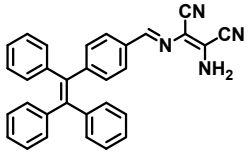
Supporting Information

1 Synthesis of TPE-MN

The details of the synthetic procedure for TPE-MN is listed below. Compound 4-(1,2,2-triphenylvinyl)benzaldehyde was synthesized according to previous report.[1] The final compound is characterized by ^{1}H NMR spectroscopy, High-resolution EI mass spectroscopy and elemental analysis.



TPE-MN

TPE-MN. To a round-bottomed flask containing 4-(1,2,2-triphenylvinyl)benzaldehyde (3.60 g, 10.0 mmol), diaminomaleonitrile (1.08 g 10.0 mmol) and acetic acid (0.1 ml) were added degassed ethanol (40 mL) under an argon atmosphere. Upon reflexing and stirring for 8 hours under an argon atmosphere, pale yellow precipitation was formed. the mixture filtered and filtrate was precipitation. The residue was purified by recrystallization by CH_2Cl_2-hexane mixed−solvent system. Pale yellow solids were achieved. Yield: 3.15 g (70 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 8.32 (s, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.11-7.13 (m, 11H), 7.05−7.02 (m, 7H); High solution EI−MS: m/z found: 450.1838 $[M]^+$; calcd for $C_{31}H_{22}N_4$: 450.1844. Anal. calcd for $C_{31}H_{22}N_4$: C 82.64, H 4.92, N 12.44; found: C 82.33, H 5.14, N 12.20.

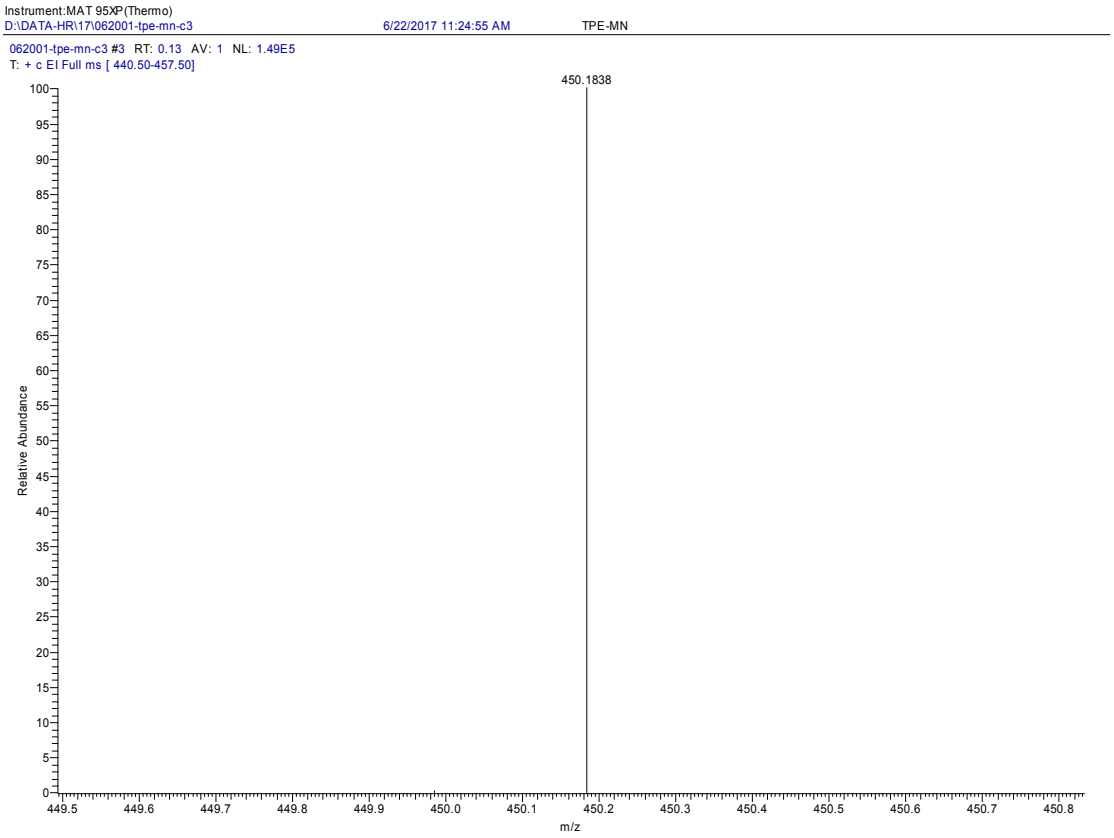


Figure S1 High Resolution EI mass spectrum of TPE-MN.

2 Physical measurements and instrumentations

^{1}H NMR spectra were achieved on a Varian Mercury-Plus 300 Nuclear Magnetic Resonance Spectrometer with chemical shifts recorded relative to tetramethylsilane (Me_4Si). Positive ion EI mass spectrum was recorded on a Thermo MAT95XP high resolution mass spectrometer. Single-crystal X-ray data of TPE-MN was determined on an Oxford Diffraction Germini S Ultra X-ray Single Crystal Diffractometer using a (Cu) X-ray source. Steady state emission spectra were recorded using a Shimadzu RF-5301pc spectrofluorophotometera and low-temperature emission studies were conducted with the same spectrofluorometer equipped with a Cryocon 22C temperature controller. The elemental analysis was performed with a Vario EL analyzer. Solid state luminescent quantum yield measurements for TPE-MN samples were performed with the Horiba Scientific Fluorolog-3 spectrofluorometer equipped with a Horiba Scientific Quanta-φ calibrated integrating sphere. pXRD spectra were recorded on a Rigaku X-ray

diffractometer (D/max-2200) with an X-ray source of Cu Kα (λ= 0.15406 nm) at 40 kV and 30 mA, at a scan rate of 10° (2θ) per 1 min. DSC studies were performed on a NETZSCH DSC 204 F1 instrument under nitrogen at a heating rate of 10 °C/min.

3 Single crystal data of TPE-MN

Single-crystal X-ray data for TPE-MN was determined on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer using graphite-monochromatized Cu-Kα radiation (λ = 1.54184 Å). The structure was solved by Olex2 v1.2 program and expanded using Fourier techniques. All non-H atoms of the compound were refined with anisotropic thermal parameters. The hydrogen atoms were included in idealized positions and refined with fixed geometry with respect to their carrier atoms. The disordered solvent molecules in TPE-MN were removed using SQUEEZE routine of PLATON. CCDC numbers for the single crystal of TPE-MN is 1497597.

Crystal data for TPE-MN; $C_{63}H_{46}Cl_2N_8$, Formula Weight = 986.03 g/mol, triclinic, space group P-1, T = 293 K, Z = 2, a = 10.5762(4) Å, b = 13.3993(4) Å, c = 21.7435(6) Å, α = 97.986(3) °, β = 100.725(3) °, γ = 112.276(3) °, V = 2726.21(18) Å^3, ρ_c = 1.2011 g cm^{-3}, μ($Cu_{K\alpha}$) = 1.435 mm^{-1}, F(000) = 1032.2. Reflections collected 25431, Independent reflections 8276 (R_{int} = 0.0443). R_1 = 0.0827 (I ＞ 2σ(I)) and wR_2 = 0.2682 , GOF = 1.050.

Table S1. Bond distances (Å) for TPE-MN

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N8	C3	1.390(4)	Cl1	C95	1.559(8)
N8	C77	1.274(4)	N4	C14	1.283(4)
C3	C24	1.362(4)	N4	C19	1.394(4)
C3	C96	1.423(5)	C8	C14	1.458(5)
C77	C6	1.462(4)	C8	C18	1.384(5)
C6	C9	1.390(4)	C8	C30	1.392(5)
C6	C10	1.389(4)	C15	C22	1.397(5)
C7	C11	1.397(5)	C15	C25	1.500(4)

C7	C13	1.381(4)	C15	C26	1.387(5)
C7	C17	1.490(4)	C18	C26	1.385(5)
C9	C13	1.391(4)	C19	C29	1.364(5)
C10	C11	1.366(4)	C19	C99	1.416(5)
N5	C96	1.138(4)	C22	C30	1.373(5)
C17	C32	1.340(5)	C23	C33	1.503(5)
C17	C35	1.509(5)	C23	C46	1.371(5)
C21	C32	1.482(5)	C23	C49	1.385(6)
C21	C34	1.382(5)	C25	C33	1.358(5)
C21	C48	1.382(5)	C25	C76	1.486(5)
C24	N7	1.337(5)	C27	C33	1.486(5)
C24	C97	1.439(5)	C27	C43	1.383(5)
C32	C37	1.497(4)	C27	C51	1.386(6)
C34	C59	1.369(6)	C29	N3	1.336(5)
C35	C47	1.388(6)	C29	C98	1.436(5)
C35	C56	1.376(6)	C38	C60	1.380(6)
C36	C37	1.377(5)	C38	C76	1.391(6)
C36	C53	1.386(6)	N1	C99	1.151(5)
C37	C50	1.393(6)	C43	C57	1.376(6)
N6	C97	1.140(5)	N2	C98	1.140(5)
C47	C71	1.377(8)	C46	C55	1.398(5)
C48	C62	1.404(7)	C49	C69	1.385(6)
C50	C66	1.394(6)	C51	C73	1.386(7)
C53	C54	1.370(8)	C52	C68	1.396(7)
C54	C66	1.359(9)	C52	C76	1.378(6)
C56	C67	1.394(8)	C55	C63	1.349(7)
C59	C65	1.371(7)	C57	C70	1.377(8)
C62	C65	1.357(7)	C60	C64	1.356(8)
C67	C72	1.371(11)	C63	C69	1.350(7)
C71	C72	1.320(11)	C64	C68	1.369(8)
Cl2	C95	1.731(9)	C70	C73	1.369(9)

Table S2. Bond angles for TPE-MN

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C77	N8	C3	121.3(3)	C30	C8	C18	118.5(3)
C24	C3	N8	117.5(3)	C8	C14	N4	122.8(3)
C96	C3	N8	122.2(3)	C25	C15	C22	119.7(3)
C96	C3	C24	120.2(3)	C26	C15	C22	118.2(3)
C6	C77	N8	120.8(3)	C26	C15	C25	122.1(3)

C9	C6	C77	120.3(3)	C26	C18	C8	121.3(3)
C10	C6	C77	121.1(3)	C29	C19	N4	118.3(3)
C10	C6	C9	118.5(3)	C99	C19	N4	122.2(3)
C13	C7	C11	118.3(3)	C99	C19	C29	119.3(3)
C17	C7	C11	118.8(3)	C30	C22	C15	121.3(3)
C17	C7	C13	122.9(3)	C46	C23	C33	122.2(3)
C13	C9	C6	120.5(3)	C49	C23	C33	119.6(3)
C11	C10	C6	120.7(3)	C49	C23	C46	118.0(3)
C10	C11	C7	121.2(3)	C33	C25	C15	122.3(3)
C9	C13	C7	120.6(3)	C76	C25	C15	115.5(3)
C32	C17	C7	123.6(3)	C76	C25	C33	122.1(3)
C35	C17	C7	113.8(3)	C18	C26	C15	120.2(3)
C35	C17	C32	122.6(3)	C43	C27	C33	121.3(3)
C34	C21	C32	121.8(3)	C51	C27	C33	120.4(3)
C48	C21	C32	120.3(3)	C51	C27	C43	118.3(3)
C48	C21	C34	117.8(4)	N3	C29	C19	124.1(3)
N7	C24	C3	123.8(3)	C98	C29	C19	118.5(3)
C97	C24	C3	119.5(3)	C98	C29	N3	117.3(3)
C97	C24	N7	116.7(3)	C22	C30	C8	120.4(3)
C21	C32	C17	122.5(3)	C25	C33	C23	123.4(3)
C37	C32	C17	121.8(3)	C27	C33	C23	114.1(3)
C37	C32	C21	115.6(3)	C27	C33	C25	122.6(3)
C59	C34	C21	121.6(4)	C76	C38	C60	120.7(5)
C47	C35	C17	120.9(4)	C57	C43	C27	121.4(4)
C56	C35	C17	120.1(4)	C55	C46	C23	120.3(4)
C56	C35	C47	118.8(4)	C69	C49	C23	120.4(4)
C53	C36	C37	121.0(5)	C73	C51	C27	120.2(5)
C36	C37	C32	119.7(3)	C76	C52	C68	120.9(5)
C50	C37	C32	122.0(3)	C63	C55	C46	121.0(4)
C50	C37	C36	118.3(3)	C70	C57	C43	119.7(5)
C71	C47	C35	119.6(6)	C64	C60	C38	120.4(5)
C62	C48	C21	120.1(4)	C69	C63	C55	119.2(4)
C66	C50	C37	119.8(5)	C68	C64	C60	120.5(4)
C54	C53	C36	120.4(5)	C64	C68	C52	119.4(5)
C66	C54	C53	119.3(4)	C63	C69	C49	121.2(4)
C67	C56	C35	120.1(5)	C73	C70	C57	119.8(4)
C65	C59	C34	120.5(4)	C70	C73	C51	120.5(5)
C65	C62	C48	120.6(4)	C38	C76	C25	120.5(4)
C62	C65	C59	119.3(4)	C52	C76	C25	121.4(4)
C54	C66	C50	121.2(5)	C52	C76	C38	118.0(4)

C72	C67	C56	119.0(6)	N5	C96	C3	176.6(3)
C72	C71	C47	121.3(7)	N1	C99	C19	177.0(4)
C71	C72	C67	121.1(6)	N6	C97	C24	178.0(5)
C19	N4	C14	119.7(3)	N2	C98	C29	178.4(4)
C18	C8	C14	119.0(3)	Cl1	C95	Cl2	112.6(5)
C30	C8	C14	122.5(3)				

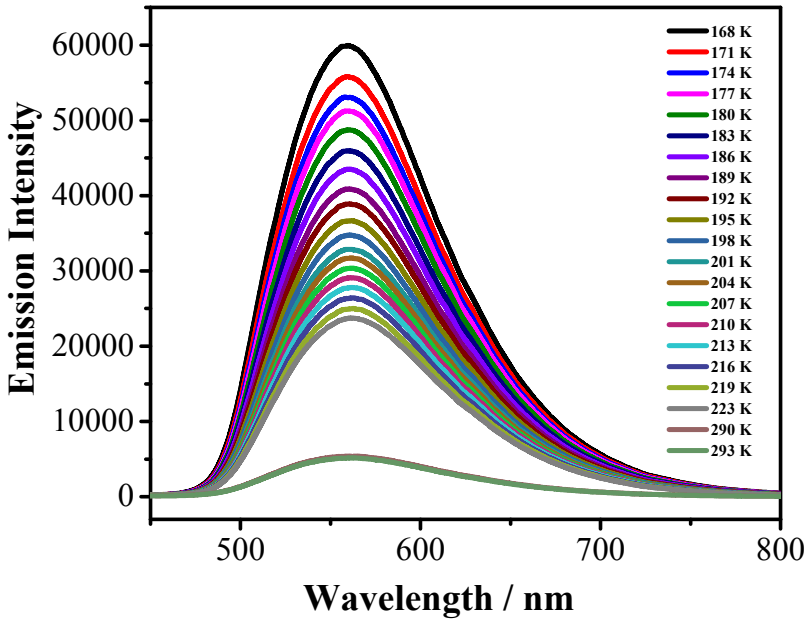


Figure S2. Temperature-dependent emission spectra of ground TPE-MN in the amorphous state (excited at 365 nm) after cooling below room temperature.

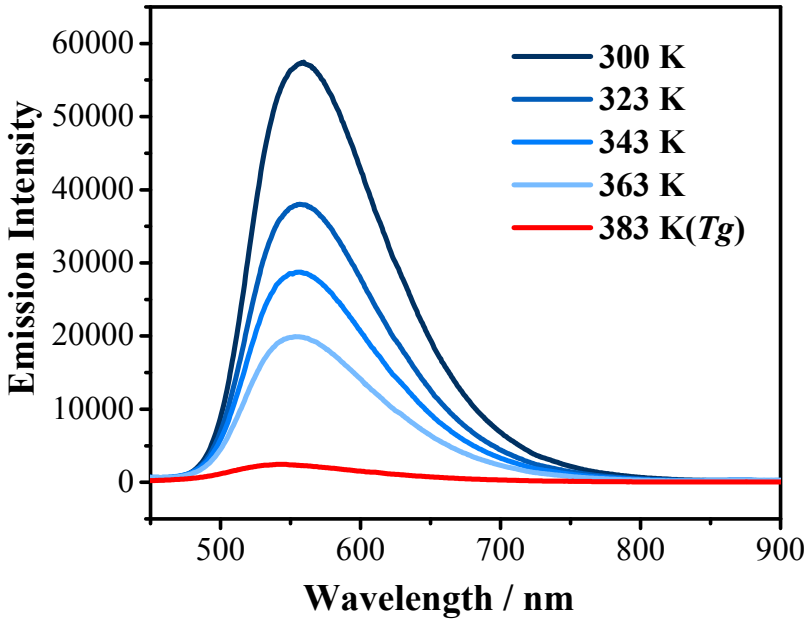


Figure S3. Temperature-dependent emission spectra of ground TPE-MN in the amorphous state after heating above room temperature.

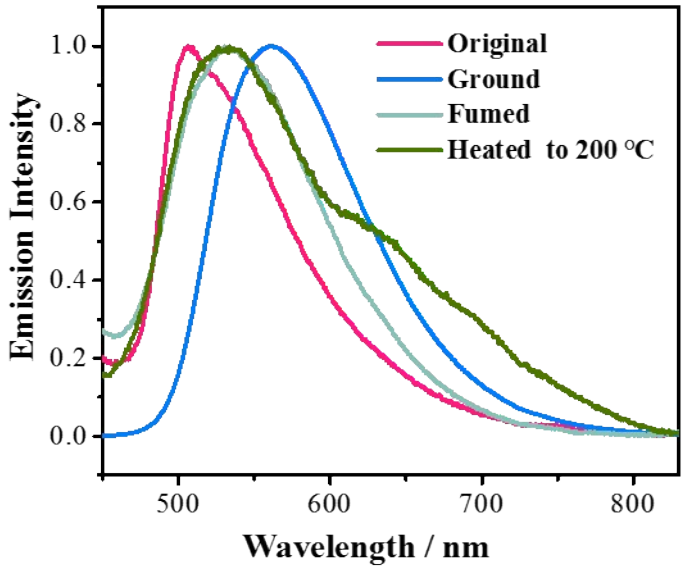


Figure S4. Normalized PL spectra of TPE-MN samples in the crystalline state (original), ground TPE-MN sample, dichloromethane fumed ground sample and

heated ground sample.

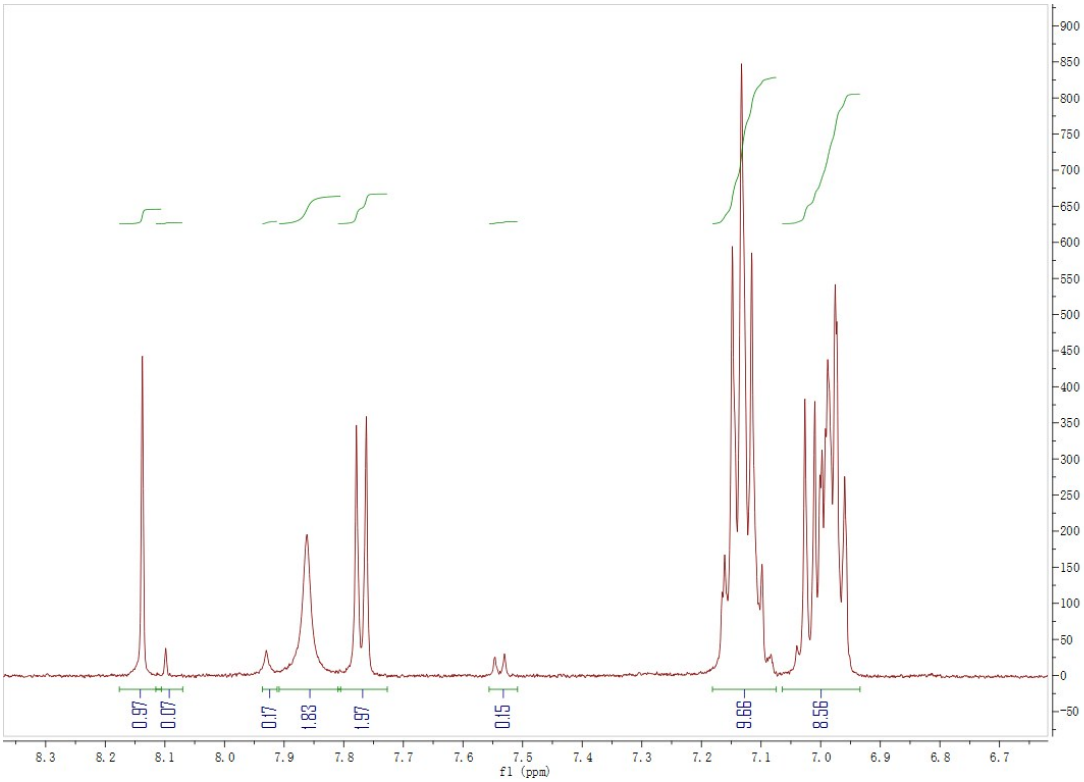


Figure S5. ^{1}H NMR spectrum of TPE-MN in deuterated DMSO.

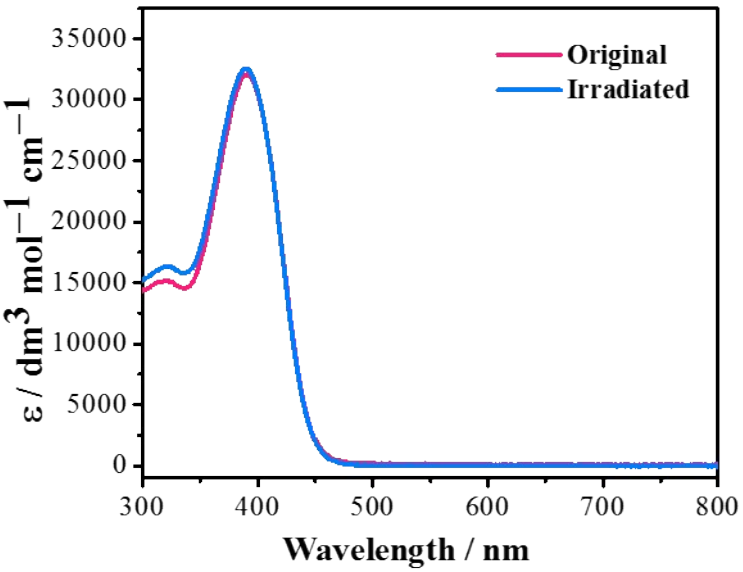


Figure S6. UV-vis absorption spectra of TPE-MN in dichloromethane (1.0×10^{-5} mol/L) solution before and after UV-light irradiation (365 nm).

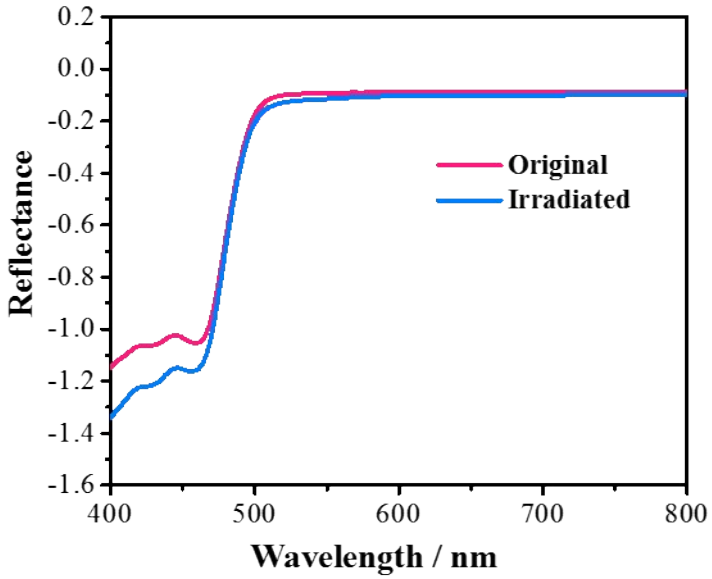


Figure S7. UV-vis reflectance spectra of TPE-MN in the crystalline state before and after UV-light irradiation.

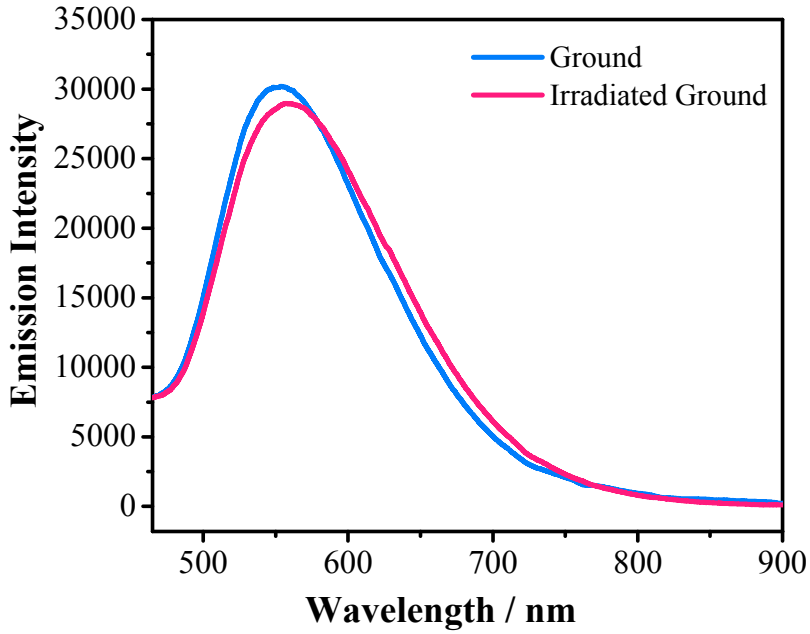


Figure S8. Emission spectra of ground TPE-MN with the excitation wavelength of 365 nm before and after UV-light (365 nm) irradiation.

Reference:

[1] Y. Wang, I. Zhang, B. Yu, X. Fang, X. Su, Y.-M. Zhang, T. Zhang, B. Yang, M. Li, S. X.-A Zhang, *J. Mater. Chem. C*, 2015, **3**, 12328.