1 wt.% MOPY-1 in PMMA films photo-activated by (a) 300 nm or (b) 365 nm (39.9 mW/cm²). c, Lifetime decay profiles of 1 wt.% MOPY-1 in PMMA film excited by 365 nm monitoring 508 nm before and after photo-activated by 365 nm. Phosphorescence spectra of 1 wt.% s-OBP-1 in PMMA films photo-activated by (d) 270 nm and (e) 365 nm (39.9 mW/cm²). f, Lifetime decay profiles of 1 wt.% s-OBP-1 in PMMA film excited by 365 nm monitoring 552 nm before and after photo-activated by 365 nm.



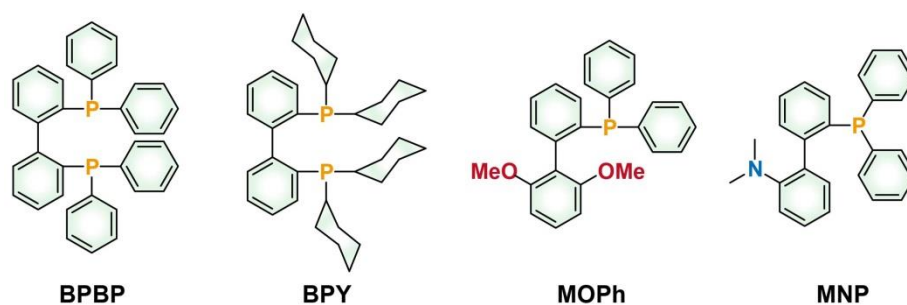
Supplementary Figure 61. Photographs of 1 wt.% MOPY-1 in PMMA film and 1 wt.% s-OBP-1 in PMMA film before and after photo-activated by 365 nm UV lamp (39.9 mW/cm²) taken under 365 nm UV lamp (39.9 mW/cm²) on and off.

Supplementary Table 15. Phosphorescence lifetimes (τ) of 1 wt.% MOPY-1 in PMMA film and 1 wt.% s-OBP-1 in PMMA film photo-activated by 365 nm with different irradiation time. ^a

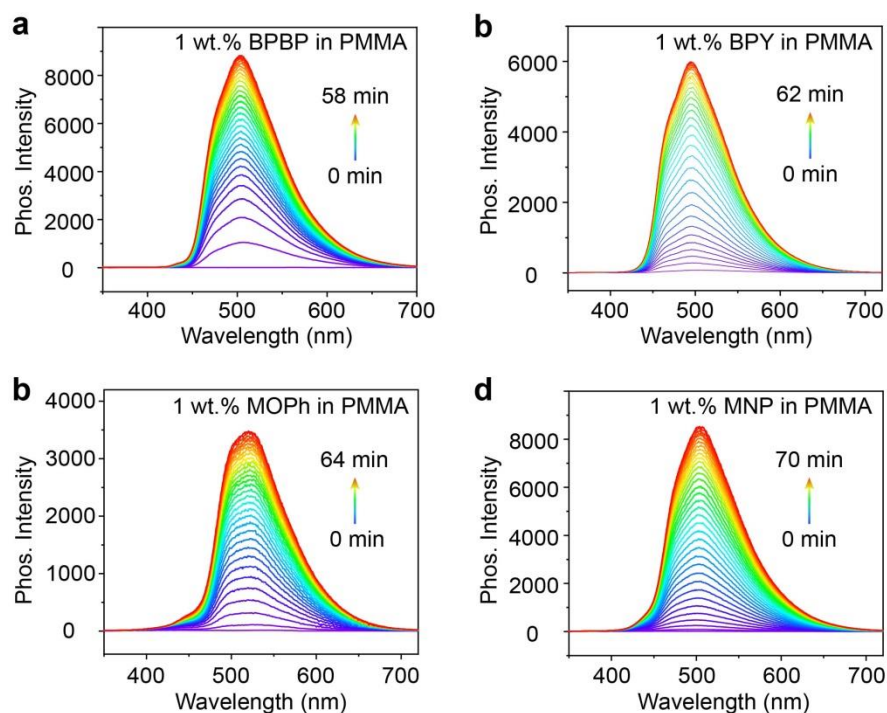
Compounds	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A ₁ (%)	τ_2 (ms)	A ₂ (%)	τ_3 (ms)	A ₃ (%)	τ_4 (ms)	A ₄ (%)
1 wt.% MOPY-1 in PMMA-0 s	508	0.001	28.41	0.222	71.59	-	-	-	-
1 wt.% MOPY-1 in PMMA-5 s	508	45.66	8.32	206.88	39.22	592.26	52.46	-	-
1 wt.% MOPY-1 in PMMA-10 s	508	50.37	8.25	216.50	40.48	594.18	51.27	-	-
1 wt.% MOPY-1 in PMMA-15 s	508	43.15	8.79	206.09	41.90	587.69	49.61	-	-
1 wt.% s-OBP-1 in PMMA-0 s	552	0.009	64.86	0.099	35.14	-	-	-	-
1 wt.% s-OBP-1 in PMMA-5 s	552	2.13	6.43	23.83	23.94	114.80	69.63	-	-
1 wt.% s-OBP-1 in PMMA-10 s	552	1.71	1.86	11.75	8.48	50.01	28.44	140.40	61.21
1 wt.% s-OBP-1 in PMMA-15 s	552	1.66	6.85	26.06	22.10	119.49	71.05	-	-

^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.

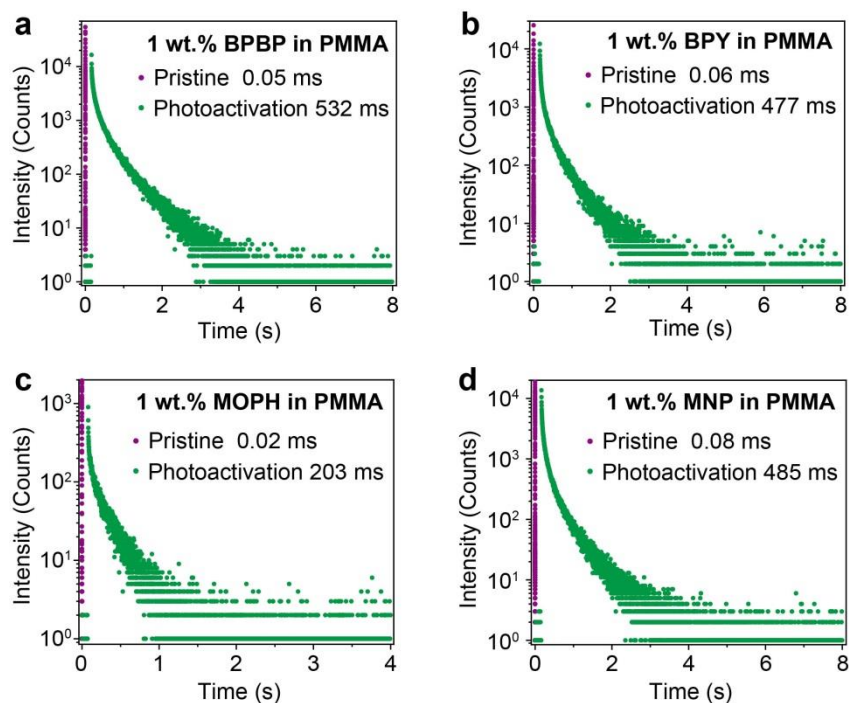
r-MOP, s-OBP, and MOPY are typical organophosphorus ligands, and they can generate free radicals upon ultraviolet light irradiation. To comprehensively validate the universality of the strategy, we supplemented four additional organophosphorus ligands, namely, BPBP, BPY, MOPh and MNP (Supplementary Fig. 62). BPBP, BPY, MOPh and MNP were doped into PMMA at the concentration of 1 wt.%, respectively. As expected, all PMMA films demonstrated green ultralong organic phosphorescence after photo-activated by UV light for approximately 1 hour (Supplementary Fig. 63). The photo-activated phosphorescence lifetimes of PMMA films doped with BPBP, BPY, MOPh and MNP at the concentration of 1 wt.% are 532, 477, 203, and 485 ms, respectively (Supplementary Fig. 64 and (Supplementary Table 16)). EPR spectra of PMMA films doped with BPBP, BPY, MOPh and MNP at the concentration of 1 wt.% revealed the generation of radical after the photo-activation (Supplementary Fig. 65). Therefore, it is a widely applicable method for achieving photo-activated ultralong organic phosphorescence by doping organic phosphorus ligands into PMMA.



Supplementary Figure 62. The chemical structures of other phosphorus ligands.



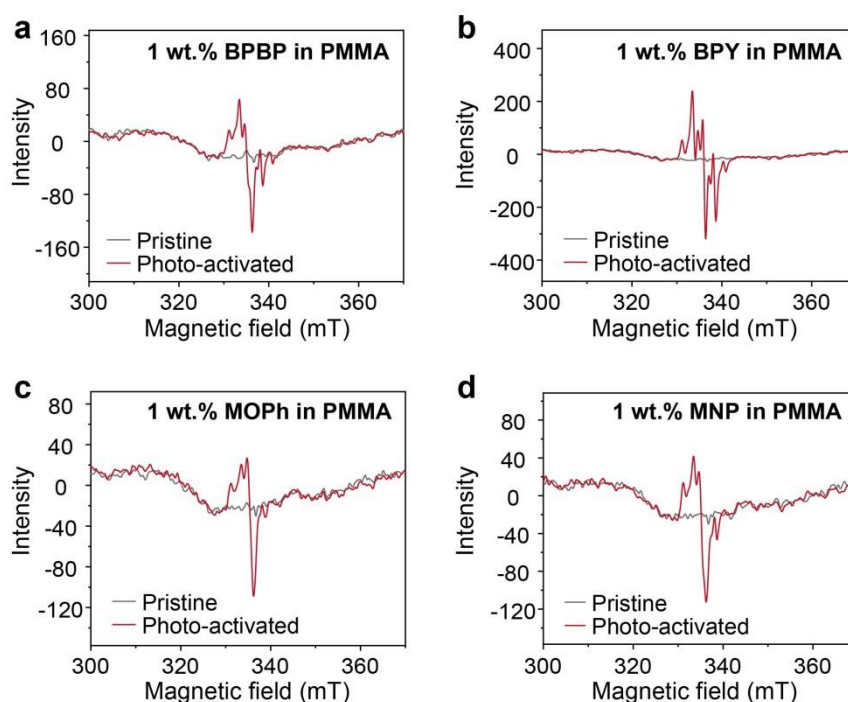
Supplementary Figure 63. Phosphorescence spectra of PMMA films doped with BPBP, BPY, MOPh, or MNP at the concentration of 1 wt.% with a photo-activation interval of 2 min (**a**, $\lambda_{\text{ex}}=280$ nm, $\text{ex}=20$, $\text{em}=10$, 750 V; **b**, $\lambda_{\text{ex}}=275$ nm, $\text{ex}=20$, $\text{em}=10$, 700 V; **c**, $\lambda_{\text{ex}}=270$ nm, $\text{ex}=20$, $\text{em}=10$, 800 V; **d**, $\lambda_{\text{ex}}=280$ nm, $\text{ex}=20$, $\text{em}=10$, 800 V).



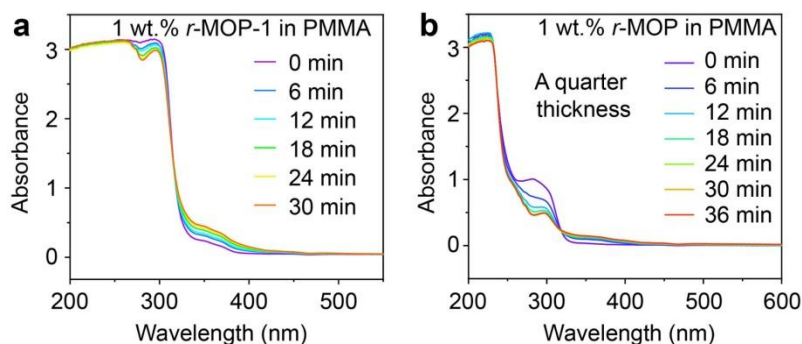
Supplementary Figure 64. Lifetime decay profiles of PMMA films doped with BPBP, BPY, MOPh and MNP at the concentration of 1 wt.% before and after the photo-activation.

Supplementary Table 16. Phosphorescence lifetimes of PMMA films doped with BPBP, BPY, MOPh or MNP at the concentration of 1 wt.% before and after the photo-activation.

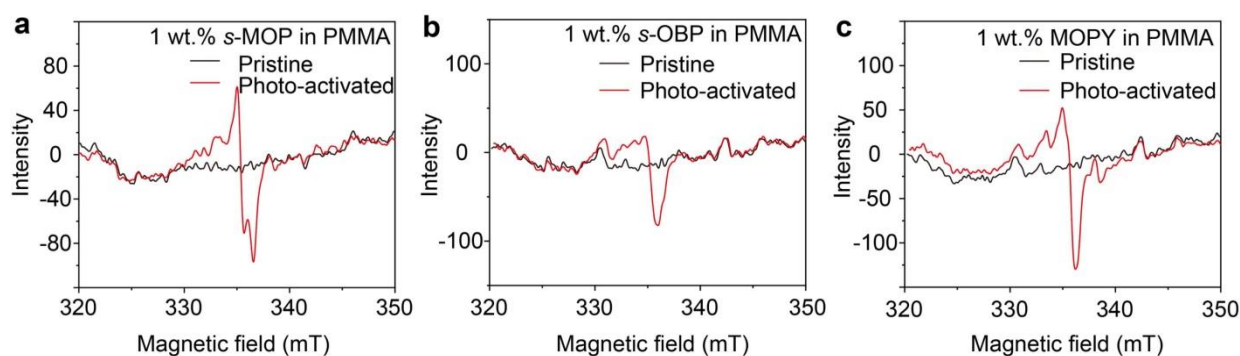
Compounds	Wavelength (nm)	Phosphorescence							
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)	τ_3 (ms)	A_3 (%)
1 wt.% BPBP in PMMA	505	0.006	63.72	0.058	36.28	-	-	-	-
1 wt.% BPBP in PMMA-UV	505	29.67	12.74	149.61	43.73	532.29	43.53	-	-
1 wt.% BPY in PMMA	499	0.008	63.82	0.064	36.18	-	-	-	-
1 wt.% BPY in PMMA-UV	499	24.12	15.46	132.08	43.17	477.30	41.37	-	-
1 wt.% MOPh in PMMA	521	0.005	89.56	0.020	10.44	-	-	-	-
1 wt.% MOPh in PMMA -UV	521	26.43	16.03	203.85	83.97	-	-	-	-
1 wt.% MNP in PMMA	501	0.008	44.13	0.082	55.87	-	-	-	-
1 wt.% MNP in PMMA-UV	501	0.002	10.7	21.75	20.23	115.82	39.31	484.85	29.75



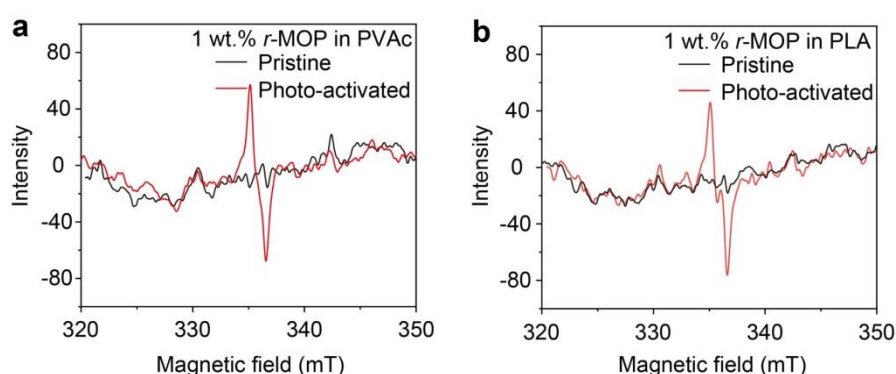
Supplementary Figure 65. EPR spectra of PMMA films doped with BPBP (λ_{ex} =280 nm), BPY (λ_{ex} =275 nm), MOPh (λ_{ex} =270 nm), and MNP (λ_{ex} =280 nm) at the concentration of 1 wt.% before and after the irradiation.



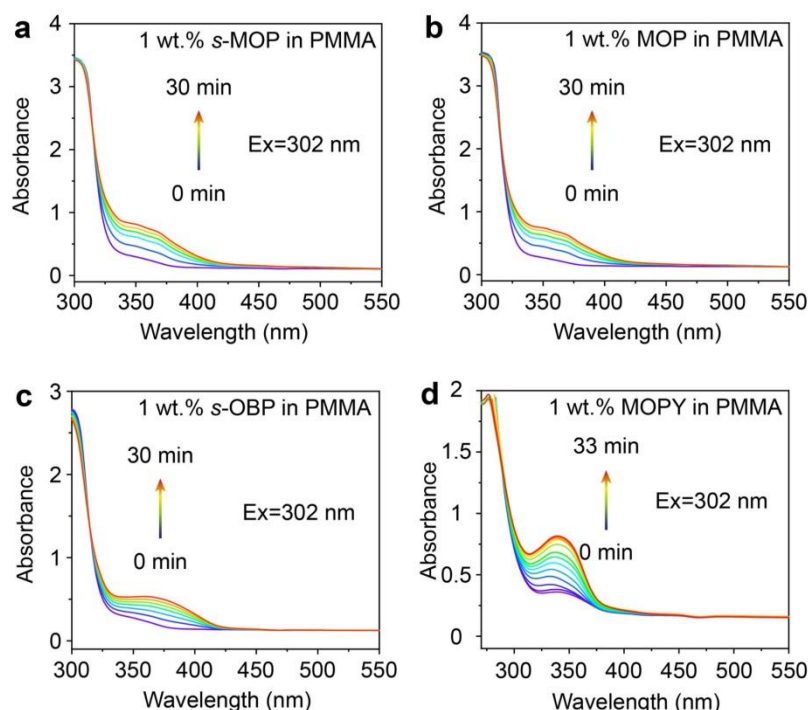
Supplementary Figure 66. a) The absorption spectra of 1 wt.% *r*-MOP-1 in PMMA films after photo-activated by 302 nm (4.04 mW/cm²) with different times. b) The absorption spectra of 1 wt.% *r*-MOP in PMMA films with a quarter thickness after photo-activated by 302 nm (4.04 mW/cm²) with different times.



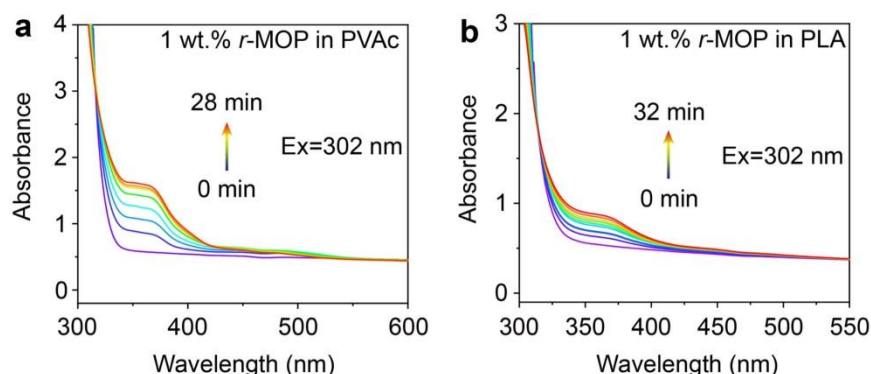
Supplementary Figure 67. EPR spectra of PMMA films doped with *s*-MOP ($\lambda_{\text{ex}} = 330$ nm), *s*-OBP ($\lambda_{\text{ex}} = 270$ nm), MOPY ($\lambda_{\text{ex}} = 300$ nm) at the concentration of 1 wt.% before and after the irradiation.



Supplementary Figure 68. EPR spectra of 1 wt.% *r*-MOP in PVAc ($\lambda_{\text{ex}} = 330$ nm) and 1 wt.% *r*-MOP in PLA films ($\lambda_{\text{ex}} = 330$ nm) before and after the irradiation.



Supplementary Figure 69. The absorption spectra of PMMA films doped with s-MOP, MOP, s-OBP and MOPY at the concentration of 1 wt.% after photo-activated by 302 nm (4.04 mW/cm^2) with an interval of 3 minutes.



Supplementary Figure 70. The absorption spectra of 1 wt.% r-MOP in PVAc and 1 wt.% r-MOP in PLA films after photo-activated by 302 nm (4.04 mW/cm^2) with an interval of 4 minutes.

To concretize the energy level of frontier molecular orbital, the energy levels of the HOMO of r-MOP and s-OBP were determined by the ultraviolet photoelectron spectroscopy (UPS) method and cyclic voltammetry (CV) study.

The UPS full spectra and a magnified view of the Fermi edge (injection barrier edge) of r-MOP and s-OBP revealed a sharp rise near 19 eV, indicating strong secondary inelastic scattering electron emission. By analyzing the cutoff, the secondary electron cutoff energy (E_{cutoff}) of r-MOP and s-OBP are determined to be 19.458 and 19.039 eV, respectively (Supplementary Fig. 71). When using the He I light source (21.22 eV photon energy), this cutoff indicates that the photon energy can excite electrons with a binding energy of 19.458 eV (r-MOP) and 19.039 eV (s-OBP), allowing them to reach the sample surface

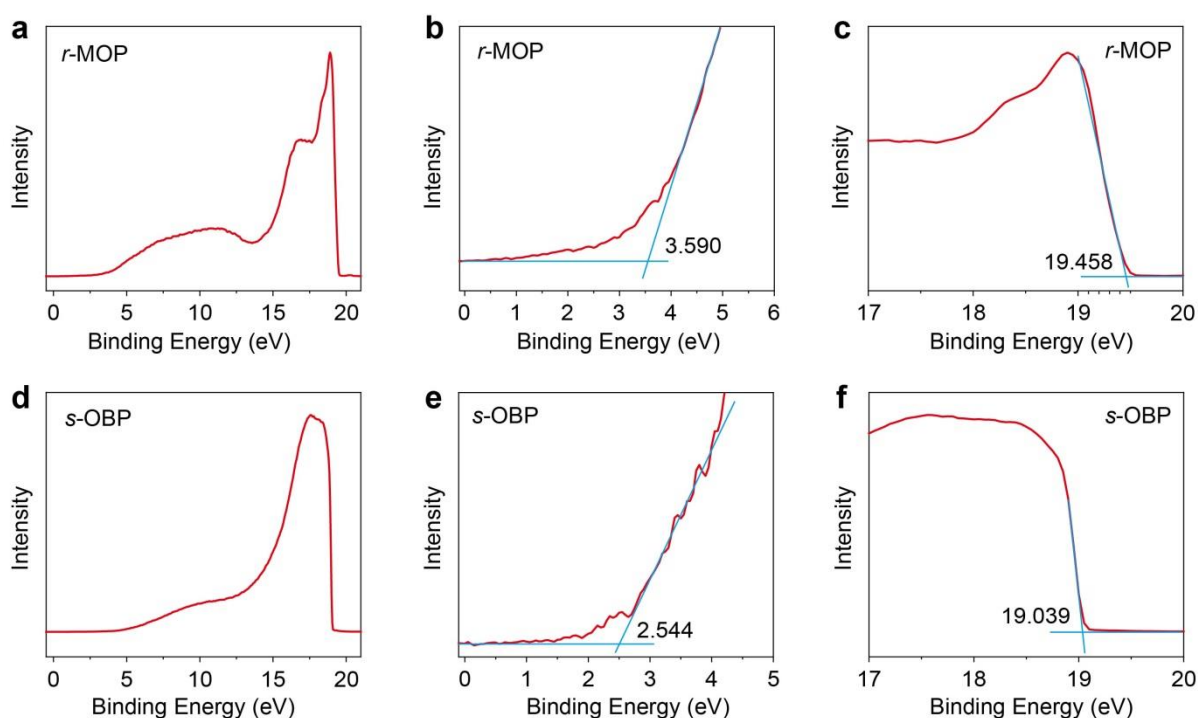
without undergoing any scattering. Furthermore, applying Formula (1), the work function (Φ) of r-MOP and s-OBP are calculated to be 1.762 eV and 2.181 eV, respectively. Taking into account the injection barrier of 3.590 eV (r-MOP) and 2.544 eV (s-OBP) relative to the substrate (Supplementary Fig. 71), the ionization potential (IP) of the sample is derived as:

$$\text{IP} = 21.22 - (19.458 - 3.590) = 1.762 + 3.590 = 5.352 \text{ eV} \quad (\text{r-MOP})$$

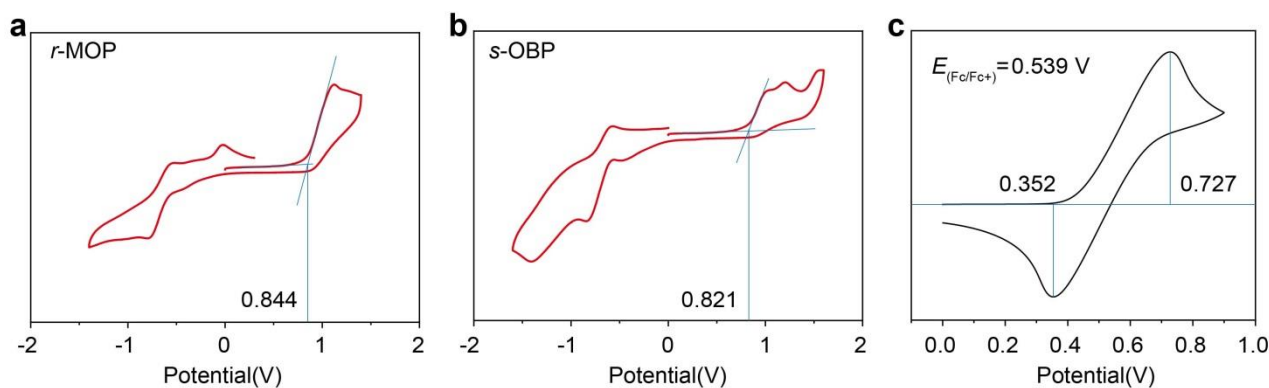
$$\text{IP} = 21.22 - (19.039 - 2.544) = 2.181 + 2.544 = 4.725 \text{ eV} \quad (\text{s-OBP})$$

Therefore, the energy level of the HOMO of r-MOP and s-OBP are 5.352 eV and 4.725 eV, respectively.

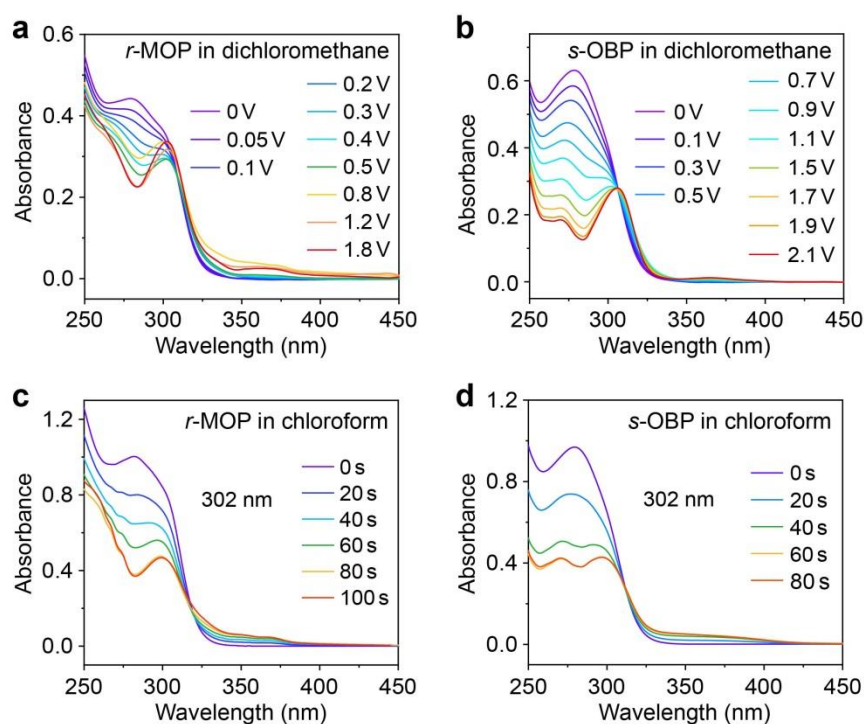
The cyclic voltammogram curves demonstrated that the E_{ox} values for r-MOP and s-OBP are 0.844 eV and 0.821 eV, respectively (Supplementary Fig. 72). The formal redox potential of ferrocene/ferrocenium, $E_{(\text{Fc}^+/\text{Fc})}$, is taken as the midpoint between the oxidation peak potential (E_{ox}) and reduction peak potential (E_{red}), i.e., $E_{(\text{Fc}^+/\text{Fc})} = (E_{\text{ox}} + E_{\text{red}})/2 = (0.352 + 0.727)/2 = 0.539 \text{ eV}$. When calculating HOMO and LUMO energy levels, the energy level corresponding to the ferrocene redox potential is typically set at -4.8 eV as a reference. The energy levels of the HOMO are estimated from $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8 - E_{(\text{Fc}^+/\text{Fc})})$ (eV). The E_{HOMO} of r-MOP and s-OBP are 5.105 eV and 5.082 eV. These results further verify the red-shift phosphorescence emission of s-OBP originates from tailoring the energy level of HOMO by chemical modification.



Supplementary Figure 71. UPS spectra of r-MOP powders and s-OBP powders.



Supplementary Figure 72. a, and b, Cyclic voltammogram (CV) curves of r-MOP and s-OBP in dichloromethane solution (0.6 mg mL⁻¹) with 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as supporting electrolyte and ferrocene as an external standard with the scan rate of 100 mV s⁻¹. c, CV curve of ferrocene.



Supplementary Figure 73. UV-Vis spectroelectrochemical response of (a) r-MOP and (b) s-OBP in dry dichloromethane solution at the concentration of 2×10^{-5} M with 0.05 M Bu₄NPF₆. The absorption spectra of (c) r-MOP and (d) s-OBP in chloroform solutions at the concentration of 5×10^{-5} M after photo-activated by 302 nm (4.04 mW/cm²) with different times.

The atomic coordinates of the optimized monomer structures of r-MOP and s-OBP are as follows:

r-MOP in monomer:

P	1.933981	0.359733	-0.528118
P	-2.653682	0.258982	0.477367
O	1.392276	-3.003995	-0.268126
O	0.561915	-4.028039	-2.127871
O	-1.462626	-1.720555	2.928547
O	-0.575664	-0.707608	4.766901
C	1.290276	0.008049	1.170548
C	2.671245	2.02713	-0.247442
C	0.137325	-0.815774	1.282406
C	-0.387061	-0.977397	2.551005
C	3.97042	-1.453299	0.397004
H	3.502325	-1.414191	1.382182
C	4.03298	2.322342	-0.365881
H	4.748696	1.527693	-0.585366
C	-0.50091	-1.481708	0.117572
C	0.175499	-2.473581	-0.561824
C	1.843197	0.596833	2.313008
H	2.720167	1.237879	2.205408
C	-4.328845	0.132505	-0.282737
C	-1.955767	1.710527	-0.426637
C	-0.340778	-3.109661	-1.689991
C	1.773605	3.06619	0.045295
H	0.706138	2.848662	0.146817
C	0.162065	-0.365839	3.676268
C	-2.306469	-1.794801	-1.492735
H	-3.29242	-1.514269	-1.866395
C	1.756981	-3.769156	-1.402953
H	2.458419	-3.183923	-2.026948
H	2.206737	-4.716165	-1.081506
C	3.436447	-0.701414	-0.65541
C	-6.924946	-0.201442	-1.295649
H	-7.933892	-0.330241	-1.690555
C	-2.186703	2.976555	0.131108
H	-2.722962	3.05546	1.080412
C	-1.756098	-1.300407	4.247441
H	-2.035458	-2.165909	4.859695
H	-2.564193	-0.546834	4.219478
C	-1.785579	-1.133589	-0.378025
C	-1.750016	4.131327	-0.517303
H	-1.948112	5.109781	-0.07623
C	-4.787436	0.933153	-1.334526
H	-4.13183	1.689412	-1.77089
C	-5.191766	-0.829074	0.263621
H	-4.844801	-1.451371	1.093322
C	1.293358	0.418979	3.592665
H	1.725476	0.886841	4.476123
C	4.488066	3.632416	-0.195642

H	5.553854	3.848267	-0.288444
C	-6.476033	-1.003434	-0.24492
H	-7.132615	-1.761585	0.185048
C	5.675637	-2.343939	-1.07307
H	6.544971	-2.983877	-1.232519
C	-1.052905	4.032605	-1.72236
H	-0.698351	4.933333	-2.226035
C	-1.593513	-2.799483	-2.173608
H	-2.005708	-3.303941	-3.046426
C	5.153195	-1.596213	-2.128387
H	5.610677	-1.648058	-3.1178
C	-1.242613	1.621454	-1.629279
H	-1.029506	0.644353	-2.06645
C	5.07921	-2.272733	0.186408
H	5.480954	-2.859779	1.014088
C	-6.080827	0.767494	-1.834133
H	-6.427203	1.3993	-2.653781
C	3.59152	4.656908	0.097931
H	3.950777	5.678453	0.232074
C	4.032817	-0.791585	-1.921651
H	3.610735	-0.224509	-2.756206
C	2.230542	4.368366	0.221889
H	1.517047	5.161678	0.4529
C	-0.791886	2.777076	-2.269526
H	-0.227036	2.692093	-3.199211

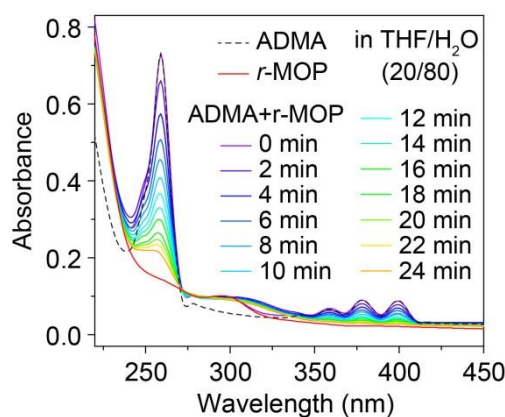
s-OBP in monomer:

P	-2.38557	0.549343	-0.33252
P	2.385617	0.549316	0.332512
O	1.580644	-2.2737	1.353213
O	-1.58066	-2.27392	-1.35288
C	-1.47363	-0.34337	1.011209
C	4.244684	-1.57287	-0.26246
H	3.623518	-1.82831	-1.12199
C	-1.93173	-0.31829	2.338041
H	-2.8445	0.227204	2.584658
C	1.931702	-0.31859	-2.33793
H	2.844433	0.226925	-2.58463
C	1.224876	-0.97707	-3.33381
H	1.586958	-0.96027	-4.36304
C	3.885215	-0.50284	0.565727
C	0.282094	-1.0122	-0.69239
C	-0.04402	-1.65563	3.033746
H	0.505096	-2.16122	3.82602
C	-0.2821	-1.01208	0.692607
C	0.044053	-1.65612	-3.03343
H	-0.50504	-2.1619	-3.82562
C	1.47362	-0.34353	-1.01109
C	2.409811	-2.80858	2.353473

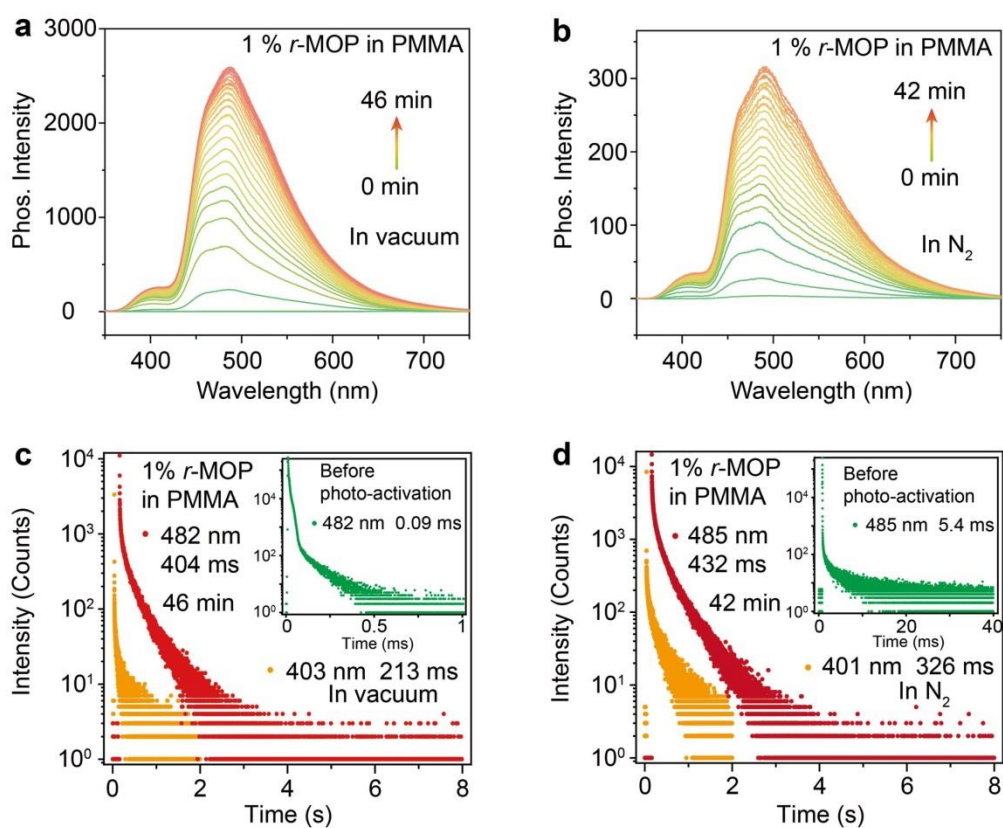
H	2.675451	-2.04265	3.100945
H	3.324714	-3.14713	1.852933
H	1.92721	-3.66101	2.859768
C	-3.88508	-0.50295	-0.56575
C	-3.08395	1.948058	0.65332
C	-4.68106	-0.22055	-1.68453
H	-4.39877	0.599109	-2.35117
C	-6.1735	-2.03553	-1.12632
H	-7.06112	-2.63229	-1.3424
C	-1.22487	-0.97658	3.334023
H	-1.58695	-0.95964	4.363251
C	5.380746	-2.33269	0.017701
H	5.646041	-3.16608	-0.63526
C	0.429279	-1.66919	1.720851
C	-4.44677	2.140467	0.902122
H	-5.17678	1.412499	0.543136
C	4.68156	-0.21983	1.684107
H	4.39947	0.600168	2.350414
C	3.083844	1.948015	-0.65347
C	-4.24477	-1.57257	0.262876
H	-3.62389	-1.82751	1.122764
C	-2.40986	-2.80871	-2.35315
H	-2.67519	-2.04281	-3.10077
H	-3.32492	-3.14692	-1.85267
H	-1.92744	-3.66135	-2.85927
C	-5.82172	-0.97445	-1.96024
H	-6.43167	-0.73726	-2.83356
C	-0.42928	-1.66947	-1.72054
C	-5.38068	-2.3326	-0.01727
H	-5.64615	-3.16568	0.636012
C	2.169205	2.898683	-1.133
H	1.099582	2.758841	-0.9503
C	-2.16939	2.898535	1.133373
H	-1.09968	2.758491	0.951264
C	5.822354	-0.97352	1.959818
H	6.432574	-0.73585	2.832821
C	4.446572	2.140195	-0.90298
H	5.176644	1.412082	-0.5444
C	-4.88438	3.258036	1.617371
H	-5.95112	3.393577	1.804084
C	-3.96825	4.190272	2.097145
H	-4.3126	5.060306	2.658315
C	2.604879	4.004958	-1.85565
H	1.878334	4.728756	-2.22851
C	6.17392	-2.035	1.126315
H	7.061654	-2.63159	1.342409
C	-2.60524	4.004853	1.855849
H	-1.87876	4.728495	2.229134
C	4.884008	3.257721	-1.6184
H	5.950675	3.393086	-1.80565

C	3.967787	4.190143	-2.09765
H	4.312002	5.060146	-2.65896

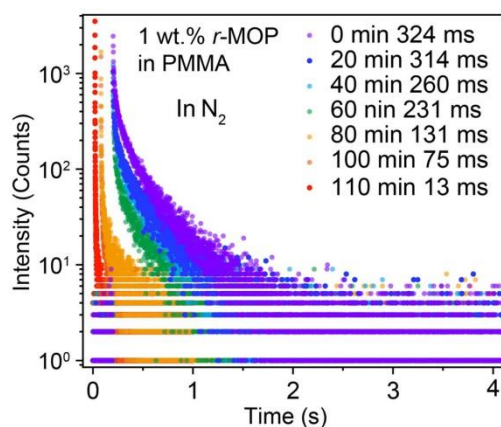
UV-Vis spectroelectrochemical spectra of r-MOP and s-OBP in dry dichloromethane solution exhibited an obvious absorption peak at 280 nm (Supplementary Fig. 73). And the absorption peak gradually decreased and a new absorption peak at 302 nm and shoulder peak about 320-360 nm appeared when the applied voltage continuously increased. The absorption spectra of r-MOP and s-OBP in chloroform solutions showed similar spectra and variation trends upon the 302 nm UV irradiation. The absorption peak at 280 nm of r-MOP and s-OBP in chloroform belong to the neutral molecules, new absorption peak at 302 nm and shoulder peak about 320-360 nm belong to the radical (Supplementary Fig. 73). Therefore, free radicals are generated from the organic small molecules during the electrolysis of organic small molecules under applied voltage.



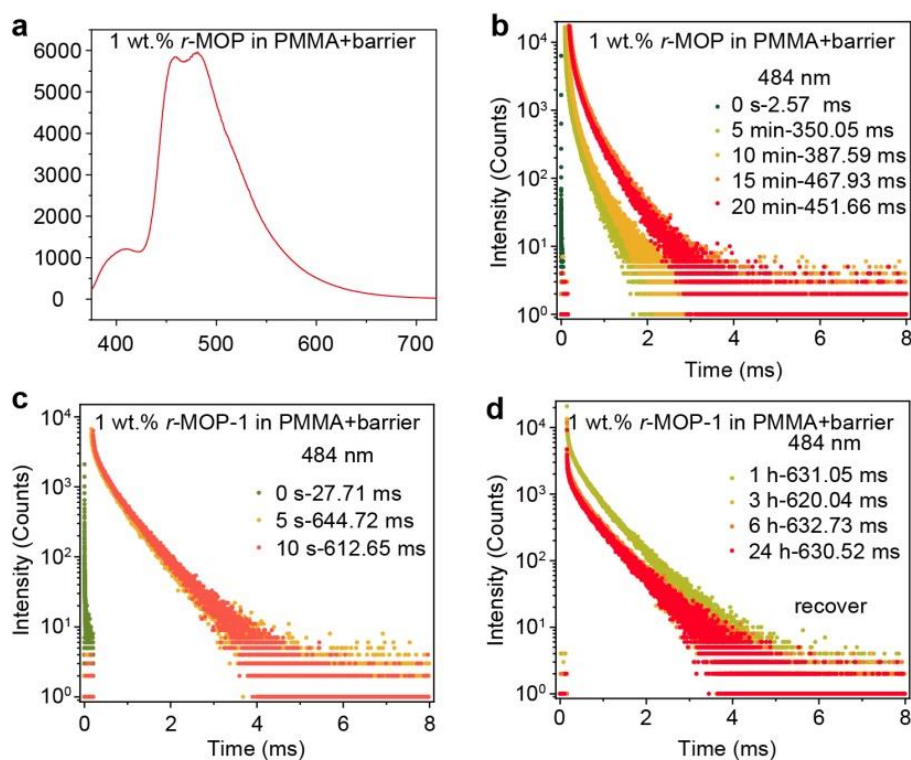
Supplementary Figure 74. The absorption spectra of a r-MOP and ADMA mixture dissolved in a THF/H₂O (20/80) solution (5 μ M) excited by 302 nm with different irradiation time.



Supplementary Figure 75. Phosphorescence spectra of 1 wt.% *r*-MOP in PMMA films before and after the photo-activation in vacuum (a) and nitrogen (b). Phosphorescence lifetimes of 1 wt.% *r*-MOP in PMMA films before and after the photo-activation in vacuum (c) and nitrogen (d).



Supplementary Figure 76. Phosphorescence spectra of photo-activated PMMA films doped with 1 wt.% *r*-MOP after recovered in nitrogen at different time.

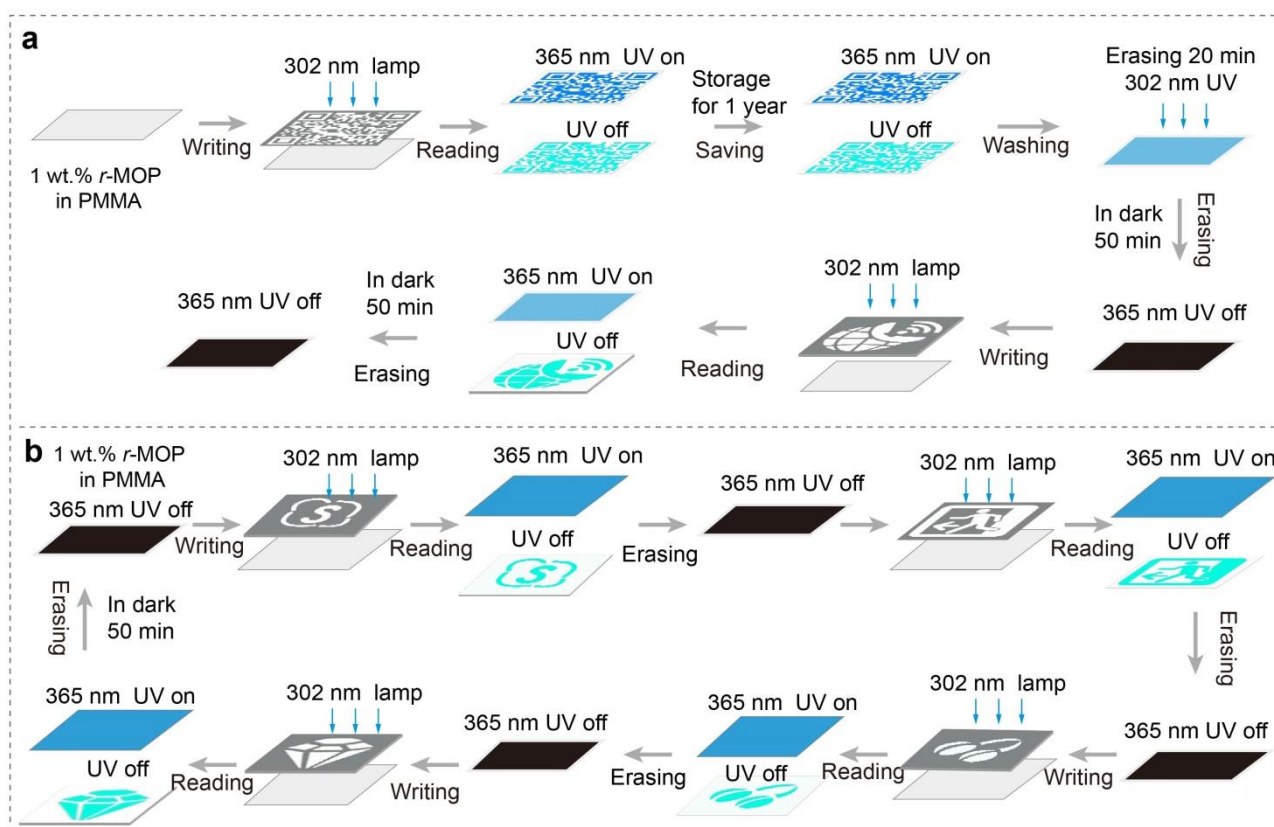


Supplementary Figure 77. a) Phosphorescence spectra of 1 wt.% r-MOP in PMMA films coated with oxygen barrier excited by 365 nm after photo-activated by 302 nm. b) Lifetime decay curves of 1 wt.% r-MOP in PMMA films coated with oxygen barrier before and after photo-activated by 302 nm (4.04 mW/cm²) with different times. c) Lifetime decay curves of 1 wt.% r-MOP-1 in PMMA films coated with oxygen barrier before and after photo-activated by 365 nm (39.9 mW/cm²) with different times. d) Lifetime decay curves of photo-activated 1 wt.% r-MOP-1 in PMMA films coated with oxygen barrier after recovered at different times.

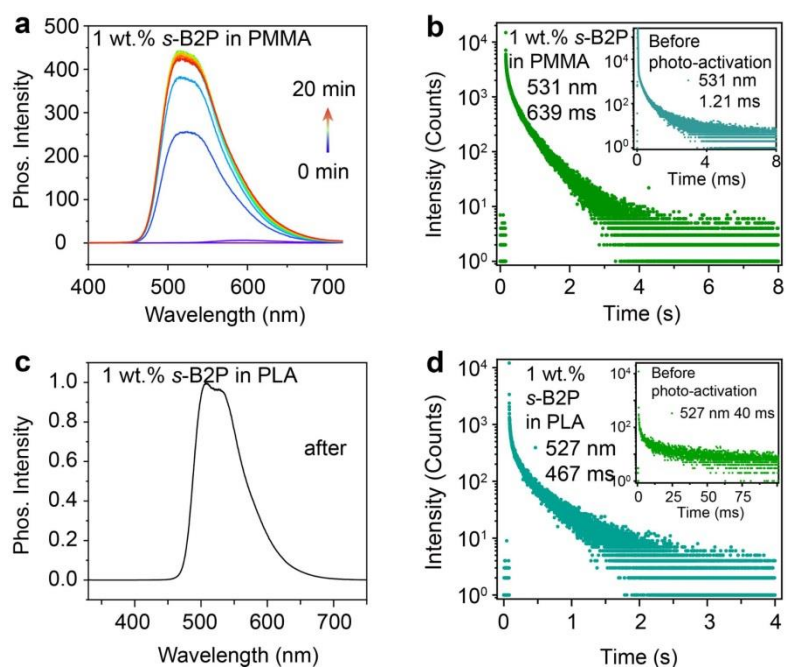
Supplementary Table 17. Phosphorescence lifetimes of 1 wt.% r-MOP in PMMA films before and after the photo-activation in vacuum or nitrogen, and after recovered in nitrogen at different time.^a

Compounds	Wavelength (nm)	Phosphorescence					
		τ_1 (ms)	A_1 (%)	τ_2 (ms)	A_2 (%)	τ_3 (ms)	A_3 (%)
r-MOP in PMMA in vacuum-0 min	480	0.008	41.17	0.087	58.83	-	-
r-MOP in PMMA in vacuum-46 min	403	28.51	30.86	212.8	69.14	-	-
	480	69.05	28.44	404.7	71.56	-	-
r-MOP in PMMA in vacuum-recover	480	0.177	53.64	0.818	46.36	-	--
r-MOP in PMMA in N ₂ -0 min	485	5.4	28.05	5.4	71.95	-	-
r-MOP in PMMA in N ₂ -42 min	401	42.7	21.97	326	78.03	-	-
	485	79	34.72	432	65.28	-	-
r-MOP in PMMA in N ₂ -recover-20 min	485	38..35	22.59	314.08	77.41	-	-
r-MOP in PMMA in N ₂ -recover-40 min	485	24.66	21.02	290.24	78.98	-	-
r-MOP in PMMA in N ₂ -recover-60 min	485	17.0	24.34	231.05	75.66	-	-
r-MOP in PMMA in N ₂ -recover-80 min	485	6.13	29.65	131.2	70.35	-	-
r-MOP in PMMA in N ₂ -recover-100 min	485	0.67	39.25	5.53	28.02	75.42	32.73
r-MOP in PMMA in N ₂ -recover-110 min	485	1.37	52.09	13.1	47.91	-	-

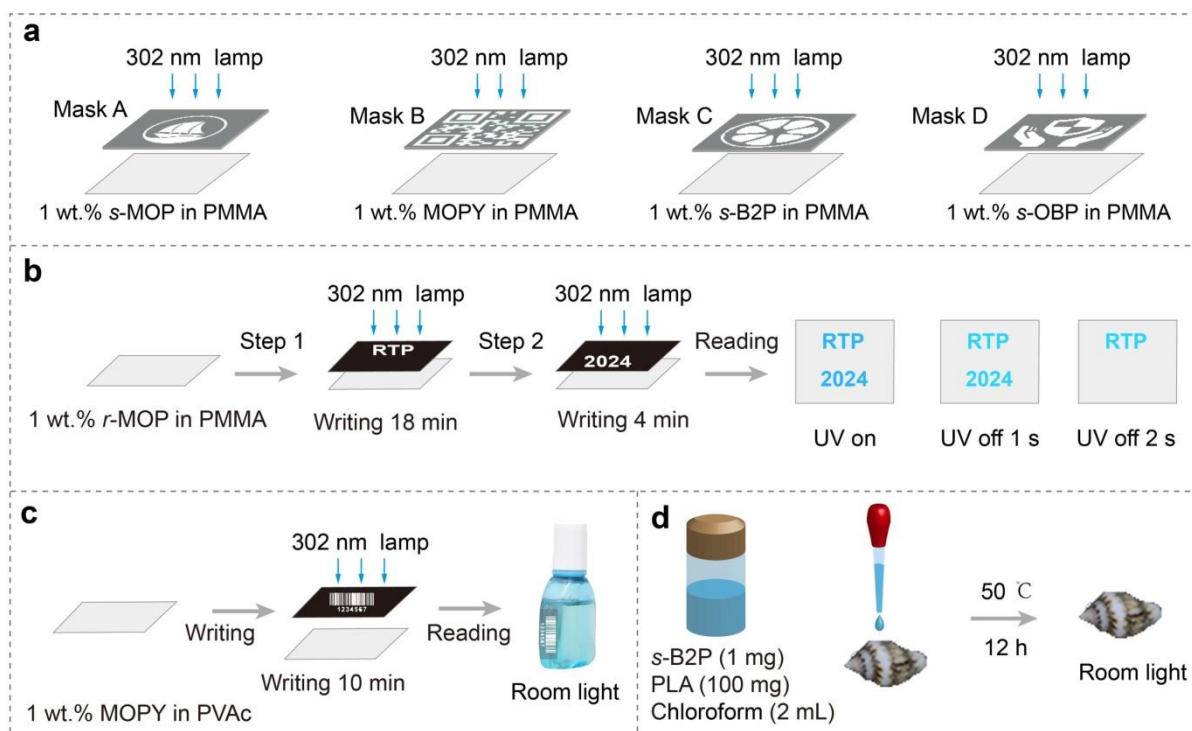
^a Determined from the fitting function of $I(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4}$, where A_i and τ_i represent the amplitudes and lifetimes of the individual components for multi-exponential decay profiles, respectively.



Supplementary Figure 78. The preparation process of writing, reading, washing, erasing the patterns on the PMMA films doped with 1 wt.% *r*-MOP in detail. a) A quick response code was wrote by 302 nm lamp upon 1 wt.% *r*-MOP in PMMA films with screen printed quick response code pattern as the mask. The pattern was read by 365 nm lamp. The pattern can be stored for a year, and can be washing by 302 nm. The phosphorescence of pattern can be erased by keeping in the dark for 50 min. Then the PMMA film can be writing other patterns by choosing other screen printed patterns as the masks. b) Different patterns were wrote by 302 nm lamp irradiation using different screen printed patterns as the masks, and read by 365 nm lamp, then erased by keeping in the dark for 50 min.



Supplementary Figure 79. a) Phosphorescence spectra of 1 wt.% s-B2P in PMMA films photo-activated by 365 nm (0.72 mW/cm^2) with a photo-activation interval of 2 min. b) Lifetime decay profiles of 1 wt.% s-B2P in PMMA films before and after the photo-activation. c) Phosphorescence spectrum of 1 wt.% s-B2P in PLA films photo-activated by 365 nm (0.72 mW/cm^2) with a photo-activation interval of 2 min. d) Lifetime decay profiles of 1 wt.% s-B2P in PLA films before and after the photo-activation.



Supplementary Figure 80. The preparation process of multicolor afterglow patterns, encrypted pattern, anti-counterfeiting pattern and afterglow artworks. a) Different patterns were wrote on the PMMA films doped with 1 wt.% s-MOP, 1 wt.% MOPY, 1 wt.% s-B2P, and 1 wt.% s-OBP by 302 nm lamp using different screen printed patterns as the masks, respectively. b) “RTP” was wrote on 1 wt.% *r*-MOP in PMMA films by the irradiation of 302 nm lamp for 18 min, followed by “2024” by the irradiation of 302 nm lamp for 4 min using screen printed “RTP” and “2024” as the masks. c) A bar code was wrote by the irradiation of 302 nm lamp for 10 min using screen printed bar code as the mask, read by 365 nm lamp. d) The artworks were covered by s-B2P in PLA solution, then dried at 50 °C for 12 h.