Supporting Information

The Dermacozines and Light: A Novel Phenazine Semiquinone Radical based Photocatalytic System from the Deepest Oceanic Trench of the Earth

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phenazine-1-carboxilic acid



Dermacozine C



Dermacozine A



Dermacozine B



Dermacozine D



Dermacozine E



Dermacozine F





Dermacozine H



Dermacozine I



Dermacozine G



Dermacozine M





Dermacozine O



Dermacozine P

S1. Dermacozines isolated to date. [Ref.2,3,4,5]



S2. Dermacozines, isolation (stationary phase: silica, mobile phase: 90% CH₂Cl₂-10% CH₃OH).

Dermacozine	Longest absorption maximum in the visible [nm]	Longest absorption maximum in the visible [m]		E _{optical_gap_calc_Joules} [J]	E _{optical_gap_calc_ev} [eV]
Dermacozine A	398	3.98E-07	7.53247E+14	4.99107E-19	3.12
Dermacozine B	419	4.19E-07	7.15495E+14	4.74092E-19	2.96
Dermacozine C	460	4.60E-07	6.51723E+14	4.31836E-19	2.70
Dermacozine D	408	4.08E-07	7.34785E+14	4.86874E-19	3.04
Dermacozine E	576	5.76E-07	5.20473E+14	3.44869E-19	2.15
Dermacozine F	566	5.66E-07	5.29669E+14	3.50962E-19	2.19
Dermacozine G	580	5.80E-07	5.16884E+14	3.42491E-19	2.14
Dermacozine H	459	4.59E-07	6.53143E+14	4.32777E-19	2.70
Dermacozine I	516	5.16E-07	5.80993E+14	3.84970E-19	2.40
Dermacozine J	435	4.35E-07	6.89178E+14	4.56654E-19	2.85
Dermacozine M	590	5.90E-07	5.08123E+14	3.36686E-19	2.10
Dermacozine N	729	7.29E-07	4.11238E+14	2.72489E-19	1.70
Dermacozine O	644	6.44E-07	4.65516E+14	3.08454E-19	1.93
Dermacozine P	465	4.65E-07	6.44715E+14	4.27193E-19	2.67
PCA	364	3.64E-07	8.23606E+14	5.45727E-19	3.41

S3. UV-Vis measured Longest AMs of dermacozines (solvent: C_2H_5OH) in the visible EM radiation in [nm] ^[Ref.2,3,4,5], [m], [Hz], [J] and [eV].



S4. Longest AMs of dermacozines in the visible EM (solvent: C_2H_5OH))^[2,3,4,5] [eV].



S5. Dermacozine B Cyclic Voltammetry measurements (0.1 M NaClO₄ in CH₃CN).



S6. Dermacozine E Cyclic Voltammetry measurements (0.1 M NaClO₄ in CH₃CN).



S7. Dermacozine F Cyclic Voltammetry measurements (0.1 M NaClO₄ in CH₃CN).



S8. Dermacozine O Cyclic Voltammetry measurements (0.1 M NaClO₄ in CH₃CN).



S9. PCA Cyclic Voltammetry measurements (0.1 M NaClO₄ in CH₃CN).



S10. Dermacozine P Cyclic Voltammetry measurements (0.1 M NaClO₄ in CH₃CN).

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DERMACOZINE	OPTICAL GAP [EV] (EXP)	ELECTRIC GAP±SE [V] (EXP)	EXPERIMENTAL ANODIC POTENTIAL±SE [V] (AG ACETONITRILE) (EXP)	EXPERIMENTAL CATHODIC POTENTIAL±SE [V] (AG ACETONITRILE) (EXP)	SHE REFERENCED ANODIC POTENTIALS [V] (EXP)	SHE REFERENCED CATHODIC POTENTIALS [V] (EXP)	ESTIMATED ANODIC POTENTIALS BASED ON OPTICAL GAP – ELECTRIC HOMO EXPERIMENTAL RELATIONSHIP (R ² =0.73)±ME [V] μ_{Anodic} [V] = $\frac{\mu_{Anodic}}{3}$)±ME	ESTIMATED CATHODIC POTENTIALS FROM μ OF THE EXPERIMENTAL CATHODICPOT ENTIALS [V]±ME
	1						CALC (SHE)	CALC (SHE)
N	1,7						+0.8±0.01	-0.9±0.02
0	1,9	1.763±0.005	+0.883±0.001	-0.880±0.005	+0.848±0.003	-0.915±0.005	+0.9±0.01	-0.9±0.02
G	2,1						+1.0±0.01	-0.9±0.02
М	2,1						+1.0±0.01	-0.9±0.02
E	2,2	1.908±0.030	+1.014±0.021	-0.894±0.021	+0.979±0.021	-0.929±0.021	+1.0±0.01	-0.9±0.02
F	2,2	1.998±0.024	+1.169±0.010	-0.829±0.022	+1.134±0.010	-0.864±0.022	+1.0±0.01	-0.9±0.02
I.	2,4						+1.1±0.01	-0.9±0.02
С	2,7						+1.1±0.01	-0.9±0.02
н	2,7						+1.1±0.01	-0.9±0.02
Р	2,7	2.849±0.053*	+1.546±0.052*	-1.303±0.018*	+1.511±0.052*	-1.338±0.052*	+1.1±0.01	-0.9±0.02
l	2,9						+1.2±0.01	-0.9±0.02
В	3,0	2.122±0.054	+1.271±0.015	-0.851±0.052	+1.236±0.015	-0.886±0.052	+1.2±0.01	-0.9±0.02
D	3,0						+1.2±0.01	-0.9±0.02
А	3,1						+1.3±0.01	-0.9±0.02
PCA	3,4	2.252±0.029	+1.291±0.025	-0.960±0.015	+1.256±0.025	-0.995±0.015	+1.4±0.01	-0.9±0.02

S11. Measured anodic and cathodic potentials of dermacozines in 0.1 M NaClO₄ in CH₃CN±Standard Errors (SE) and calculated anodic and cathodic values±Mean Errors (ME) based on 13.a. linear regression (calculated anodic potentials) and arithmetic mean of measured cathodic potentials (μ)±ME. *Dermacozine P excluded from calculations as the cathodic and anodic current overlaps too much with the solvent decomposition.

NB: Since the errors of the AMs in Ethanol are not known, no standard propagation of error but mean error (ME) was given for calculated values. Whereas the measured potentials expressed as ± standard error (SE).



Dermacozine	(x) <u>A</u> L electric [V]	(y) <u>A</u> E Optical [eV]
PCA	2,3	3,4
В	2,1	3
E	1,9	2,2
F	2	2,2
0	1,8	1,9

S12.a. Dermacozine B, E, F, O and PCA's experimental optical (Solvent: C_2H_5OH) and experimental electric HOMO-LUMO energy gaps (solvent: CH_3CN) correlation.

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0,960027177							
R Square	0,92165218							
Adjusted R Square	0,89553624							
Standard Error	0,203903351							
Observations	5							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	1,46727027	1,46727027	35,2907909	0,009535859			
Residual	3	0,12472973	0,041576577					
Total	4	1,592						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95,0%	Upper 95,0%
Intercept	-3,82027027	1,074519785	-3,555327993	0,037946247	-7,23987179	-0,40066875	-7,23987179	-0,40066875
X Variable 1	3,148648649	0,530021523	5,940605264	0,009535859	1,461883611	4,835413686	1,461883611	4,835413686

S12.b. Dermacozine B, E, F, O and PCA's experimental optical [eV] (Solvent: C_2H_5OH) and experimental electric HOMO-LUMO energy gaps [V] (solvent: CH_3CN) multiple regression (Microsoft Excel).



Dermacozine	HOMO [V]	(y) Z E Optical [eV]			
PCA	1,3	3,4			
В	1,2	3			
E	1	2,2			
F	1,1	2,2			
0	0,8	1,9			

S13.a. Linear correlation between the experimental anodic potentials of dermacozine B, E, F, O and PCA [V] with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0,914704005							
R Square	0,836683417							
Adjusted R Square	0,782244556							
Standard Error	0,294392029							
Observations	5							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	1,332	1,332	15,36923077	0,029518265			
Residual	3	0,26	0,086666667					
Total	4	1,592						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95,0%	Upper 95,0%
Intercept	-0,7	0,836875355	-0,836444753	0,464292127	-3,363310883	1,963310883	-3,363310883	1,963310883
X Variable 1	3	0,765235641	3,920361051	0,029518265	0,564678663	5,435321337	0,564678663	5,435321337

S13.b. Multiple Regression (Microsoft Excel) between the experimental anodic potentials of dermacozine B, E, F, O and PCA [V] measured with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].



Dermacozine	(x) Electric LUMO [V]	(y) ∆ E Optical [eV]			
PCA	-1	3,4			
В	-0,9	3			
E	-0,9	2,2			
F	-0,9	2,2			
0	-0,9	1,9			

S14.a. Linear correlation between the cathodic potentials of dermacozine B, E, F, O and PCA [V] measured with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].

SUMMARY OUTPUT								
Regression Statistics								
Multiple R	0,762047295							
R Square	0,58071608							
Adjusted R Square	0,440954774							
Standard Error	0,471699057							
Observations	5							
ANOVA								
	df	SS	MS	F	Significance F			
Regression	1	0,9245	0,9245	4,15505618	0,134253828			
Residual	3	0,6675	0,2225					
Total	4	1,592						
	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95,0%	Upper 95,0%
Intercept	-7,35	4,856439025	-1,513454604	0,227379012	-22,80535643	8,105356431	-22,8053564	8,105356431
X Variable 1	-10,75	5,273755777	-2,038395492	0,134253828	-27,53344459	6,033444589	-27,5334446	6,033444589

S14.b. Multiple regression (Microsoft Excel) between the experimental cathodic potentials of dermacozine B, E, F, O and PCA [V] measured with Cyclic Voltammetry (solvent: CH_3CN) and the experimental optical HOMO-LUMO gaps measured with UV-Vis Spectroscopy (solvent C_2H_5OH) [eV].



S15. Dermacozine O semiquinone radical's reaction with water, EPR Spectroscopy, He atmosphere, 298 K, 550±50 nm filter in CHCl₃.



S16. Dermacozine E neutral semiquinone radical EPR (a) in chloroform (red line, experimetnal 550±50 nm filter, blue dashed line modelled EPR spectrum) and (b) UV Vis Spectrum before (blue) and after (red) the the dermacozine O semiquinone radical formed in chloroform (inlet: confirmed dermacozine E radical structure).



S17. Dermacozine O neutral semiquinone radical EPR (a) in chloroform (red line, experimetnal 550±50 nm filter, blue dashed line modelled EPR spectrum) and (b) UV Vis Spectrum before and after the the dermacozine O semiquinone radical formed in chloroform (inlet: confirmed dermacozine O radical structure).



S18. Dermacozine O radical UV-Vis Spectrum in CHCl₃.



S19. Dermacozine O UV-Vis Spectrum in CHCl₃.



S20. Dermacozine E UV-Vis Spectrum in CHCl₃ (solution is blue).



S21. Dermacozine E UV-Vis Spectrum, after EPR and with 550 nm filter irradiation, in $CHCl_3$ (solution is orange), a near infrared band (arrow) appeared at ~1000 nm, 298 K.



S22. Dermacozine E UV-Vis Spectrum, after EPR and with 550 nm filter irradiation, in CH₃OH (colour of the solution changed to blue from orange), 298 K.



S23. Dermacozine E (LC)-HR-(ESI)-MSⁿ after irradiation and EPR in CH₃OH.



S24. Dermacozine E dimer (LC)-HR-(ESI)-MSⁿ after irradiation dissociated in CH₃OH and dermacozine E is detectable again.

🔛 Compass Da	itaAnalysis - BJ32	LP1-E-3_1_43	37.d (modi	fied) [Data/	Analysis o	-TOF Default	m (modified)]											- 0	\times
SmartFor	mula Manually					×	tation Method	(iew <u>T</u> ools Cg	mpass <u>W</u> indow <u>H</u> e	lp									
Lower formula	C11					ienerate	s 🖓 🖓 💉	^1 I I' II'	= 1. B /	a da 🖂 🖂 🖬	۵ 🗈								
Upper formula	1					Help													
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1	Note: for m < 20	00 the element	s C, H, N, a	nd O are cor	sidered im	ploty.													
Adducts, pos.	M+H			~		lect adducts													
Adducts, neg.	мн				4					V				~	\sim			-	-
Measured m/z	400.0906	Tolerance	4	mDa ▼	Charge	: 1 0													
Meas. m/z	# Ion Formula	m/z e	err (ppm) i	nSigma #	mSigma	Score rdl				/									
400.0906	1 C16H18NO11	400.0874	-7.9	7.2	1	19.03 9.0													
400.0906	2 C19H12N8O6 3 C14HdN15O	400.0874	-7.9	8.5	2	18.52 14.													
400.0906	4 C17H14N5O7	400.0888	-4.6	15.4	4	51.74 14.													
400.0906	5 C16H8N12O2	400.0888	-4.6	21.6	5	45.27 19.													
400.0906	6 C19H16N2O8	400.0901	-1.2	22.4	6 1	00.00 13.	3.55		3.60	3.65	3.70	3.	75	3.80	3.85	3.90	3.95		Time [min]
400.0906	7 C18H10N9O3	400.0901	-1.2	28.3	7	87.13 19.0													
400.0906	8 C20H12N6O4	400.0915	2.1	35.1	8	60.89 18.													
400.0906	9 C22H14N3O5	400.0928	5.5	42.0	9	20.54 18.0													X
400.0905	11 C24H16O6	400.0941	8.9	49.0	11	4.73 17							40	0.0005			+MS2(400.0903), 20.3-	50.7eV, 3.6min	#374 ^
400.0906	12 C23H10N7O	400.0941	8.8	55.2	12	3.92 23.4							~	•					
400.0906	13 C31H12O	400.0883	-5.8	79.5	13	5.13 26.													
400.0906	14 C29H10N3	400.0869	-9.2	84.8	14	1.12 27.0													
<						>													
Automatica	illy locate monoisoti	opic peak Ma	ximum numb	ber of formul	lae	500													
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		Ele	ctron config	uration		both ~						30.							
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S25. Dermacozine O (LC)-HR-(ESI)-MSⁿ after irradiation and EPR in CH₃OH.



S26. LC MS Mass Spectrometry Chromatogram of Dermacozine B (Orbitrap)



S27. Dermacozine B 1D ¹H NMR Spectrum in DMSO-*d*₆ 400 MHz (x: contaminant)



S28. LC MS Mass Spectrometry Chromatogram of Dermacozine E (Orbitrap)



S29. Dermacozine E 1D ¹H NMR Spectrum in DMSO-d₆ 400 MHz



S30. LC MS Mass Spectrometry Chromatogram of Dermacozine F (qToF)



S31. Dermacozine F 1D ¹H NMR Spectrum in DMSO- d_6 400 MHz



S32. LC MS Mass Spectrometry Chromatogram of PCA (qToF)



S33. PCA 1D ¹H NMR Spectrum in DMSO-*d*₆ 400 MHz



S34. Dermacozine O 1D ¹H NMR Spectrum in DMSO-*d*₆ 400 MHz

(† N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).



S35. LC MS Mass Spectrometry Chromatogram of Dermacozine O (qToF)

([†] N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).



S36. Dermacozine P 1D ¹H NMR Spectrum in DMSO-d₆ 400 MHz

(† N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).



S37. LC MS Mass Spectrometry Chromatogram of Dermacozine P (Orbitrap)

([†] N.B. Identical spectral data of dermacozine O and P appearing in SI which have already been published in Reference [5]. However, for clarity and for completeness the authors present them in the SI with appropriate citation).