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Original Citation:

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NIR-sensitized Dye-Sensitized Solar Cells: effect of the different molecular moieties on the photovoltaic performances

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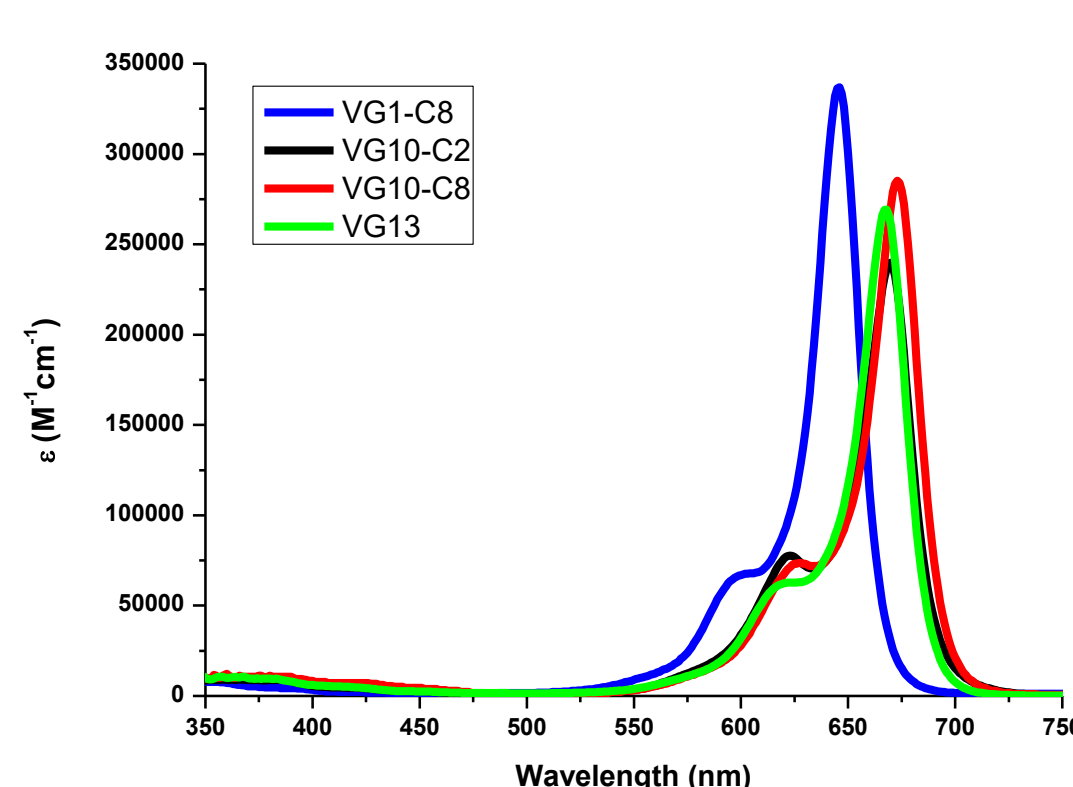
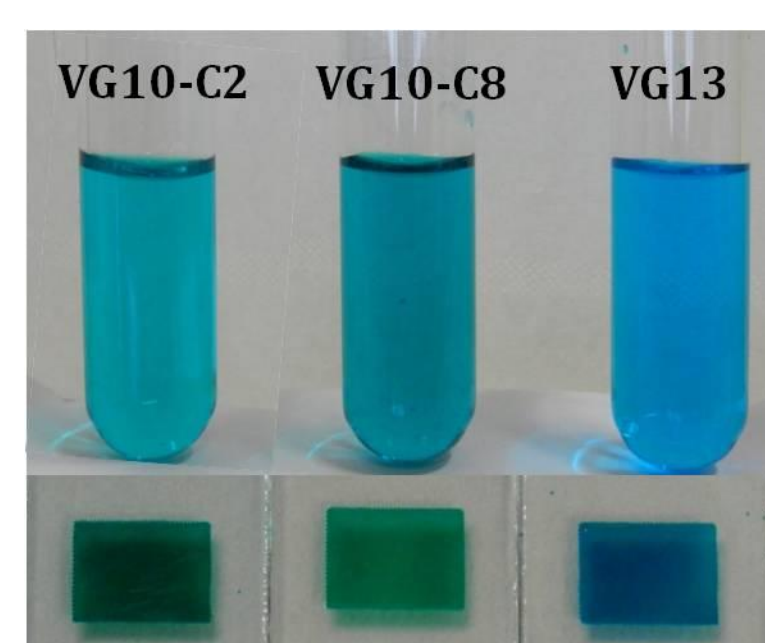
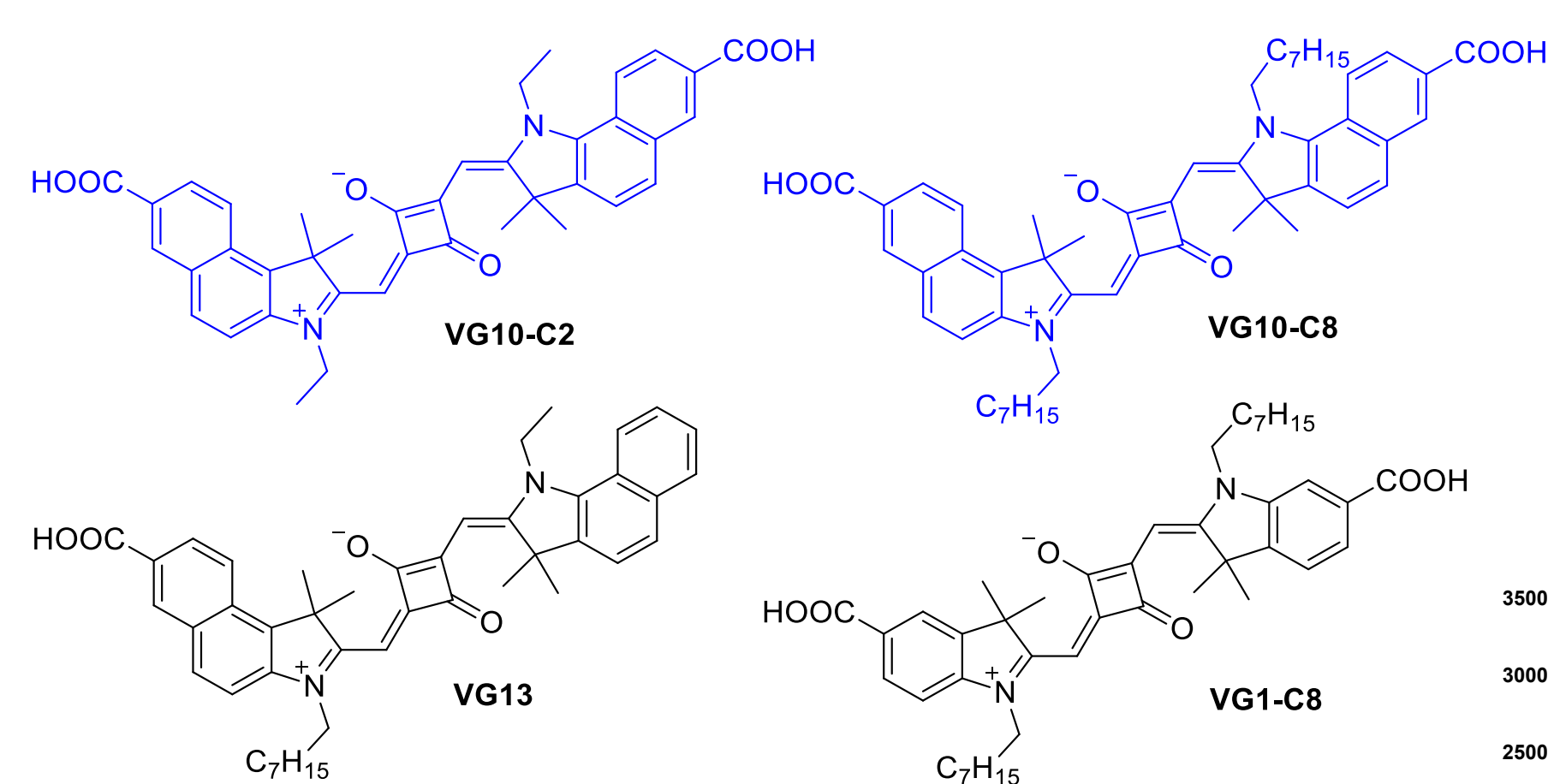
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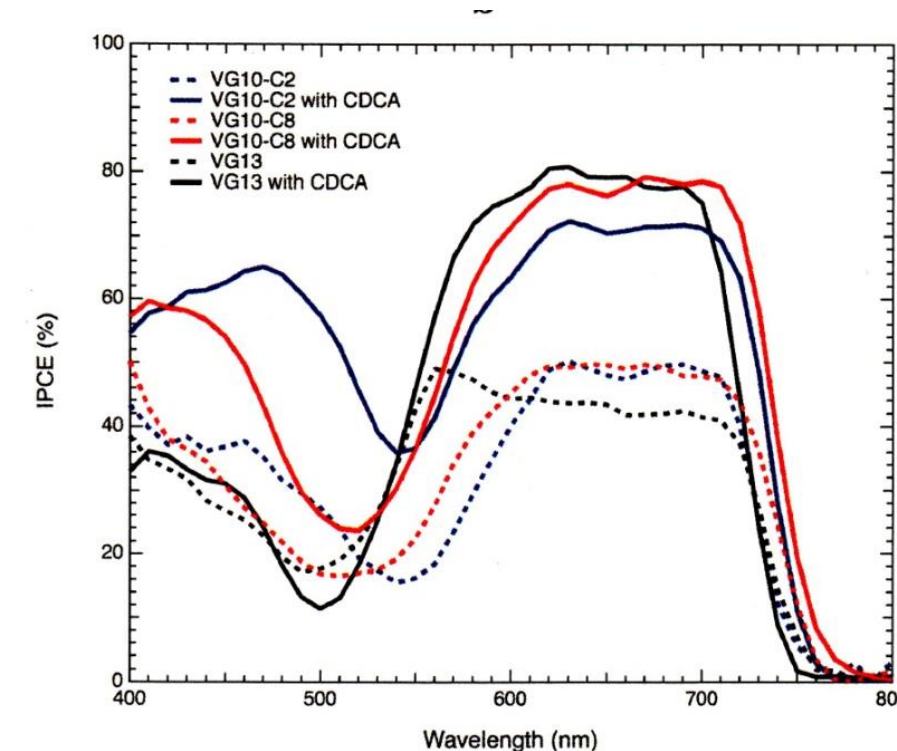
Dye-sensitized solar cells (DSSCs) are nowadays one of the most interesting alternatives when looking at solar harvesting technologies able to provide enhanced performance under low or weak irradiation and for building integrated applications (BIPV) [1]. However, most of these cells absorb only the visible domain of the light spectrum that is why these devices are not transparent or no less than semi-transparent. Far-red/near infra-red (NIR) light is indubitably interesting to widen solar harvesting. Of course, the photoconversion expected by the exploitation of these frequencies (700-1000 nm) is lower with respect to the visible region. But, NIR sensitizers allow to tune the colors of final devices from green to blue, even to transparent. Transparent cells without any coloration would allow the visible light to pass through unhampered reaching a fully integration of PV devices in BIPV [2]. Our group have already developed several squaraine dyes for DSSC absorbing in the NIR region [4,5]. A few series of new efficient organic sensitizers based on squaraine [6], cyanine and croconine core-units with a shifted absorption as high as 830 nm have been synthesized and fully characterized. DSSCs based on these new efficient sensitizers are able to convert up to 36% IPCE until 850 nm.

VG10 SQUARINE for DSSCs [3]



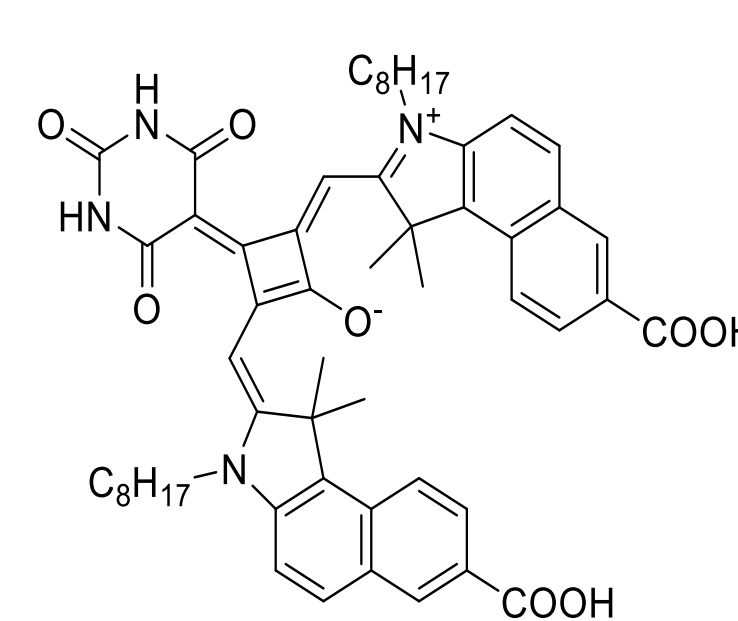
panchromatic spectral response and a record efficiency over 6%

	λ_{max} (nm)	Log ϵ	λ_{em} (nm)	τ (ns)	Φ_{fl}
VG1-C8	646	5.55	657	1.09	0.35
VG13	667	5.43	678	1.11	0.37
VG10-C2	670	5.37	677	1.18	0.36
VG10-C8	673	5.49	679	1.51	0.47

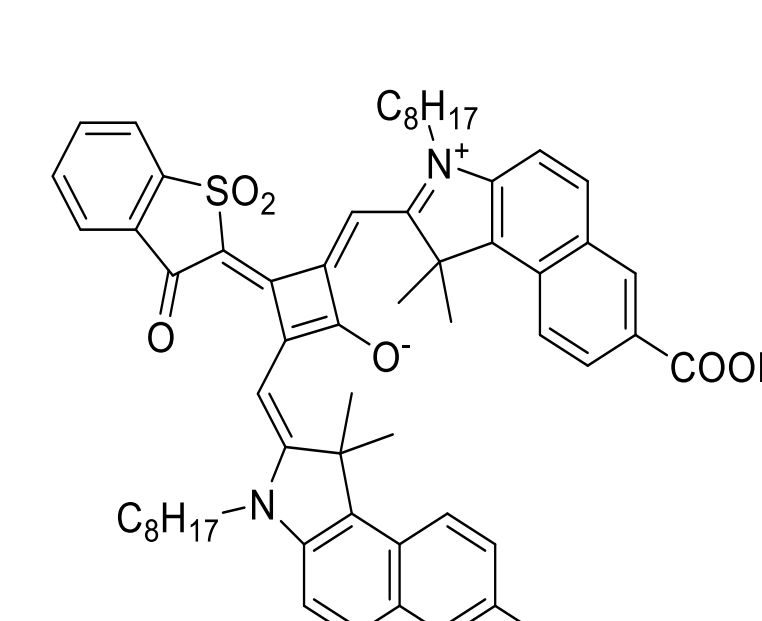


Dye	CDCA (mM)	J_{sc} (mA/cm ²)	V_{oc} (mV)	Fill Factor	η (%)
VG10-C2	0 ^a	8.60	544	0.67	3.11
	10 ^a	14.3	623	0.69	6.18
	2.5 ^b	13.3	617	0.71	5.81
VG10-C8	0 ^a	8.81	585	0.64	3.28
	10 ^a	13.6	641	0.70	6.10
	2.5 ^b	14.0	634	0.69	6.11
VG13	0 ^a	8.74	567	0.62	3.10
	10 ^a	12.1	665	0.68	5.50
	2.5 ^b	12.6	640	0.68	5.44

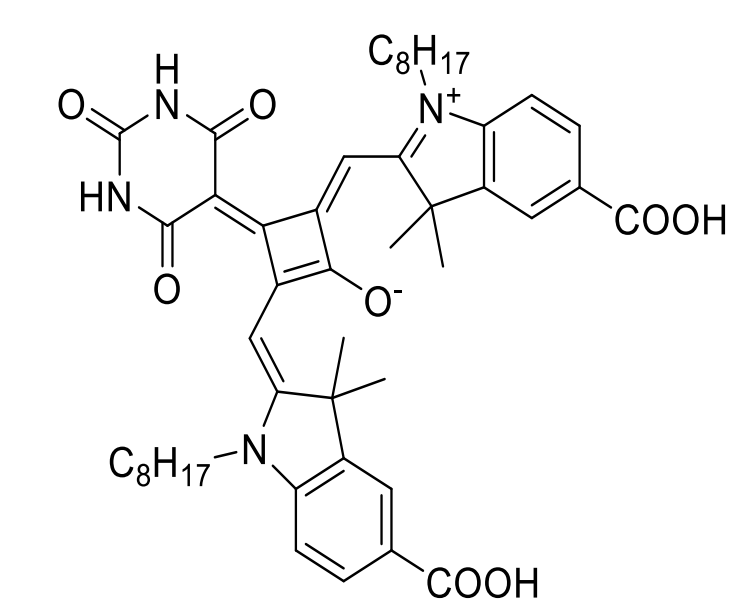
SQUARINE for aqueous DSSCs



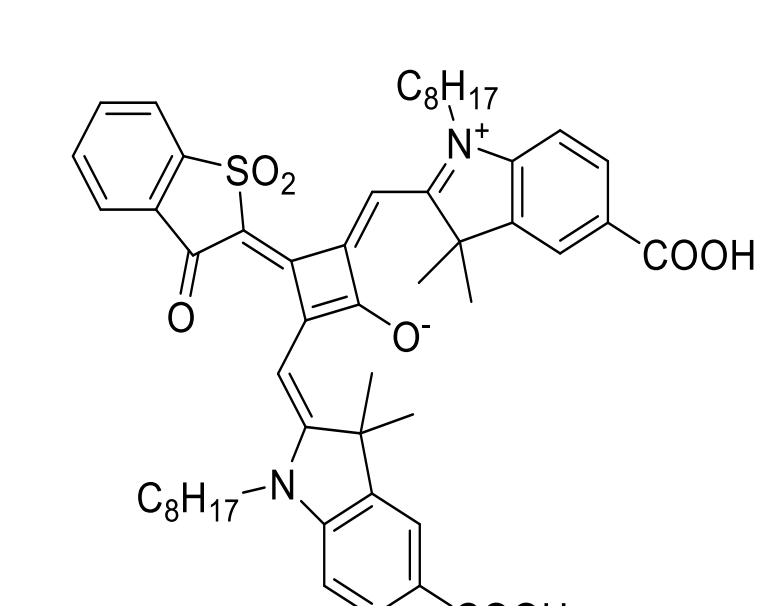
VG8-C8



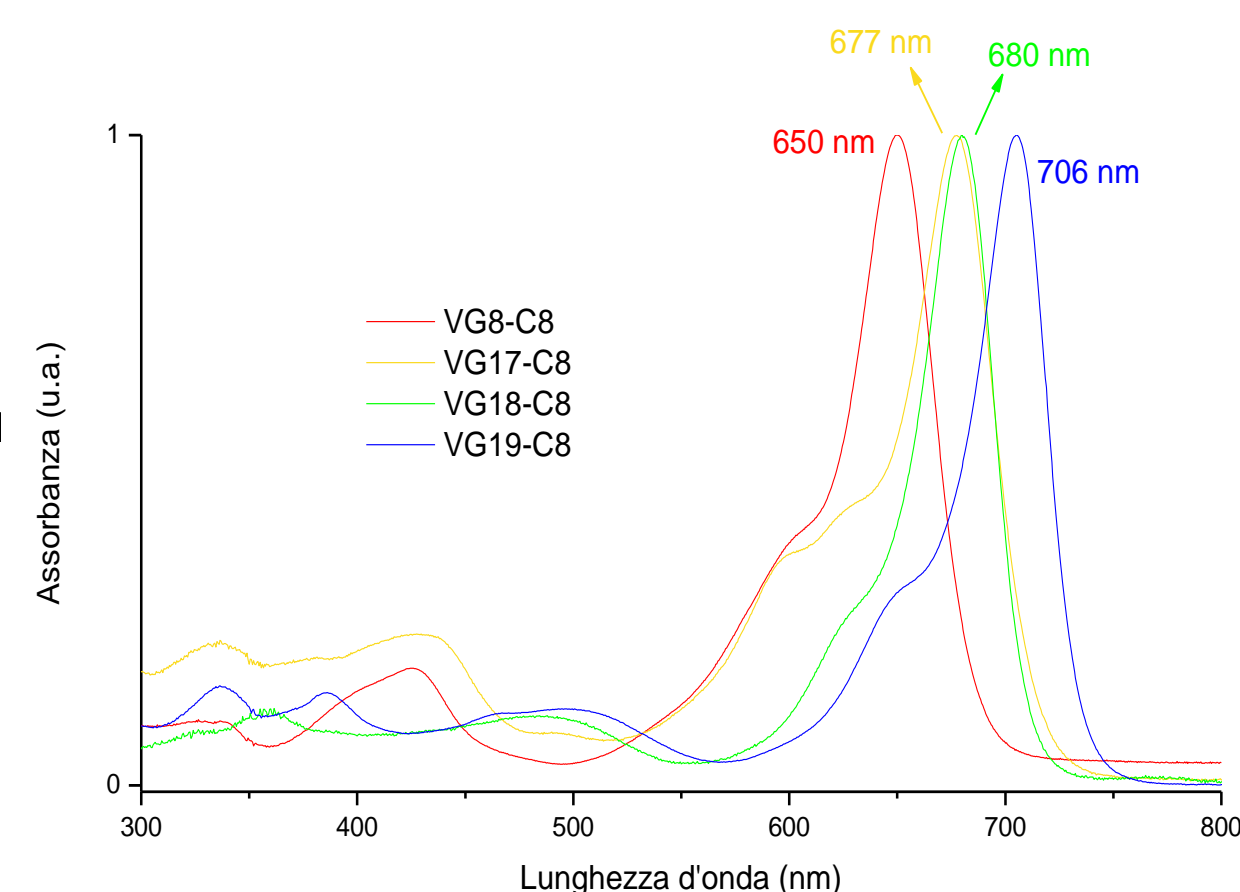
VG17-C8



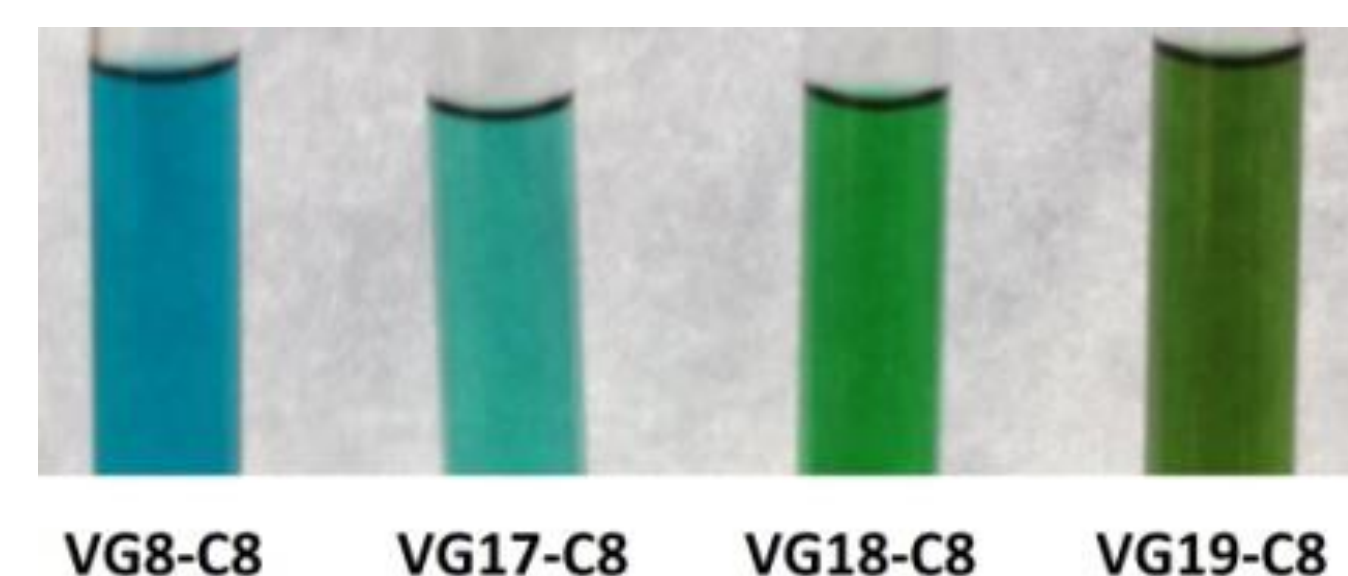
VG18-C8



VG19-C8



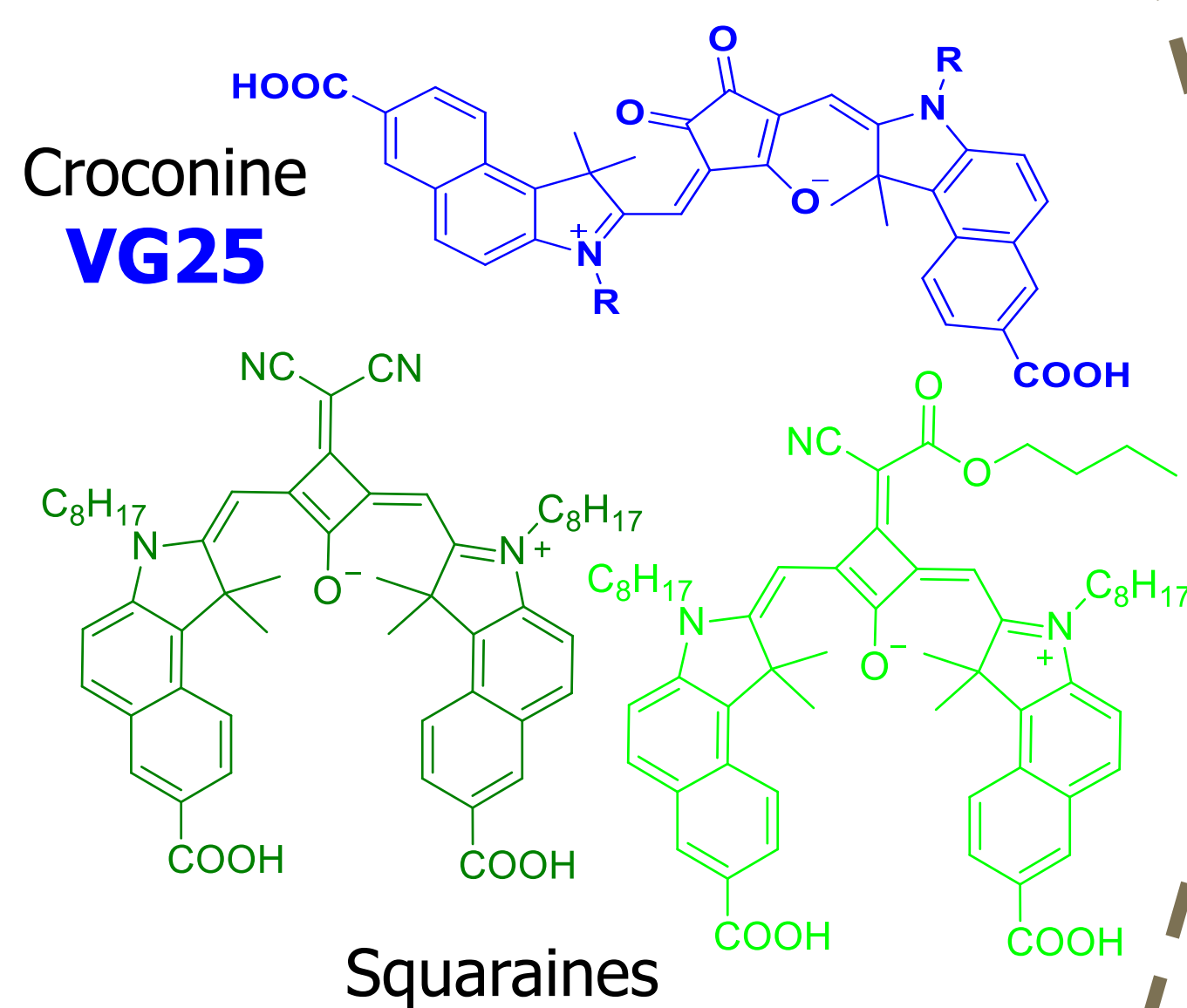
The central functionalization of the squaric acid with either barbituric acid (VG8 and VG17) and sulfoxide tioindanone (VG18 and VG19) is also interesting for the application in water-based DSSC (hydrogen bonds interactions)



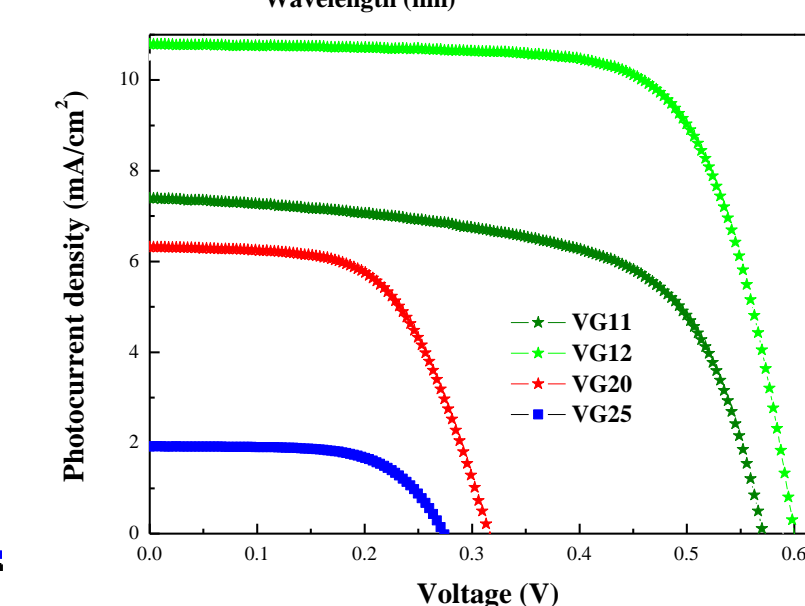
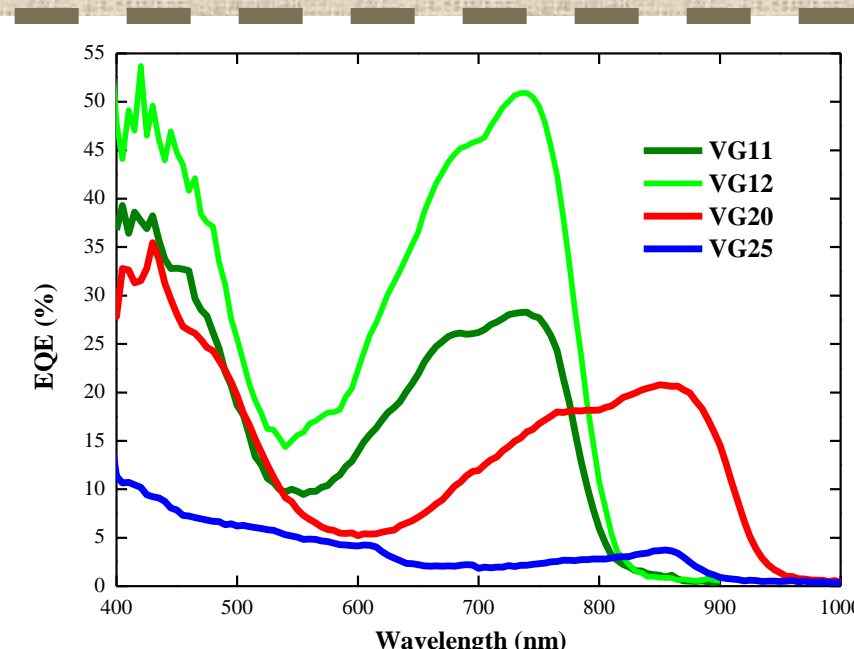
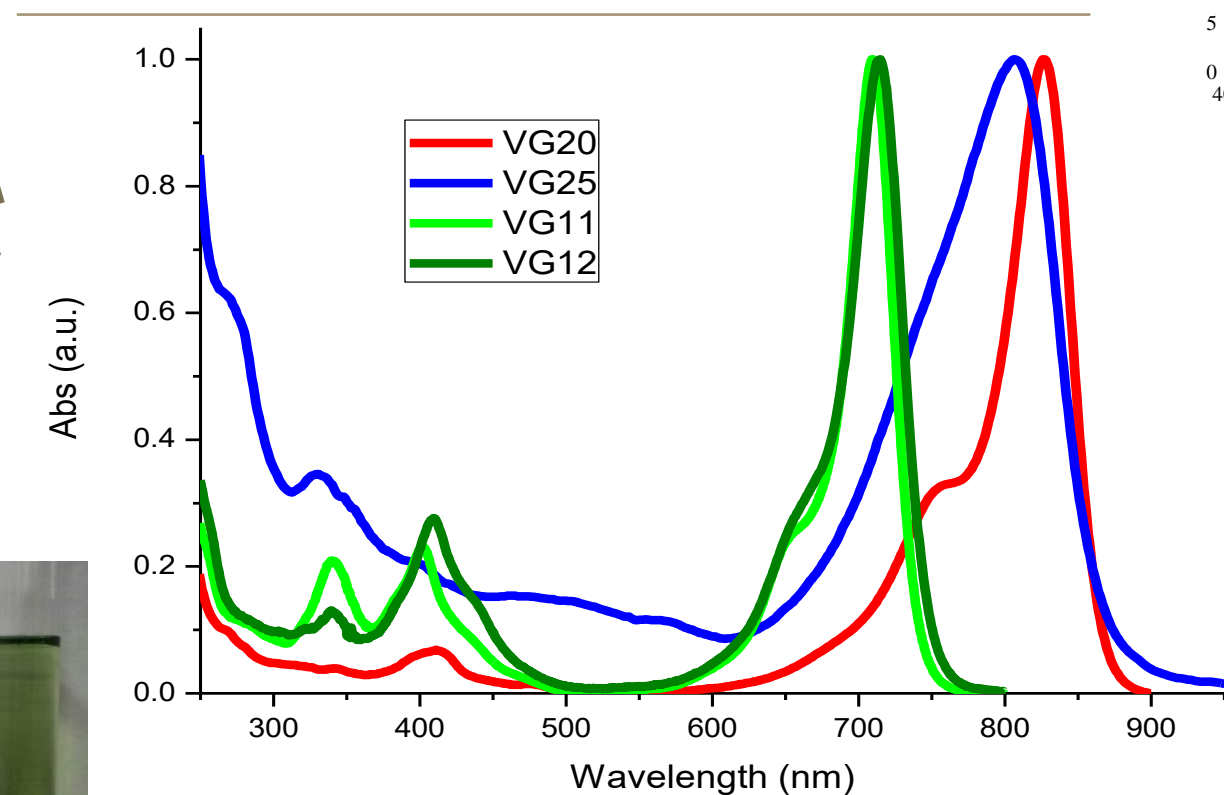
Dye	J_{sc} / mA/cm ²	V_{oc} / mV	Fill Factor	η / %
VG1-C8	-1,34	544	0,76	1,42
VG10-C8	-4,89	586	0,66	1,89
VG8-C8	-2,81	558	0,74	1,17
VG17-C8	-3,84	547	0,71	1,50
VG18-C8	-2,33	511	0,71	0,85
VG19-C8	-3,67	564	0,70	1,45

Initial results with iodine-based (organic) electrolyte (TiO₂ thickness = 6 μ m without any further pre or post-treatment)

NIR DYES for DSSCs [5]

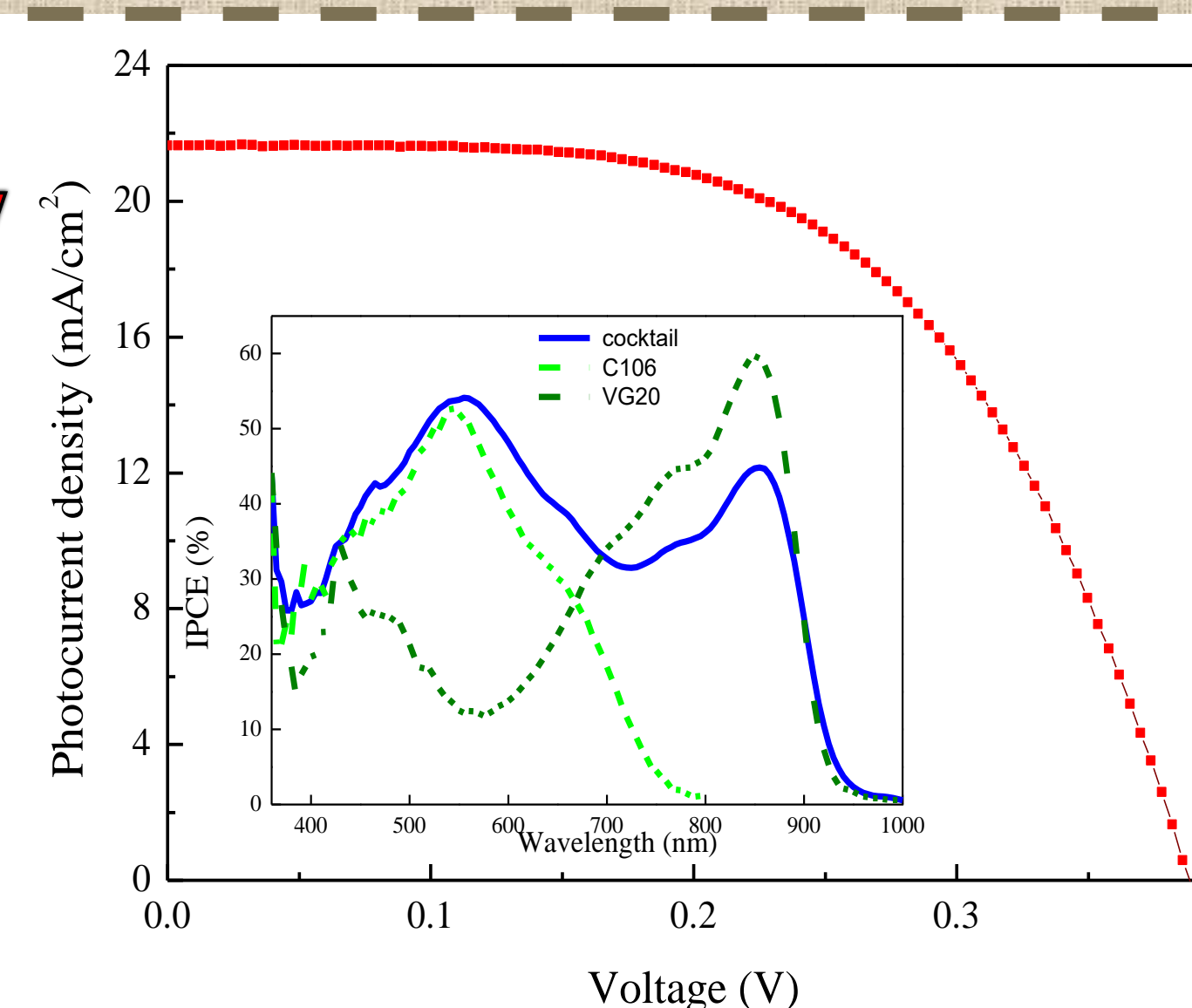
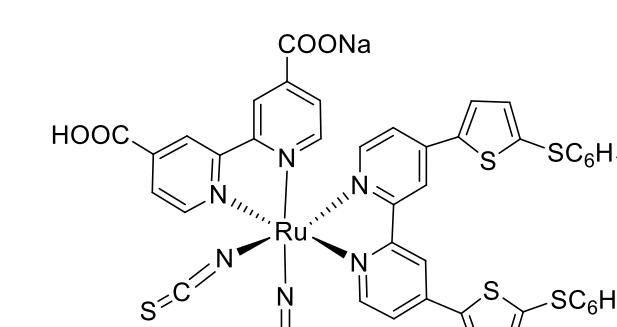


Dye	λ_{max} (nm) in MeOH
VG11	710
VG12	715
VG20	827
VG25	807



CO-SENSITIZATION with VG20

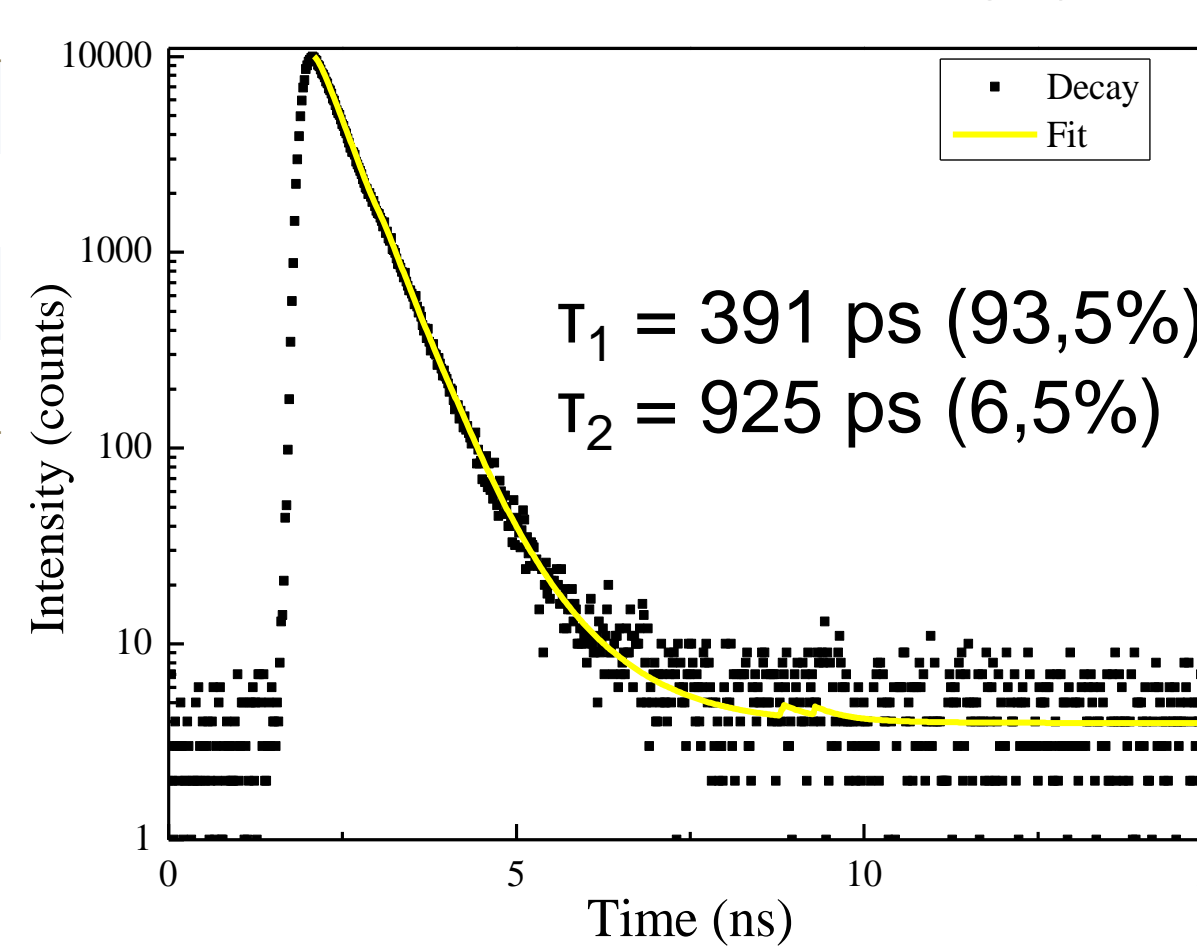
C106 $\lambda=550$ nm VG20 $\lambda=830$ nm



$J_{sc} = 21.6$ mA/cm² $V_{oc} = 389$ mV $ff = 0.57$ $\eta = 4.9\%$

Photo-dynamic of VG20

Excitation at 640 nm Emission at 870 nm



Very fast fluorescence < 1ns

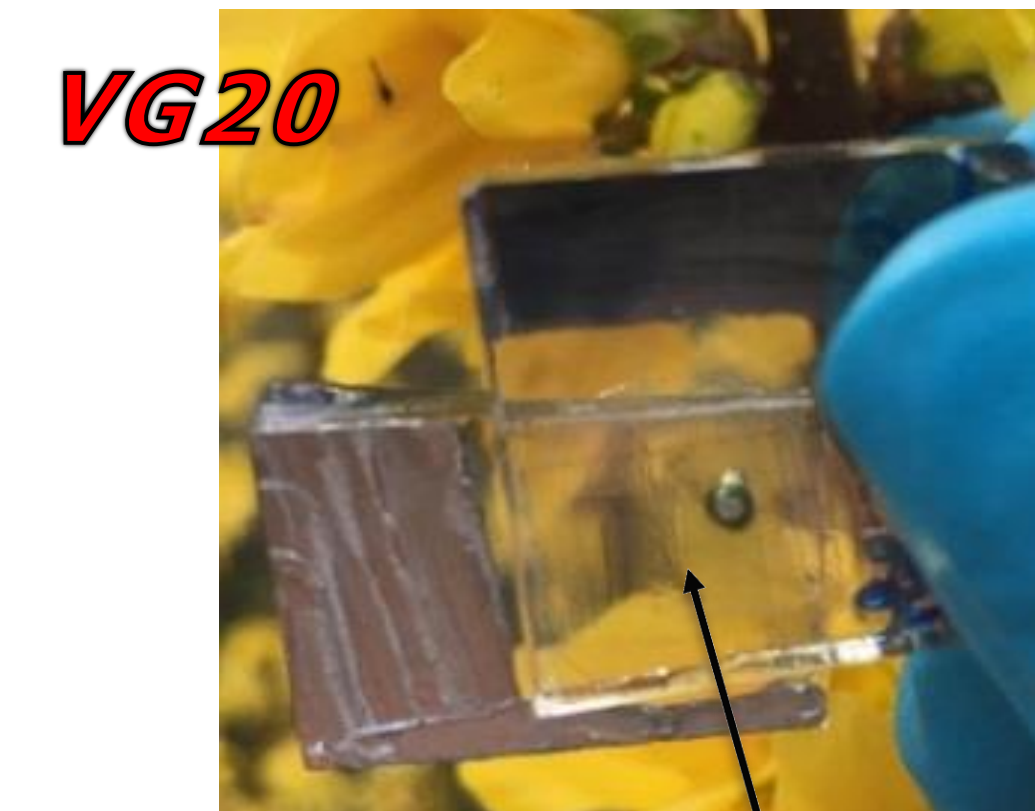
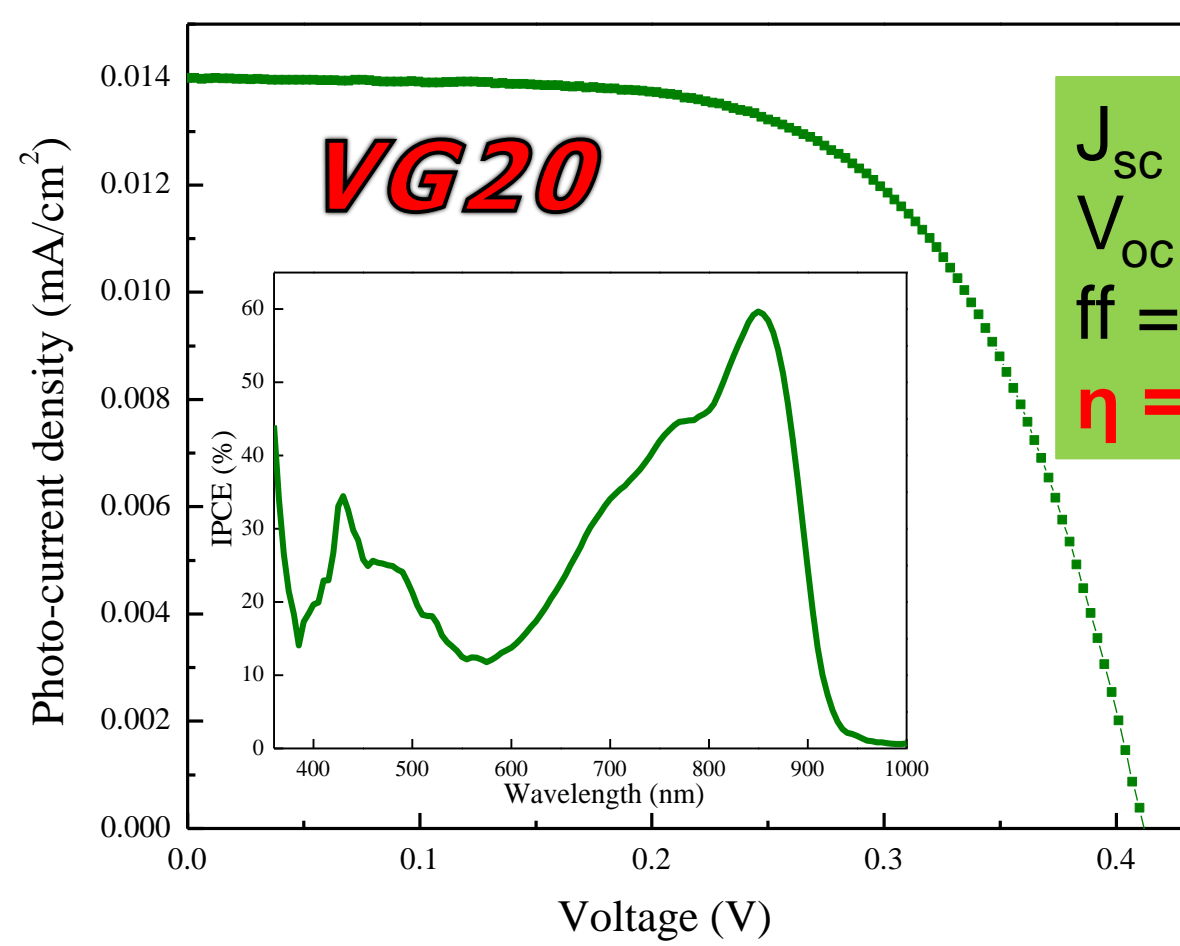


Photo-active Electrode



$J_{sc} = 14.0$ mA/cm² $V_{oc} = 412$ mV $ff = 0.62$ $\eta = 3.6\%$

Conversion up to 950 nm with a 3.6% efficiency (AM 1,5G)

TiO ₂	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)
VG11	0.587	5.3	76	2.5
VG12	0.599	10.8	71	4.6
VG20	0.412	14.0	62	3.6
VG25	0.274	1.9	63	0.33

VG20
•Dye solution: 0.1 mM + CDCA 50 mM
•Electrolyte: [I₃]=50mM; [I⁻]=1M; [LiI]=1M

VG25
•Dye solution: 0.01 mM + CDCA 1 mM
•Electrolyte: 1M DMII, 30 mM I₂, 500mM LiI

VG11 & VG12
•Dye solution: 0.1 mM + CDCA 10 mM
•Electrolyte: Z960 + LiI 50 mM
•Dipping 5 h

Acknowledgments: Authors acknowledge financial support by IMPRESSIVE H2020 project (Grant number: 826013)

References: [1] M. Freitag, J. Teuscher, Y. Saygili, X. Zhang, F. Giordano, P. Liska, J. Hua, S. M. Zakeeruddin, J.-E. Moser, M. Grätzel, M. et al. Nature Photonics, 2017, 11, 372-379; [2] N. Barbero, F. Sauvage, in Materials for Sustainable Energy Applications: Conversion, Storage, Transmission and Consumption (Eds.: X. Moya, D. Muñoz-Rojas), CRC Press, 2016, pp. 87-147; [3] T. Ono, T. Yamaguchi, H. Arakawa Sol. Energy Mater. Sol. Cells, 2009, C, 831-835; [4] C. Magistris, S. Martiniani, N. Barbero, J. Park, C. Benzi, A. Anderson, C. Law, C. Barolo, B. O'Regan Renew. Energ., 2013, 60, 672-678; [5] S. Galliano, V. Novelli, N. Barbero, A. Smarra, G. Viscardi, R. Borrelli, F. Sauvage, C. Barolo Energies, 2016, 9, 486; [6] N. Barbero, C. Magistris, J. Park, D. Saccone, P. Quagliotto, R. Buscaino, C. Medana, C. Barolo, G. Viscardi Org. Lett., 2015, 17, 3306-3309.