

Supporting Information

Synergistic Effect of Anomalous Solvatochromism and Fast Relaxation on the Enhancement of BEMT UV Photoprotection Performance

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Experimental Methods

Chemicals

Bis-Ethylhexyloxyphenol Methoxyphenol Triazine (BEMT, 99%) were obtained from COSMOS; n-Hexane (C₆H₁₂), Isooctane (C₈H₁₈), 1,4-Dioxane (C₄H₈O₂), Cyclohexane (C₆H₁₂), Ethyl acetate (C₄H₈O₂), Tetrahydrofuran (C₄H₈O), Dichloromethane (CH₂Cl₂), n-Butanol (C₄H₁₀O), Isopropanol (C₃H₈O), Ethanol (C₂H₆O), Methanol (CH₄O), N,N-Dimethylformamide (C₃H₇NO), Acetonitrile (C₂H₃N) and Dimethyl sulfoxide (C₂H₆OS) were purchased from Aladdin, 5,5-Dimethyl-1-Pyrroline-N-oxide (DMPO, 98.0%) was purchased from DOJINDO. N; Tetrabutylammonium bromide (TBAB, 99.0%), Tetrabutylammonium perchlorate (TBAP, 99.0%) and Tetrabutylammonium phosphate (TBAP, 99.0%) were purchased from Macklin; All reagents were used as analytical grade without further purification.

Impact of Microenvironment on the UV Absorption Spectrum of BEMT

Equal amounts of BEMT standard were dissolved in n-hexane ($\epsilon \approx 1.9$), toluene ($\epsilon \approx 2.4$), dioxane ($\epsilon \approx 2.2$), ethyl acetate ($\epsilon \approx 6.0$), acetone ($\epsilon \approx 20.7$), ethanol ($\epsilon \approx 24.6$), methanol ($\epsilon \approx 32.7$), and water ($\epsilon \approx 78.5$) to prepare solutions at identical concentrations. The absorption spectra were then recorded using a UV-Vis spectrophotometer.

BEMT was dissolved in an 80% dioxane/20% water mixture, and the pH of the system was adjusted to 2, 4, 7, 9, and 11 using formic acid and ammonia solution. The UV absorption spectra were measured at each pH value.

In a fixed-concentration BEMT solution prepared in 80% dioxane/20% water, The organic salt of tetrabutylammonium bromide, tetrabutylammonium hexafluorophosphate, and tetrabutylammonium perchlorate were added respectively. Subsequently, the UV absorption spectra of each system were recorded.

Photostability Testing

Firstly, BEMT was dissolved in various solvents and oils. 20 mL solution was placed in a quartz vial and subjected to irradiation in an Atlas constant-temperature aging chamber. The reaction temperature was maintained at 37°C using a cooling device. Samples were collected at irradiation time points of 0 h, 3 h, 6 h, 9 h, and 13 h. The UV absorption spectra of the samples within the 250~400 nm range were recorded. Subsequently, using the initial

concentration before irradiation as a benchmark, the retention rate of BEMT after irradiation was determined and calculated via high-performance liquid chromatography (HPLC).

SPF measurements

30 mg sample was weighed out and evenly applied onto a roughened PMMA plate. The application process lasted approximately 40 seconds. The plate was then kept in a light-protected, constant temperature and humidity environment for 15 minutes to allow the film to stabilize. The UV transmittance spectrum of the applied sample was measured over the 290~400 nm wavelength range using a UV transmittance analyzer. The in vitro sun protection factor (SPF) value was calculated according to the relevant standard. For each formulation, a minimum of three parallel samples were tested, and the mean values and standard deviations were reported.

ROS measurement

To evaluate the biosafety of BEMT under ultraviolet (UV) irradiation, the photo-induced generation of reactive oxygen species (ROS) was determined using the 3,3',5,5'-Tetramethylbenzidine (TMB) chromogenic method. TMB is a classic peroxidase substrate, can be oxidized by ROS (such as $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and H_2O_2) to form blue oxidized TMB (ox-TMB), enabling the detection of ROS.

10.0 mg BEMT was placed in a 10 mL centrifuge tube, followed by the addition of 5.0 mL of acetic acid/ammonium acetate buffer (pH=4.5). The mixture was dispersed by ultrasonication for 15 min to form a homogeneous suspension. Then, 1.0 mL 0.5 mmol L^{-1} TMB working solution was added. After mixing by inversion, the mixture was transferred to a quartz reaction vessel and sealed without any residual air bubbles. The reaction vessel was placed in an Atlas Suntest CPS+ aging chamber and irradiated with UV light for 0.5 h. After irradiation, the sample was centrifuged, and the supernatant was collected in a quartz cuvette. The absorption spectrum was scanned from 400 to 800 nm with a UV-2600 spectrophotometer.

Computational method

The theoretical calculations were performed using the Gaussian 16 program with B3LYP functional. Geometries were optimized and TD-DFT using the 6-31G(d) basis set, The Electron excitation analysis were performed through the Multiwfn 3.8 software.

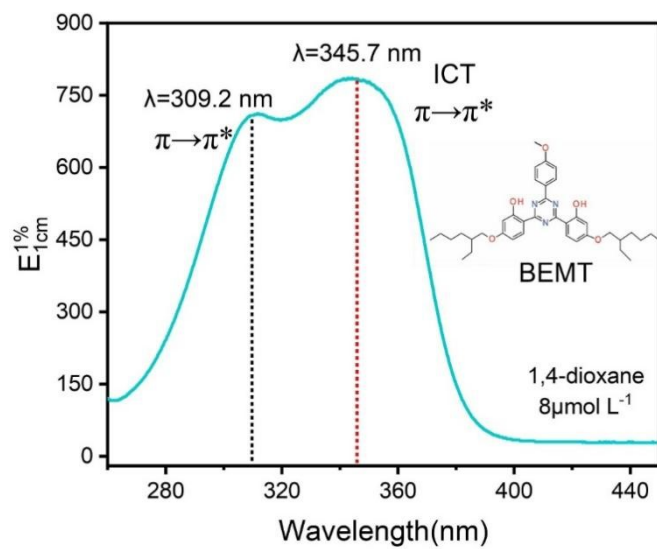


Figure. S1 UV absorption spectra of BEMT in 1,4-dioxane.

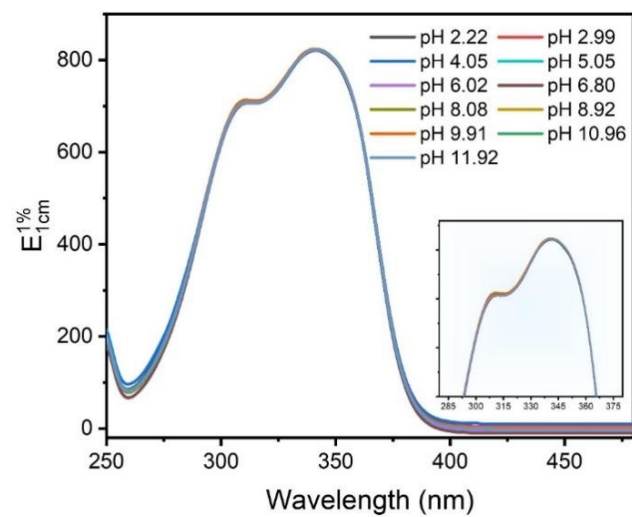


Figure S2. UV absorption spectra of BEMT in 1,4-dioxane with different pH.

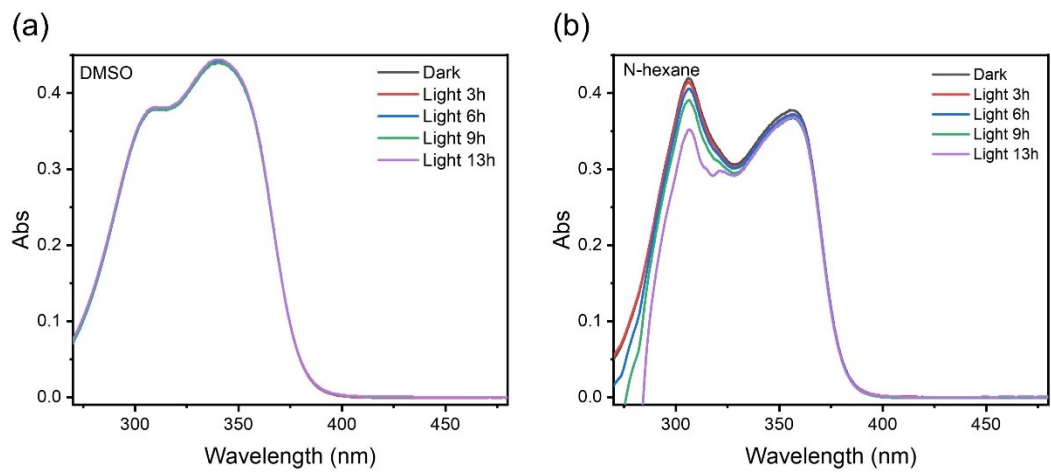


Figure S3. UV absorption spectra of BEMT in DMSO and N-hexane after light.

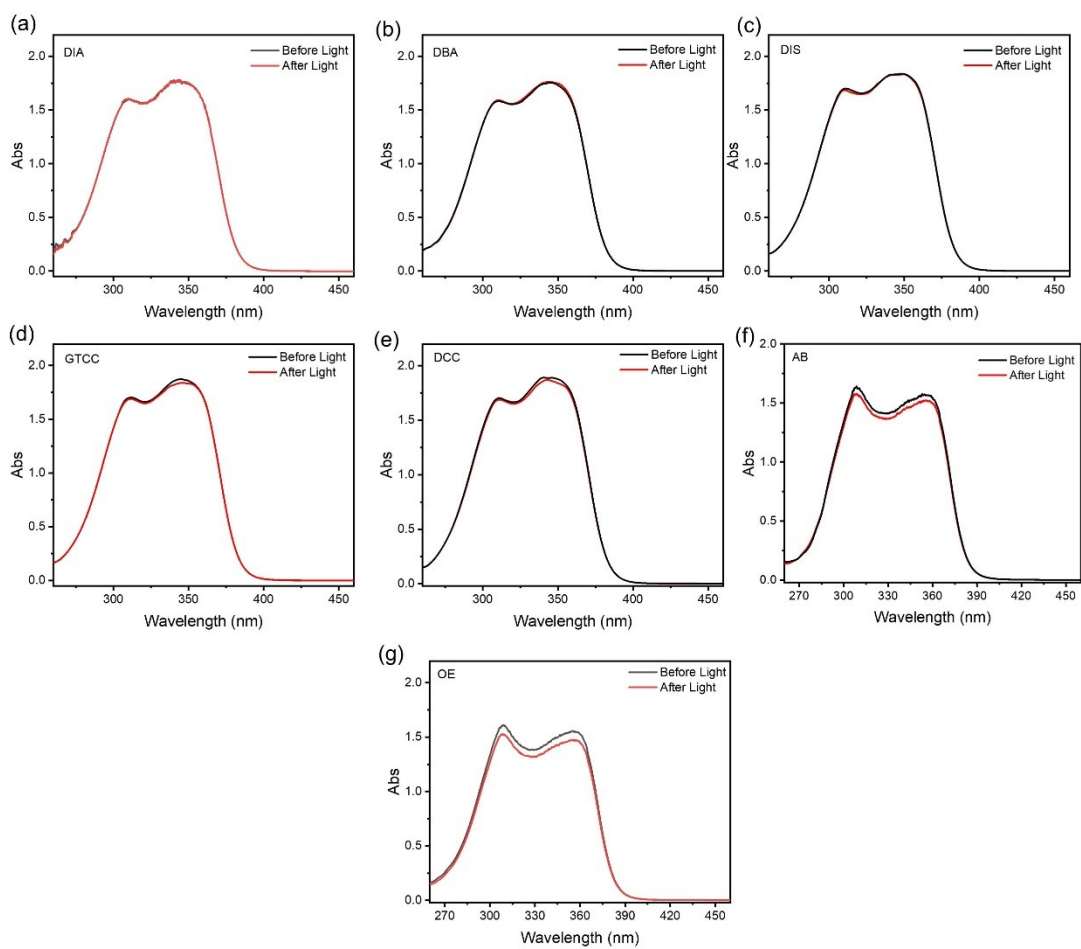


Figure S4. UV absorption spectra of BEMT in different oil before and after light.

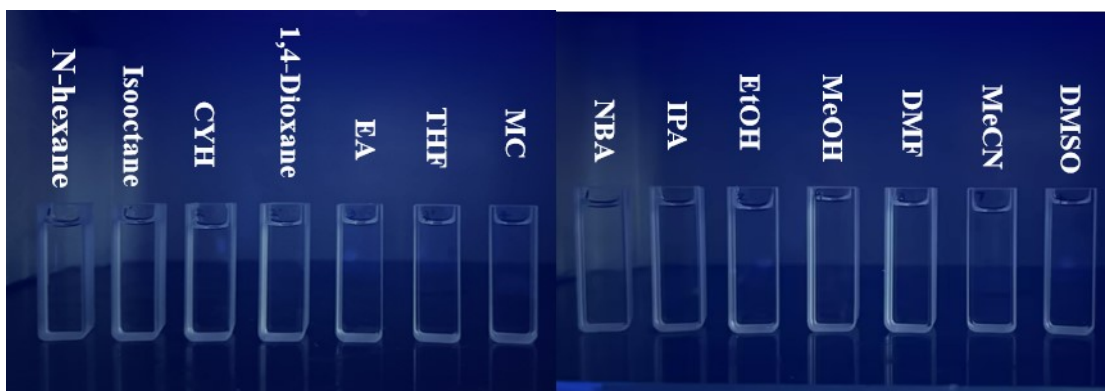


Figure S5. Fluorescence images of BEMT in different solvents at an excitation wavelength of 360 nm.

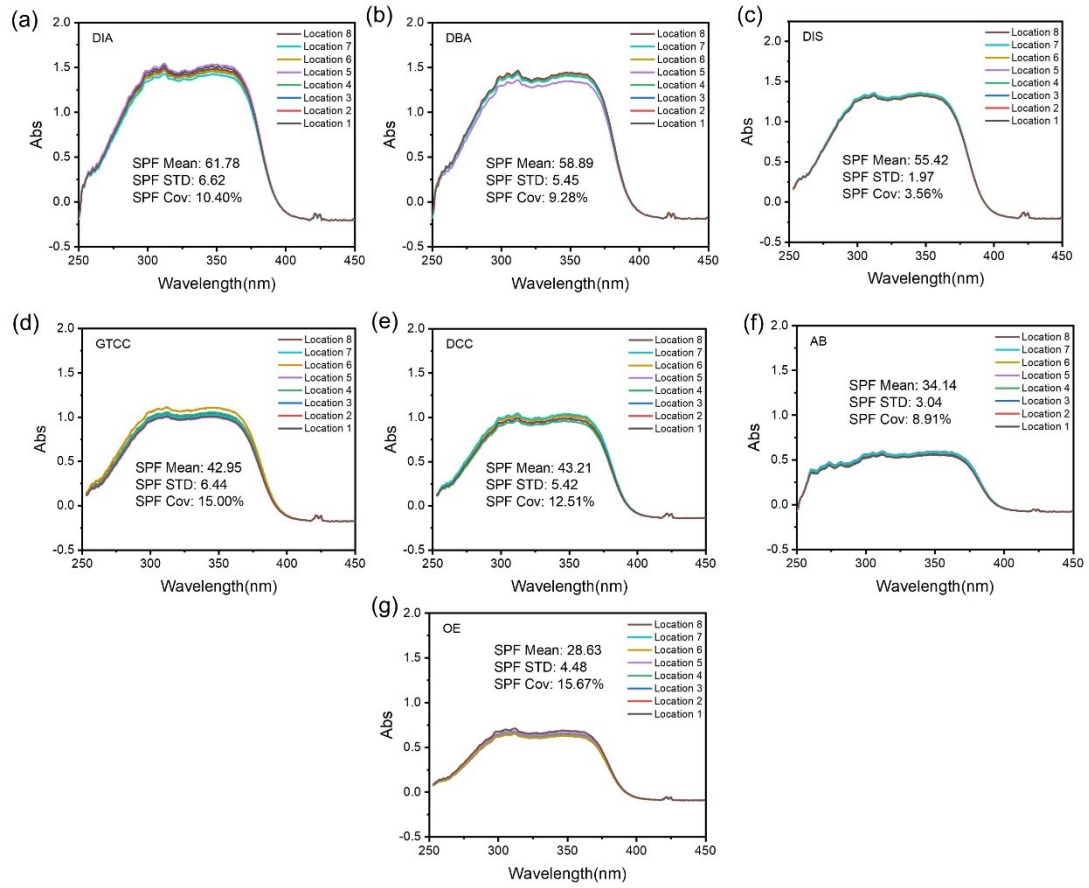


Figure S6. The SPF of BEMT in different oil.

Table S1 Summary of dielectric constants of different solvents and the correspond λ_{max} of BEMT.

Solvent	Dielectric constant	λ_{max} (nm)	$E_{1\text{cm}}^{1\%}$
DMSO	46.68	339.8	916
MeCN	37.5	340.2	888
DMF	36.71	340.5	860
MeOH	32.7	341	856
EtOH	24.5	341.4	828
IPA	20.4	341.8	824
NBA	17.5	342.8	822
MC	9.1	343.4	814
THF	7.58	343.8	812
EA	6.02	344	806
1,4-dioxane	2.2	347.2	784
CYH	2.023	355	746
Isooctane	1.94	356.8	792
N-hexane	1.88	357.6	754

Table S2. Kinetic fitting parameters of the fs-TAS for BEMT in solvents of different polarities.

Solvent	τ_1 (ps)	Standard Error	95% Confidence Interval
1,4-Dioxane	8.61	± 0.72	7.89~9.33
80% 1,4-Dioxane/20% H ₂ O	5.47	± 0.58	4.89~6.05
DMSO	4.65	± 0.51	4.14~5.16

Solvent	τ_1	τ_2	τ_3	A ₁	A ₂	A ₃
1,4-Dioxane	8.61	18.54	69.38	7404.7	2265.3	265.44
80% 1,4-Dioxane/20% H ₂ O	5.47	13.28	46.75	8260.5	2365.8	214.00
DMSO	4.65	12.62	39.45	7744.0	2400.1	253.33

Table S3. SPF-related parameters of BEMT in different oils.

Oil	SPF Mean	SPF Std	SPF Cov
DIA	61.78	6.62	10.40%
DBA	58.89	5.45	9.28%
DIS	55.42	1.97	3.56%
GTCC	42.95	6.44	15.00%
DCC	43.21	5.42	12.51%
AB	34.14	3.04	8.91%
OE	28.63	4.48	15.67%