

Role of aromatic amino acid tryptophan UVA-photoproducts in the determination of drug photosensitization mechanism: a comparison between methylene blue and naproxen

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Abbreviations. API-ES, atmospheric pressure ionization-electrospray; Trp, tryptophan; MB, methylene blue; NAP, naproxen; 6-MAN, 6-methoxy-2-acetonaphthone; DAD, photodiode array detector; ECD electrochemical detector; NSAID, non steroidal antiinflammatory drug; MSD, mass spectrometer detector; $^1\text{O}_2$, singlet oxygen; PB, phosphate buffer; ROS, reactive oxygen species;.

Fig. S1 comparison of absorption spectra of PB solutions of 50 μM Trp, 30 μM MB + 50 μM Trp, 300 μM NAP+ 50 μM Trp and emission spectrum of the black phosphor lamp

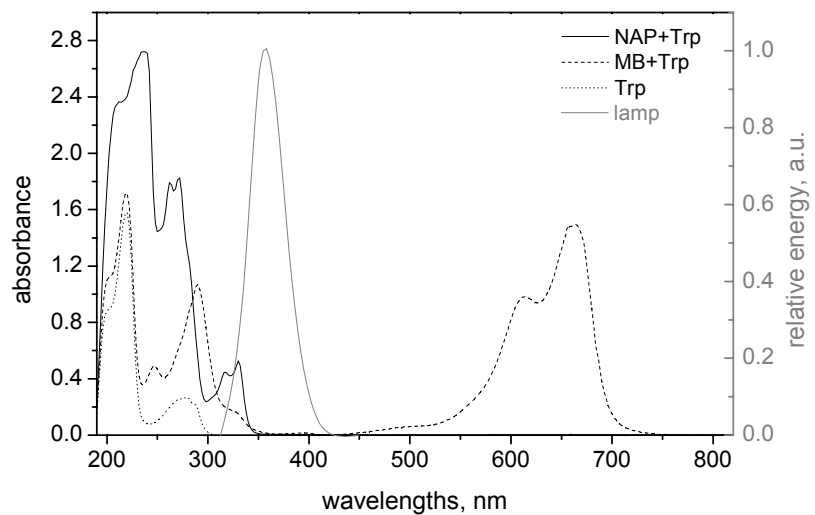


Figure S1

	SYSTEM 1		SYSTEM 2		SYSTEM 3		SYSTEM 4		SYSTEM 5
	Isocratic H ₂ O/ACN		Gradient ACN/pentane-sulfonic buffer		Isocratic formate buffer/ MeOH		Isocratic SOS buffer/MeOH		MeOH
	t _R	detector	t _R	detector	t _R	detector	t _R	detector	
MB			7.9	DAD ₂₈₀ MSD ₃₂₀₊					MSD ₂₈₄₊
10-H-phenothiazine	3.8	DAD ₂₈₀	4.2	DAD ₂₈₀					MSD ₂₈₅₊
NAP					20	DAD ₂₈₀ FLD _{278/356} MSD ₂₃₁₊			
6-MAN	4.2	DAD ₂₈₀ FLD _{278/356} MSD ₂₀₀₊			22	FLD _{278/356} DAD ₂₈₀ MSD ₂₀₀₊			
NAP alcohol deriv.					21	FLD _{278/356} DAD ₂₈₀ MSD ₁₉₈₊			
NAP decarb. deriv.					19	DAD ₃₃₀ FLD _{330/400} MSD ₁₈₅₊			
Trp	6.5	DAD ₂₈₀ FLD _{278/356} MSD ₂₀₅₊	5.5	DAD ₂₈₀ FLD _{278/356}	8.1	DAD ₂₈₀ FLD _{278/356} MSD ₂₀₅₊	22	ECD FLD _{278/356} DAD ₂₈₀	
4-OH-chinoline					10	DAD ₂₈₀ FLD _{278/356} MSD ₁₄₆₊			
tryptamine					9.5	DAD ₂₈₀ FLD _{278/356} MSD ₁₆₁₊			
3-OH-kynurenine	3.1	DAD ₃₆₀ FLD _{372/425} MSD ₂₂₅₊			3.8	DAD ₃₆₀ FLD _{372/425} MSD ₂₂₅₊	3.4	DAD ₃₆₀ ECD	
kynurenine	4.5	DAD ₃₆₀ FLD _{360/480} MSD ₂₀₉₊			5.5	DAD ₃₆₀ FLD _{360/480} MSD ₂₀₉₊	7.2	DAD ₃₆₀ ECD	
N-formylkynurenine					5.8	DAD ₃₃₀ FLD _{325/435} MSD ₂₃₇₊	6.5	DAD ₃₂₀ FLD _{319/430}	
xanthurenic acid							6.1	DAD ₃₄₀ ECD _{340/500} MSD ₂₀₆₊	
kynurenic acid					8.3	DAD ₃₃₀ FLD _{330/375} MSD ₁₉₀₊			
alanine					2.2	MSD ₉₀₊			
serine					2.5	MSD ₁₀₆₊			
aspartic acid					2.8	MSD ₃₁₂₊			
5-OH-tryptophan					7.2	DAD ₂₈₀ FLD _{278/356} MSD ₂₂₁₊			

Table S1. HPLC detector setup and retention times

t_R : retention time; DAD₂₈₀: diode array detector at 280 nm; FLD 278/356: fluorescence detector $\lambda_{ex}/\lambda_{em}$; ECD: electrochemical detector; MSD: mass spectrometer; (see also **Experimental Section**)