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Electronic Supplementary Information (ESI)

Multi-photoresponsive Triphenylethylene Derivatives with Photochromism, Photodeformation and Room Temperature Phosphorescence

Yunhao Fan^a, Mengmeng Han^a, Arui Huang^a, Qiuyan Liao^a, Jin Tu^a, Xiuxing Liu^a, Bohan Huang^a, Qianqian Li^{*a} and Zhen Li^{*a,b}

^a Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Sauvage Center for Molecular Sciences, Department of Chemistry, Wuhan University, Wuhan 430072, China.

^b Institute of Molecular Aggregation Science, Tianjin University, Tianjin 300072, China



Figure S1 Time-dependent reflectance spectra after UV-irradiation (365 nm) for 5 s: (a) TPM; (b) TPMBr; (c) TPMBr2; (d) TPF; (e) TPFBr.



Figure S2 Photographs of triphenylethylene derivatives at powder state before and after UV irradiation for 5 s.



Figure S3 Recycling of the photochromic process by UV-irradiation (365 nm) for 5 s and under visible light for 30 s, (a) TPM; (b) TPMBr; (c) TPMBr2; (d) TPF; (e) TPFBr; (f) TPFBr2.



Figure S4 The pictures of PET films under different conditions.



Figure S5 Fatigue resistance test of TPM-PET film by stretching and photo-induced shrinking process.



Figure S6 Fatigue resistance test of TPMBr-PET film by stretching and photo-induced shrinking process.



Figure S7 Fatigue resistance test of TPMBr2-PET film by stretching and photo-induced shrinking process.



Figure S8 Fatigue resistance test of TPF-PET film by stretching and photo-induced shrinking process.



Figure S9 Fatigue resistance test of TPFBr-PET film by stretching and photo-induced shrinking process.



Figure S10 Fatigue resistance test of TPFBr2-PET film by stretching and photo-induced shrinking process.

cm 1 2 3	stretching	cm 1 2 3 4 5	UV 5s	cm 1 2 3
ТРМ				
cm 1 2 3	stretching	cm 1 2 3 4 5	UV 5s	cm 1 2 3
TPMBr				
cm 1 2 3	stretching	cm 1 2 3 4 5	UV 5s	Cm 1 2 3
TPMBr2				

Figure S11 Photographs of TPM, TPMBr, TPMBr2 after stretching to break limit and under UV irradiation (365nm) for 5 s.



Figure S12 Photographs of TPF, TPFBr, and TPFBr2 after stretching to break limit and under UV irradiation (365 nm) for 5 s.



Fig S13 Afterglow photographs of triphenylethylene derivatives taken by chemiluminescent imaging system.



Figure S14 Room temperature phosphorescence spectra of triphenylethylene derivatives at crystalline and ground state.



Figure S15 Room temperature phosphorescence decay of triphenylethylene derivatives at crystalline and ground state.



Figure S16 Photoluminescence spectra of triphenylethylene derivatives at crystalline and ground state.



Figure S17 Time-resolved fluorescence of triphenylethylene derivatives at crystalline and ground state.

Crystal Sample	λex	λpl	τ	λPhos	τ	PLQY
TPM	340 nm	400 nm	1.73 ns	400 nm	13.6 ms	47.88%
TPMBr	380 nm	458 nm	2.26 ns	425 nm	285.0 ms	67.47%
				510 nm	297.0 ms	
TPMBr2	390 nm	480 nm	1.82 ns	482 nm	210.1 ms	26.04%
				578 nm	26.4 ms	
TPF	371 nm	394 nm	2.18 ns	443 nm	77.1 μs	2.61%
		434 nm	4.69 ns			
TPFBr	354 nm	418 nm	4.81 ns	418 nm	28.8 ms	12.87%
		438 nm	4.86 ns	438 nm	27.9 ms	
TPFBr2	380 nm	438 nm	2.27 ns	443 nm	93.4 ms	11.26%

Table S1 Photoluminescence parameters of triphenylethylene derivatives as single crystals.

Table S2 Photoluminescence parameters of triphenylethylene derivatives at ground state.

Ground Sample	λex	λpl	τ	λPhos	τ	PLQY
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TPM	340 nm	405 nm	1.86 ns	368 nm	6.8 ms	48.01%
				463 nm	7.6 ms	
TPMBr	382 nm	445 nm	2.39 ns	531 nm	281.0 ms	72.65%
TPMBr2	375 nm	458 nm	2.64 ns	486 nm	44.8 ms	8.27%
				578 nm	13.3 ms	
TPF	383 nm	408 nm	4.89 ns	442 nm	76.8 µs	3.77%
		434 nm	5.41 ns			
TPFBr	354 nm	418 nm	4.84 ns	418 nm	26.4 ms	5.36%
		438 nm	4.86 ns	438 nm	26.9 ms	
TPFBr2	380 nm	437 nm	4.42 ns	443 nm	280.2 ms	17.93%

 Table S3 Crystal data and structure refinement summary.

Name	TPM	TPMBr	TPMBr2	TPF	TPFBr	TPFBr2
Formula	C ₂₁ H ₁₈	C ₂₁ H ₁₇ Br	C ₂₁ H ₁₆ Br ₂	C ₂₁ H ₁₅ F ₃	C ₂₁ H ₁₄ BrF ₃	$C_{21}H_{13}Br_2F_3$
Mr	270.35	349.25	428.14	324.33	403.22	481.77
Space Group	P-1	P21/c	P21/c	Pca2 ₁	P21/c	P2 ₁ /c
a /Å	8.321(3)	8.773(4)	12.880(9)	31.90(3)	13.672(5)	16.448(5)
b /Â	9.678(4)	9.273(5)	8.745(6)	8.761(9)	7.976(3)	6.0973(19)
c /Å	9.879(4)	20.333(10)	18.874(10)	5.796(6)	16.909(6)	19.528(6)
α /°	94.541(6)	90	90	90	90	90
β /°	96.864(6)	90.317(8)	121.39(3)	90	99.786(6)	105.073(5)
γ /°	94.634(6)	90	90	90	90	90
Temperature /K	293	296	296	296	296	296
Volume /Å ³	784.1(5)	1654.1(14)	1815(2)	1620(3)	1817.1(12)	1891.1(10)
Z	2	4	4	4	4	4
Density /g cm ⁻³	1.145	1.402	1.567	1.330	1.474	1.692
μ /mm ⁻¹	0.064	2.479	4.463	0.100	2.290	4.316
F(000)	288.0	712.0	848.0	672.0	808.0	943.4
h _{max} , k _{max} , I _{max}	12,14,14	13,13,30	14,10,21	39,10,7	20,11,25	21,8,25
T _{min} , T _{max}	0.992,0.994	0.743,0.780	0.356,0.640	0.999,0.999	0.896,0.955	0.856,0.917
CCDC	2094578	2094580	2094581	2094582	2094582	2094588



Fig S18 Intermolecular interactions of TPM from each molecule with adjacent ones in single crystal.



Fig S19 Intermolecular interactions of TPMBr from each molecule with adjacent ones in single crystal.



Fig S20 Intermolecular interactions of TPMBr2 from each molecule with adjacent ones in single crystal.



Fig S21 Intermolecular interactions of TPF from each molecule with adjacent ones in single crystal.



Fig S22 Intermolecular interactions of TPFBr from each molecule with adjacent ones in single crystal.



Fig S23 Intermolecular interactions of TPFBr2 from each molecule with adjacent ones in single crystal.



Fig S24 Molecular packing of triphenylethylene derivatives in single crystals.



Fig S25 Molecular packing along the layers in crystal structures of triphenylethylene derivatives.



Fig S26 *In situ* photoluminence spectra of triphenylethylene derivatives at solid state under UV irradiation (365 nm).



Scheme S1 Synthetic routes for triphenylethylene derivatives.





145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 5 (ppm)

Figure S28 ¹³C NMR of TPM in CD₂Cl₂ (100 MHz).







Figure S30¹³C NMR of TPMBr in CD₂Cl₂(100 MHz).







Figure S32 ¹³C NMR of TPMBr2 in CDCl₃ (100 MHz).



00.0----

-1.51

Figure S33 ¹H NMR of TPF in CDCl₃ (400 MHz).







Figure S34 ¹³C NMR of TPF in CDCl₃ (100 MHz).



Figure S36¹³C NMR of TPFBr in CD₂Cl₂(100 MHz).

-1.57









Figure S38 ¹³C NMR of TPFBr2 in CD₂Cl₂ (100 MHz)

-0.00

-1.55

Supplementary Videos

Video S1. Photochromism of TPM at crystalline state.

Video S2. Photochromism of TPMBr at crystalline state.

Video S3. Photochromism of TPMBr2 at crystalline state.

Video S4. Photochromism of TPF at crystalline state.

Video S5. Photochromism of TPFBr at crystalline state.

Video S6. Photochromism of TPFBr2 at crystalline state.

Video S7. Stretched PET film under UV irradiation.

Video S8. Photo-induced bending of stretched TPM-PET film under UV irradiation.

Video S9. Photo-induced bending of stretched TPMBr-PET film under UV irradiation.

Video S10. Photo-induced bending of stretched TPMBr2-PET film under UV irradiation.

Video S11. Photo-induced bending of stretched TPF-PET film under UV irradiation.

Video S12. Photo-induced bending of stretched TPFBr-PET film under UV irradiation.

Video S13. Photo-induced bending of stretched TPFBr2-PET film under UV irradiation.