Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

Nanographene / Porphyrin Hybrids – Preparation, Characterization, and Application in Solar Energy Conversion Schemes

Daniel Kiessling,[a‡] Rubén D. Costa,[a] Georgios Katsukis,[a] Jenny Malig,[a] Fabian Lodermeyer,[a] Sebastian Feihl,[a] Alexandra Roth,[a] Leonie Wibmer,[a] Matthias Kehrer,[a] Michel Volland,[a] Pawel Wagner,[b] Gordon G. Wallace,[b] David L. Officer,[b] and Dirk M. Guldi*[a]

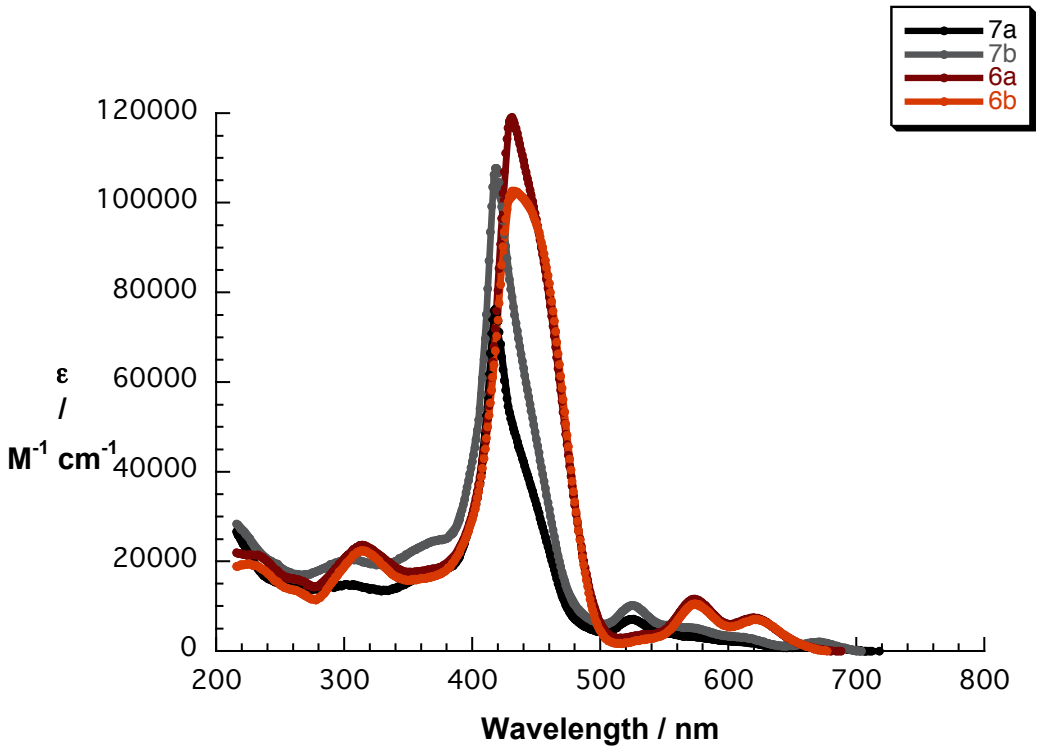


Figure S1. Absorption spectra of **6a/b** and **7a/b** in THF:water (1:1 v/v).

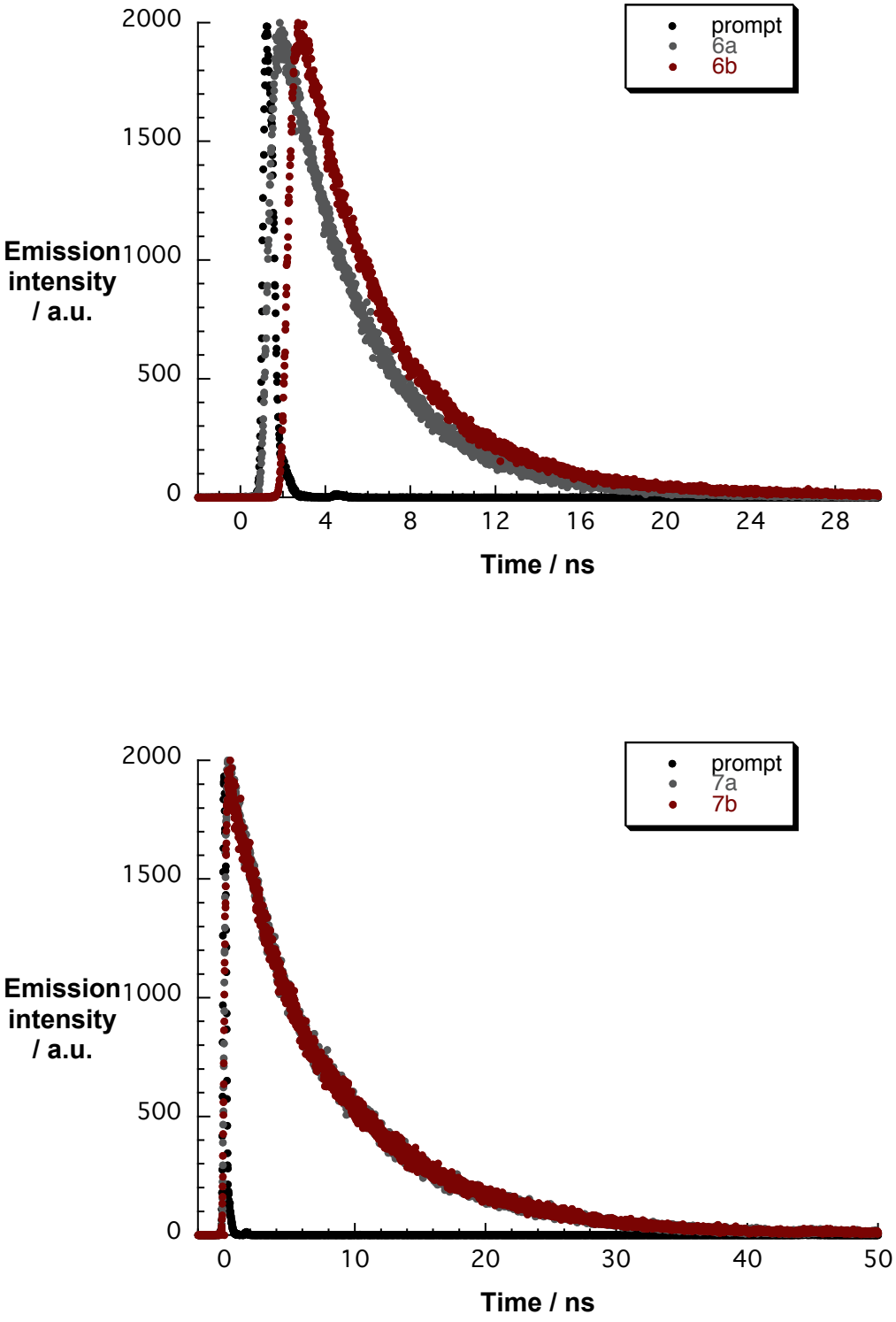


Figure S2. Upper part – TCSPC-histogram upon excitation at 403 nm of **6a/b** in THF. Lower part – TCSPC-histogram upon excitation at 403 nm of **7a/b** in THF. The detection was performed at the corresponding emission maxima – see Figure 2 in main text. The optical density was 0.2.

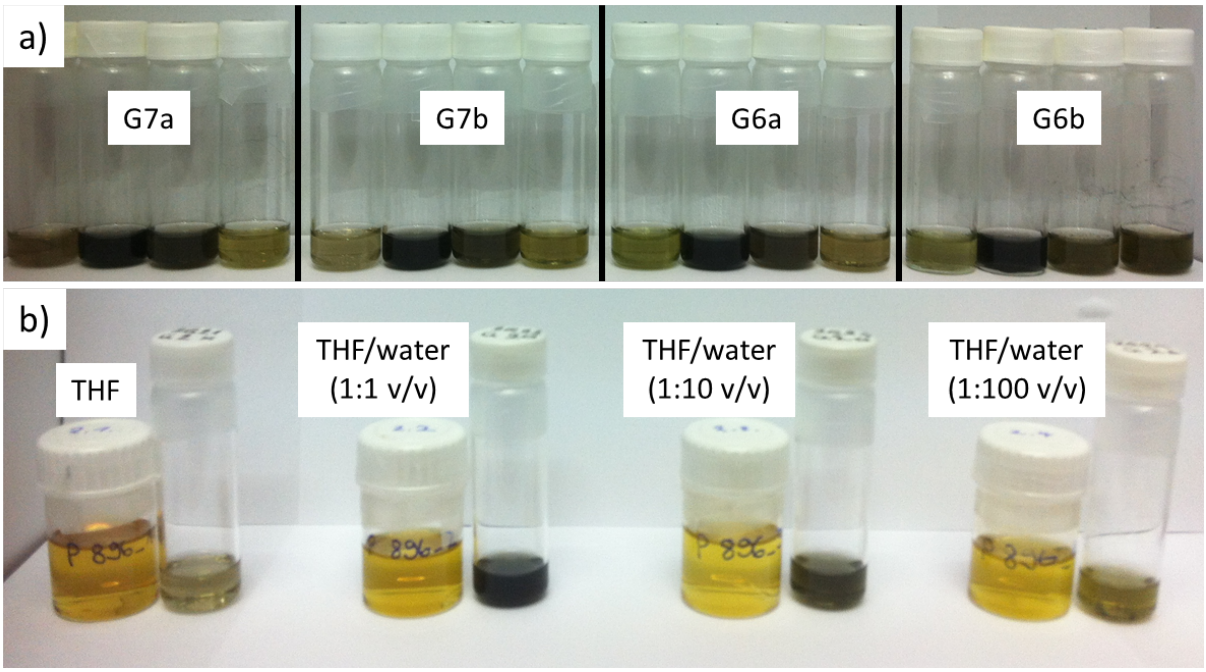
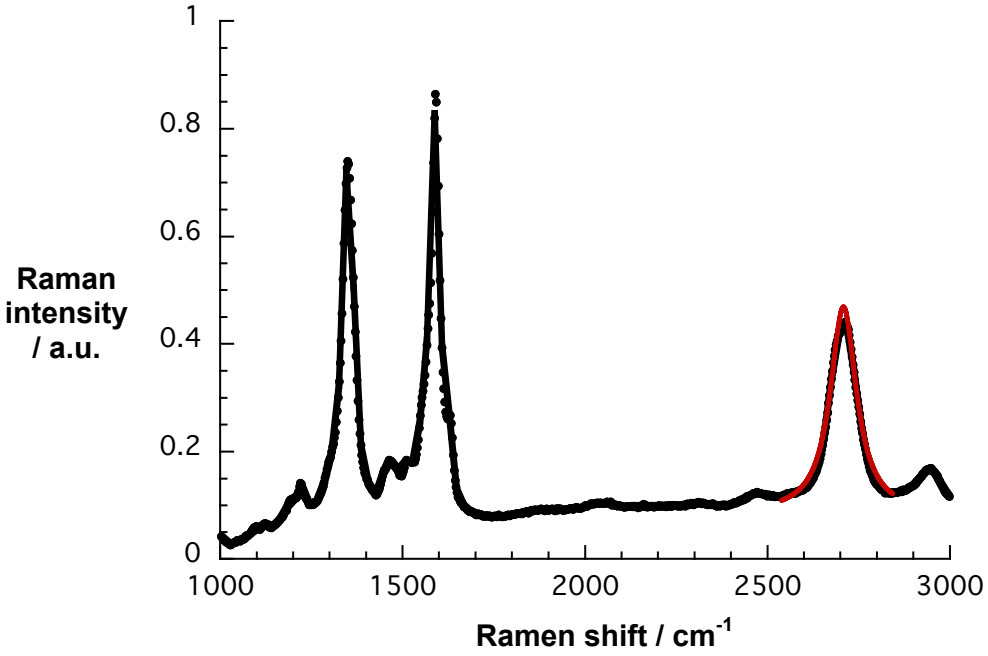
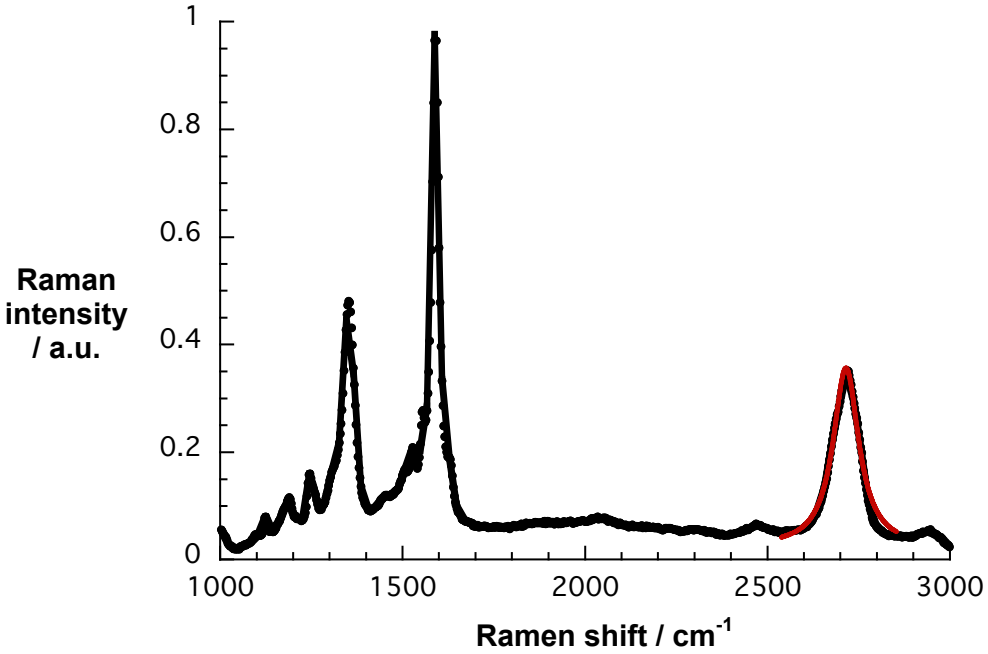


Figure S3. Upper part – Dispersions of exfoliated NG in **7a/b** and **6a/b** in THF and THF:water mixtures (1:1, 1:10, and 1:100 v/v), respectively. Lower part – Comparison of stock solution (2 x 10^{-5} M) of **7b** with its corresponding nanographene dispersion in THF and THF:water mixtures (1:1, 1:10, and 1:100 v/v).





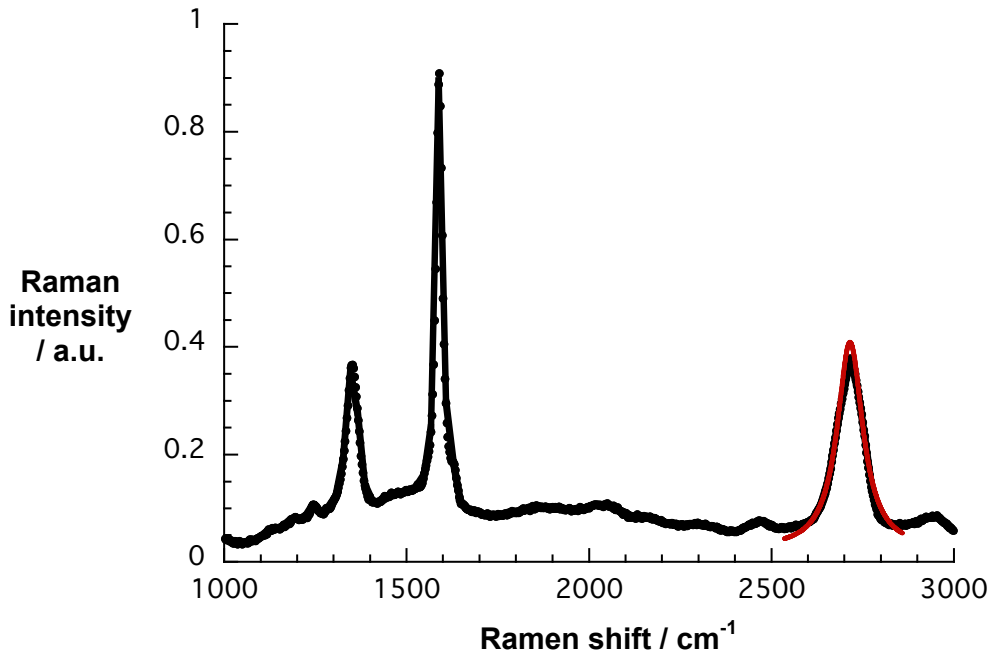
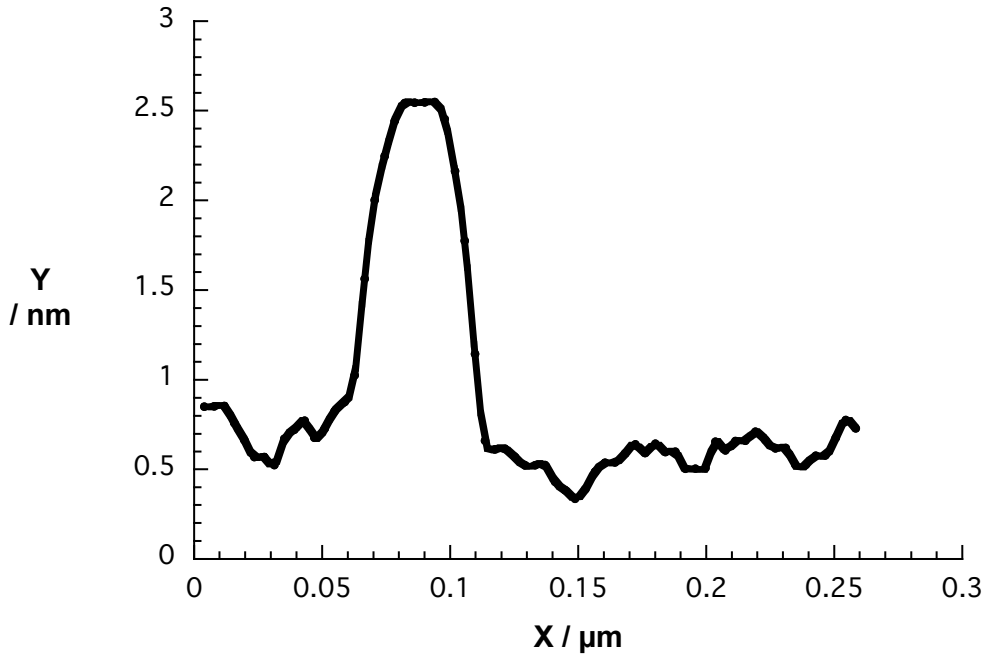
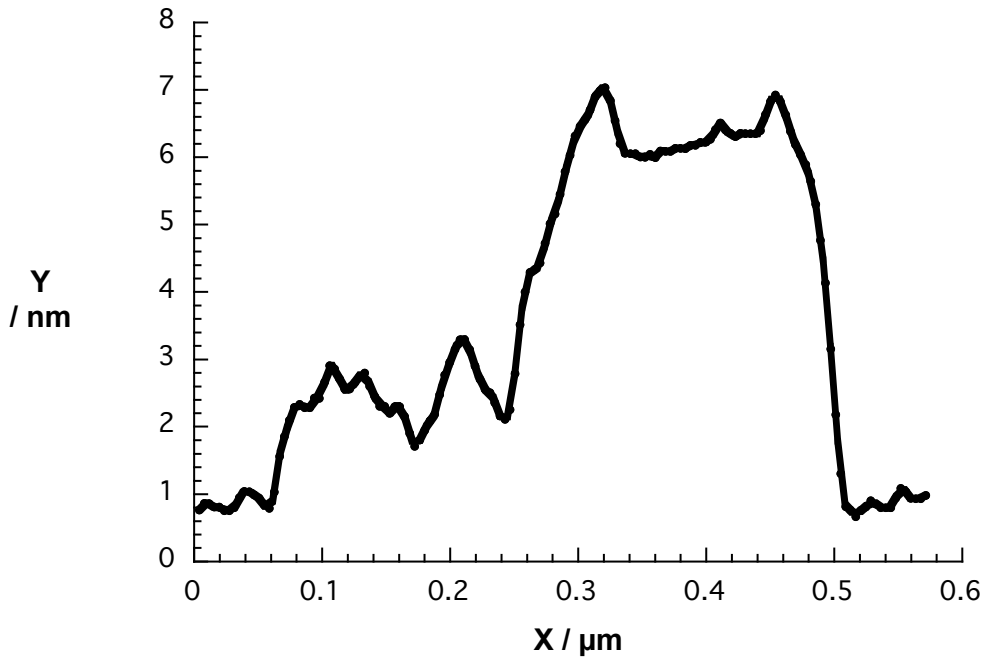


Figure S4. Upper part – Raman spectrum (black) of **G7a** upon laser excitation at 532 nm – drop-coated from THF:water (1:1 v/v) onto silicon oxide wafers – and Lorentzian fit of the 2D peak (red). Central part – Raman spectrum of **G6a** upon laser excitation at 532 nm – drop-coated from THF:water (1:1 v/v) onto silicon oxide wafers – and Lorentzian fit of the 2D peak (red). Lower part – Raman spectrum of **G6b** upon laser excitation at 532 nm – drop-coated from THF:water (1:1 v/v) onto silicon oxide wafers – and Lorentzian fit of the 2D peak (red).





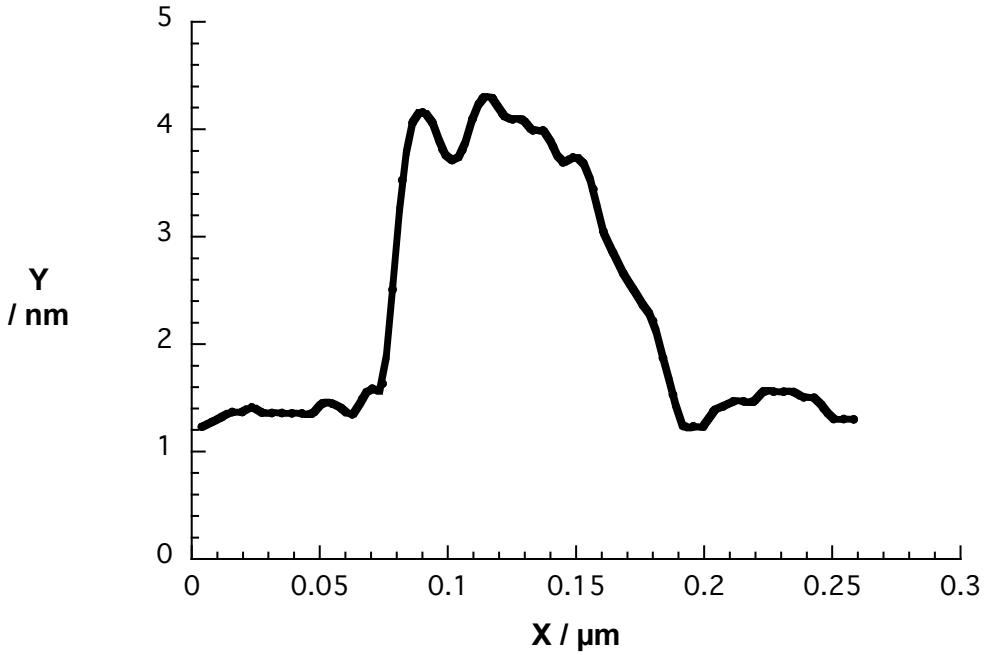


Figure S5. Upper part – Height profile across line 2 in Figure 4. Central part – height profile across line 3 in Figure 4. Lower part – Height profile across line 4 in Figure 4.

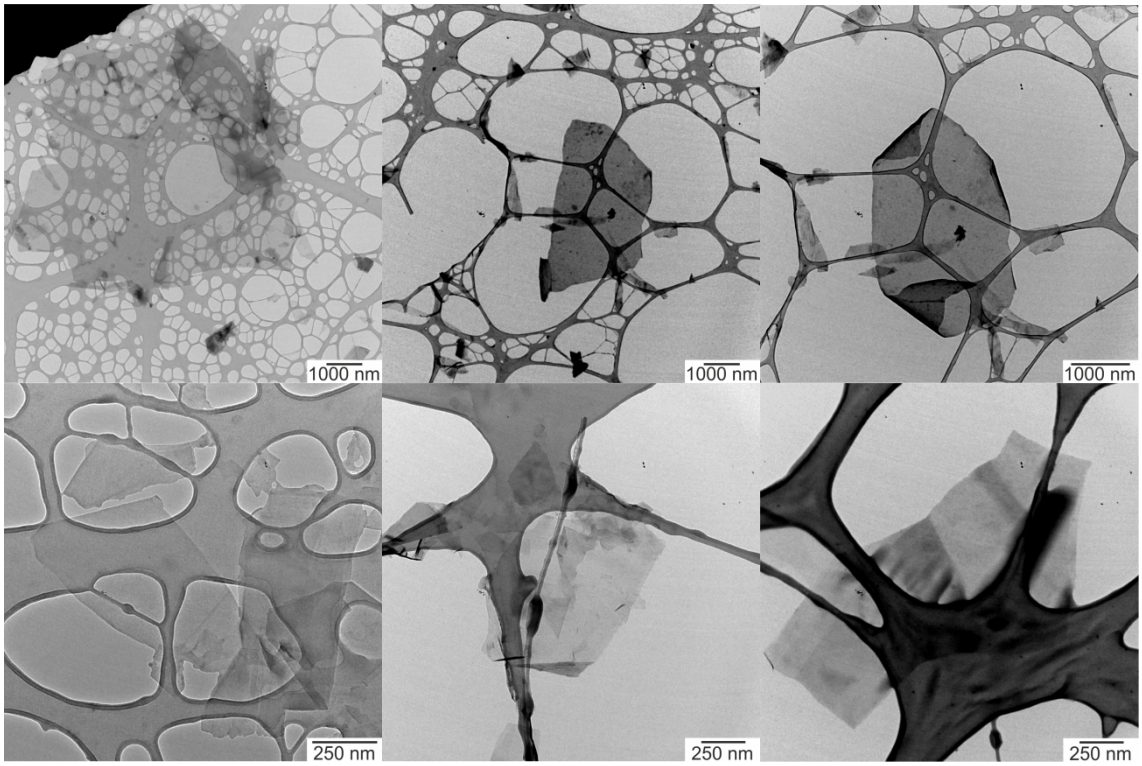


Figure S6. Upper part - TEM images of a drop casted dispersion of **G7b** in THF onto lacey carbon grid right after preparation with scale bars of 1000 nm. The flake size is around 45 μm^2 (left) and rolling up of a few-layer graphene flakes during electron beam irradiation (middle and right). Lower part - TEM images of drop casted dispersions of **G6a** (left), **G6b** (middle), and **G7a** (right) in THF:water (1:1 v/v) onto lacey carbon grid with scale bars of 250 nm.

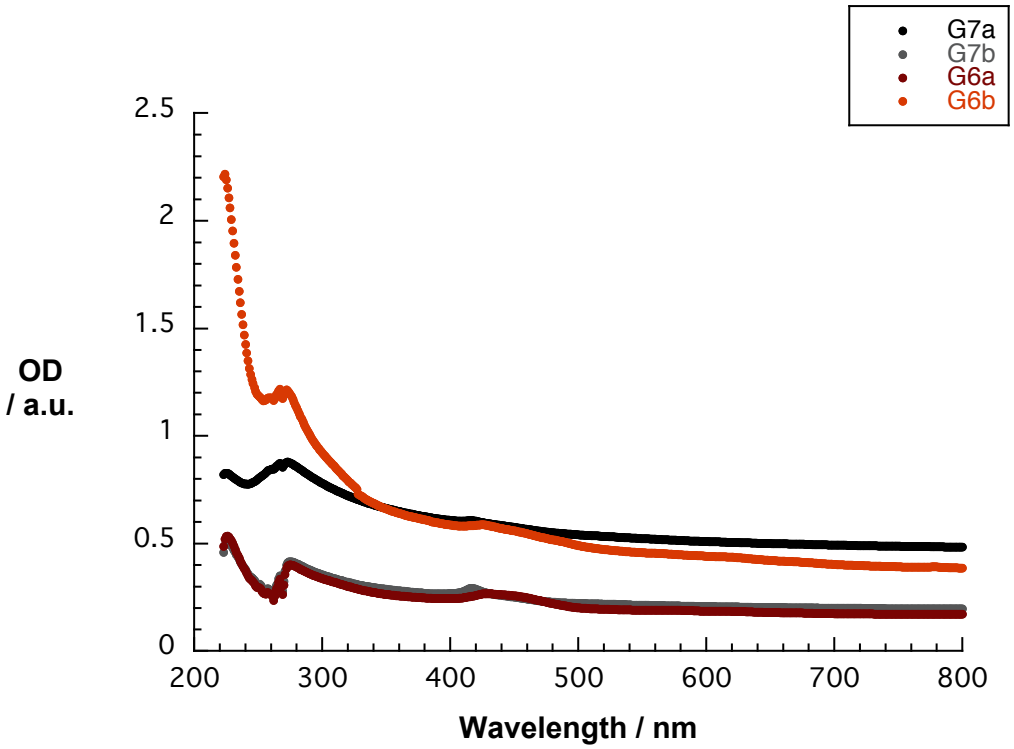


Figure S7. Absorption spectra of **G6a/b** and **G7a/b** in THF:water (1:1 v/v). The initial concentration of **6a/b** and **7a/b** was 2 x 10^{-5} M.

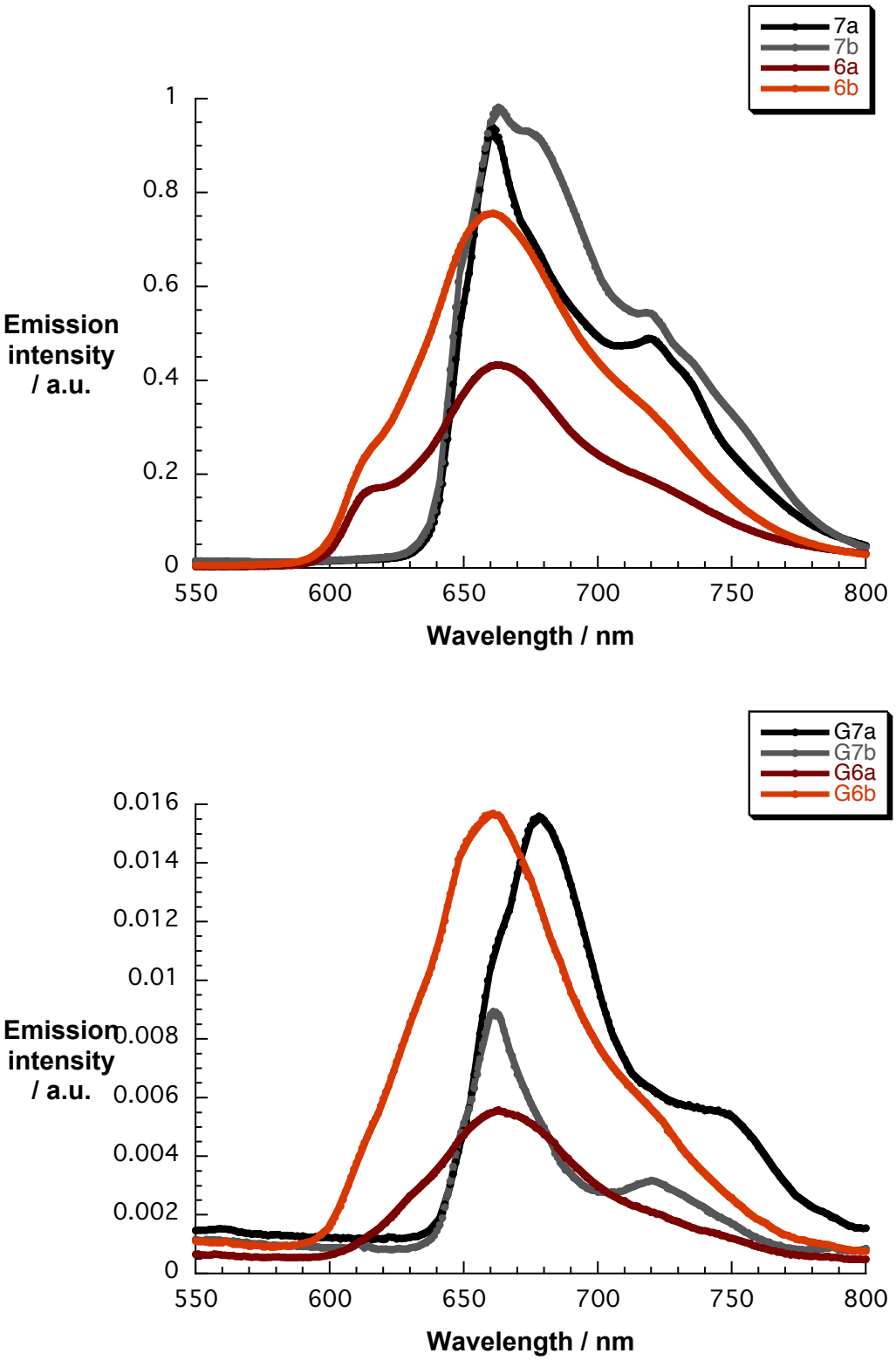


Figure S8. Upper part – Fluorescence spectra of **6a/b** and **7a/b** in THF upon excitation at 420 and 410 nm for the zinc porphyrins and the free base porphyrins, respectively. The initial concentration of **6a/b** and **7a/b** was 2 x 10^{-5} M. Lower part – Fluorescence spectra of **G6a/b** and **G7a/b** in THF upon excitation at 420 and 410 nm for the zinc porphyrins and the free base porphyrins, respectively. The initial concentration of **6a/b** and **7a/b** was 2 x 10^{-5} M.

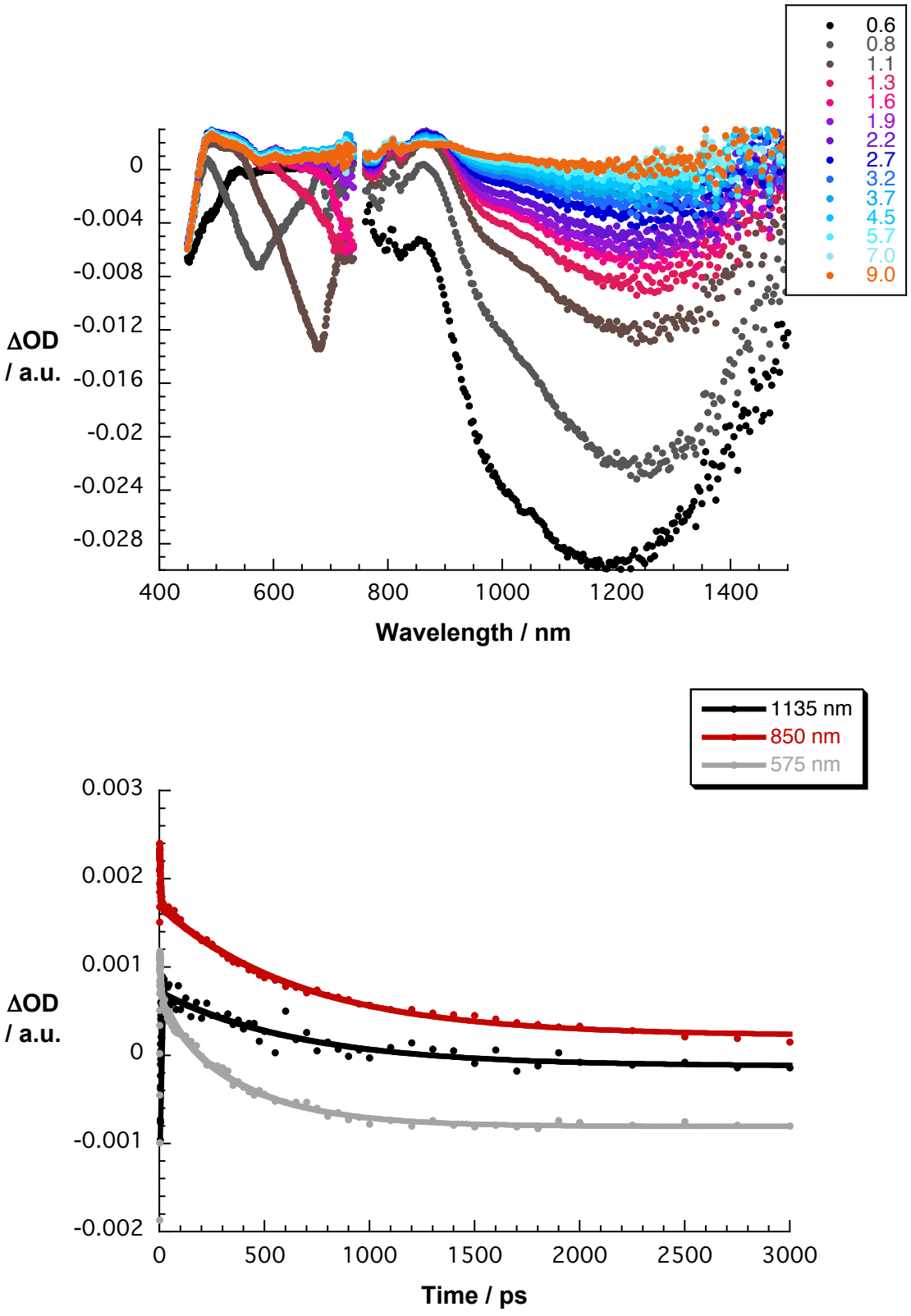


Figure S9. Upper part – Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of **G6a** in THF with several time delays between 0.6 and 9.0 ps at room temperature. Lower part – Time absorption profiles at 575, 850, and 1135 nm monitoring the charge recombination.

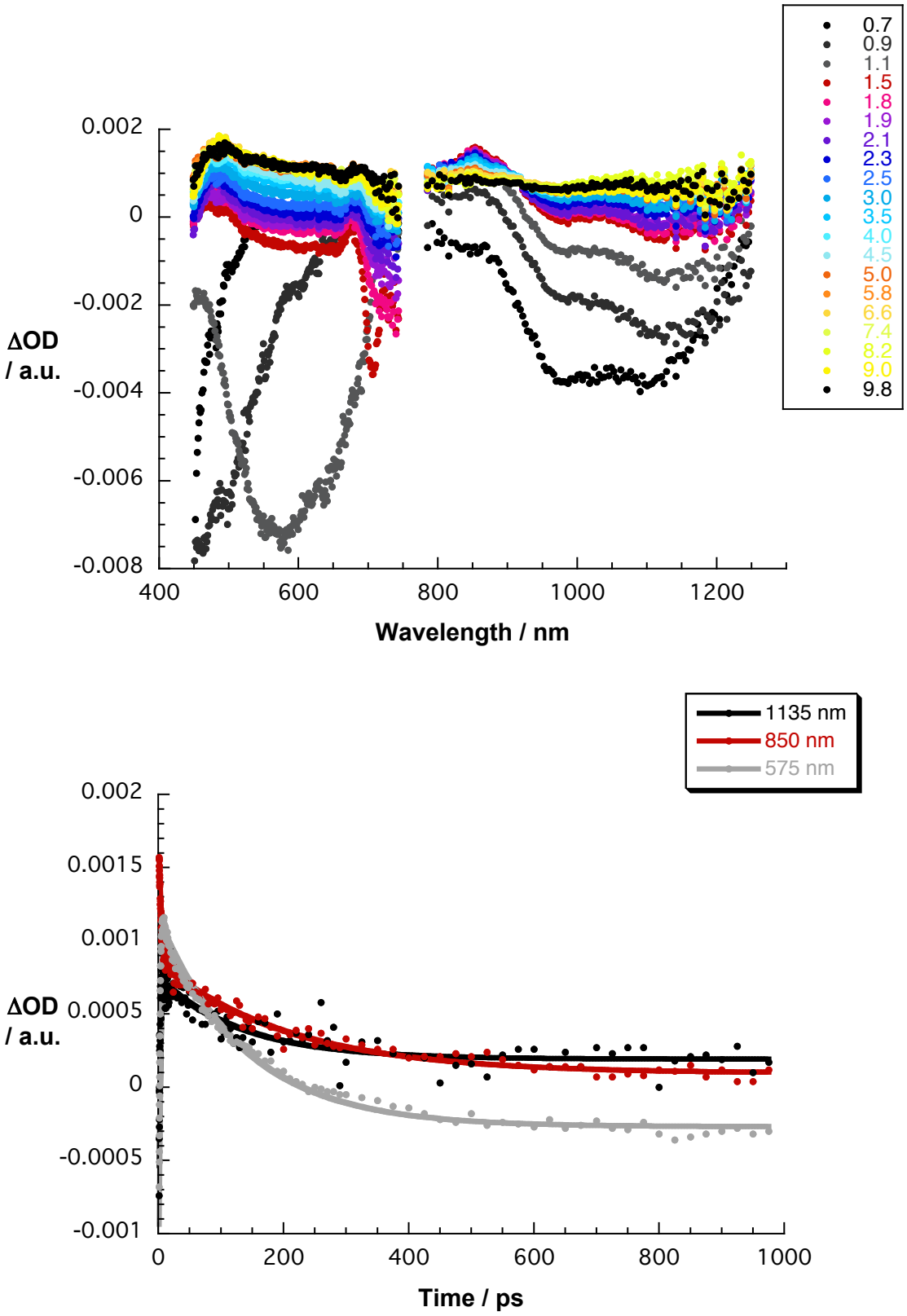


Figure S10. Upper part – Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of **G7a** in THF/water (1:1 v/v) with several time delays between 0.7 and 9.8 ps at room temperature. Lower part – Time absorption profiles at 575, 850, and 1135 nm monitoring the charge recombination.

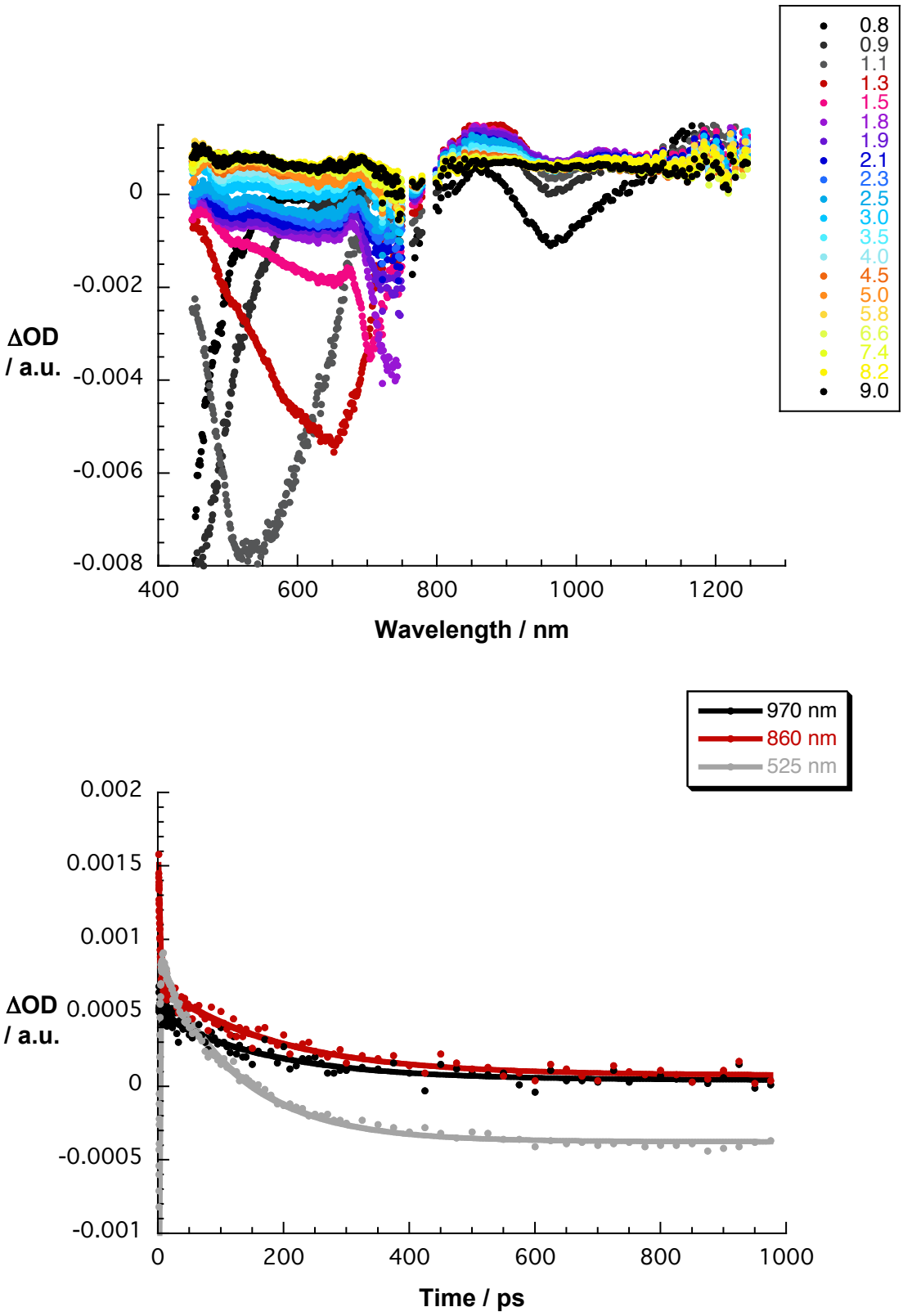


Figure S11. Upper part – Differential absorption spectra (visible and near-infrared) obtained upon femtosecond pump probe experiments (387 nm) of **G6a** in THF/water (1:1 v/v) with several time delays between 0.7 and 9.8 ps at room temperature. Lower part – Time absorption profiles at 525, 860, and 970 nm monitoring the charge recombination.

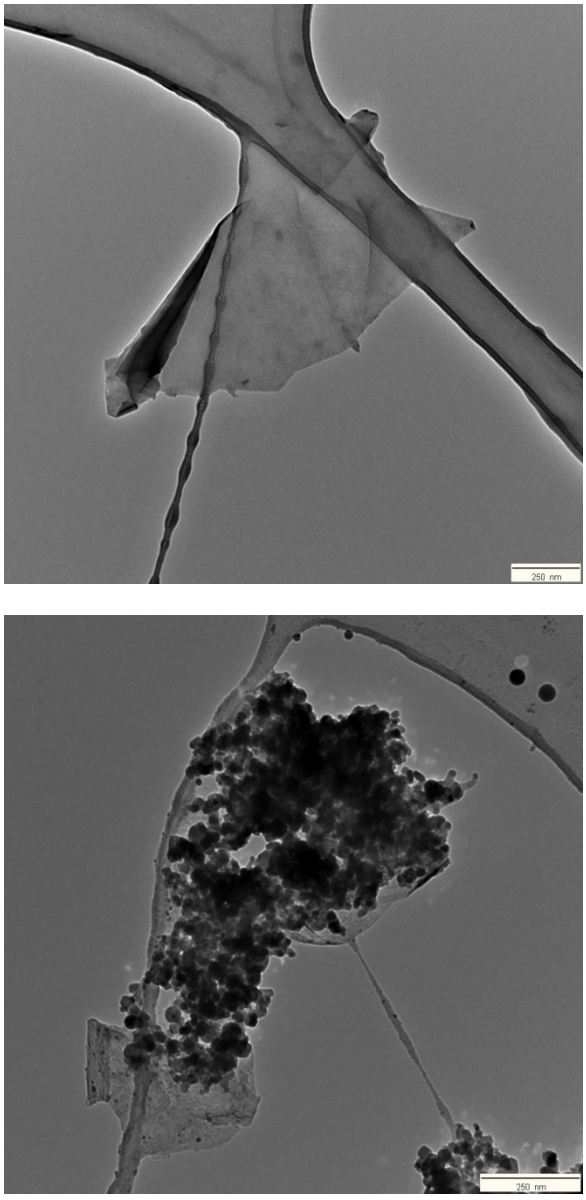


Figure S12. Upper part – TEM image of a drop-casted **G7a** dispersion in THF onto lacey carbon grids in the absence of TiO_2. Lower part – TEM image of a drop-casted **G7a** dispersion in THF onto lacey carbon grids in the presence of an excess amount of TiO_2.

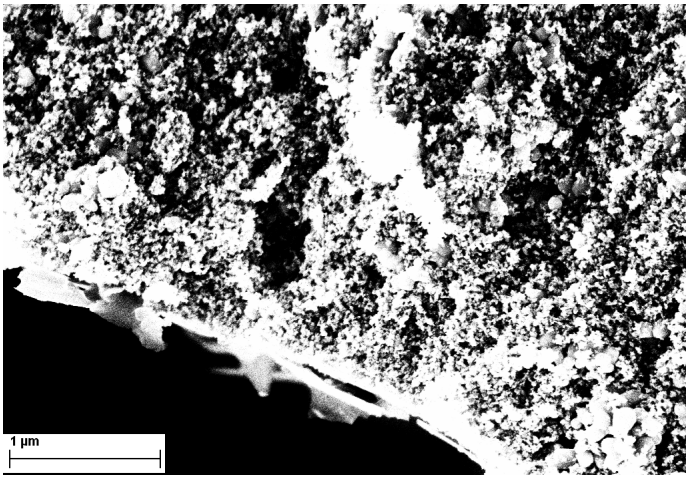


Figure S13. Cross-sectional SEM images of the TiO_2-S electrodes soaked with **G7b** in THF for 120 hours at low magnification.

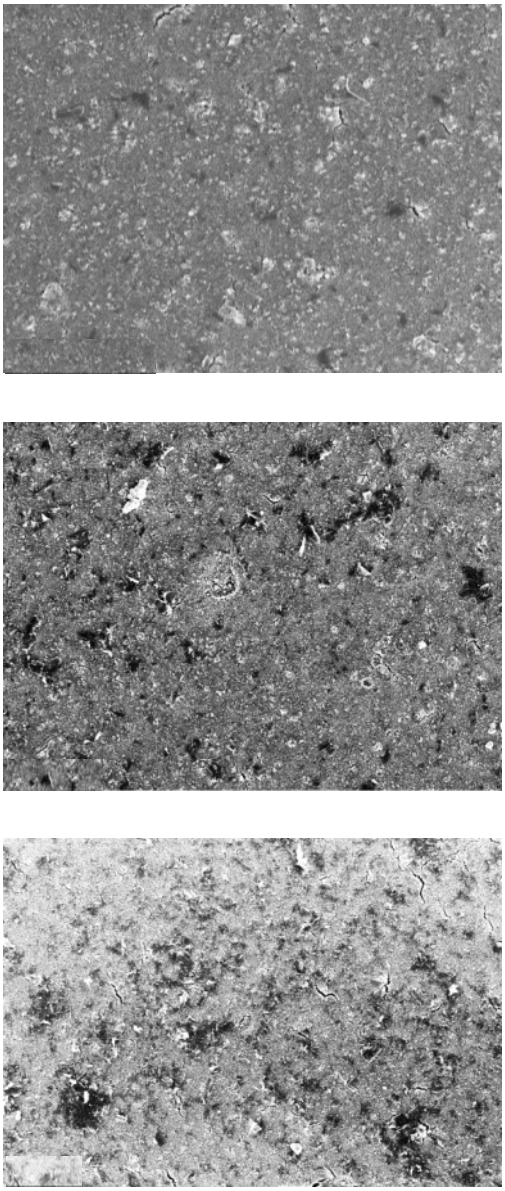


Figure S14. SEM images of TiO_2-S electrodes soaked with **G7b** (top), **G6a** (middle), and **G6b** (bottom) in THF for 120 hours at low magnifications.

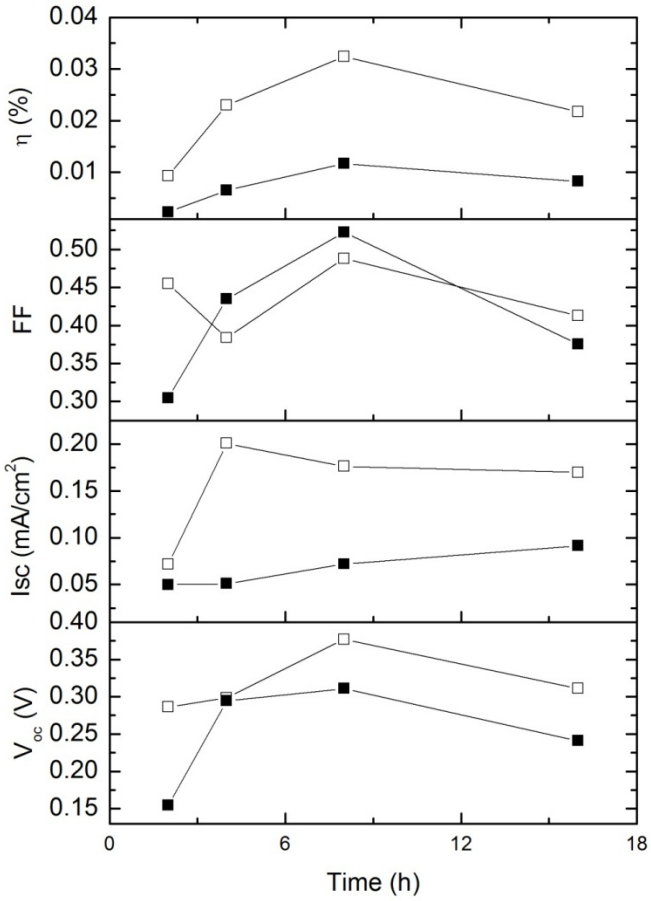


Figure S15. Device performance as a function of soaking time for devices with 4μm TiO_2 electrodes and **G7b** (open symbols) and **7b** (close symbols) in THF.

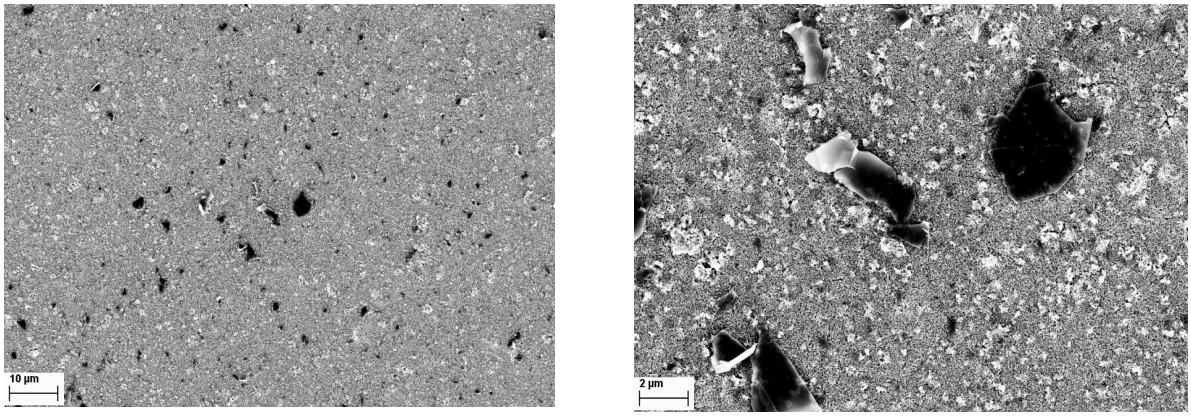


Figure S16. SEM images of TiO_2-S electrodes soaked with graphene suspension (NMP) for 120 hours at low (left) and high (right) magnifications

Table S1. Performance of the DSSCs using TiO_2-S electrodes soaked with the different porphyrins and nanographene / porphyrin hybrids in THF suspensions.

Dye	Soaking time (h)	V_{oc}[a] (V)	I_{sc}[b] (mA/cm^2)	FF[c] (%)	η[d] (%)
7a	2	0.20	0.09	0.39	$7.0\ 10^{-4}$
	4	0.36	0.05	0.51	$8.0\ 10^{-4}$
	8	0.15	0.05	0.37	$2.5\ 10^{-3}$
	16	0.20	0.05	0.41	$4.3\ 10^{-3}$
G7a	2	0.35	1.34	0.40	0.19
	4	0.39	1.22	0.42	0.20
	8	0.38	1.68	0.40	0.25
	16	0.33	1.23	0.49	0.20
7b	2	0.27	0.09	0.45	$1.1\ 10^{-2}$
	4	0.38	0.23	0.49	$4.4\ 10^{-2}$
	8	0.33	0.11	0.49	$1.8\ 10^{-2}$
	16	0.29	0.08	0.50	$1.2\ 10^{-2}$
G7b	2	0.24	0.09	0.45	0.10
	4	0.25	1.12	0.49	0.11
	8	0.29	2.50	0.49	0.27
	16	0.21	1.47	0.50	0.11
6a	2	0.37	0.40	0.45	$6.5\ 10^{-2}$
	4	0.33	0.24	0.43	$3.3\ 10^{-2}$
	8	0.28	0.19	0.43	$2.3\ 10^{-2}$
	16	0.24	0.11	0.43	$1.1\ 10^{-2}$
G6a	2	0.25	1.33	0.44	0.14
	4	0.25	1.83	0.47	0.22
	8	0.25	2.02	0.41	0.21
	16	0.23	1.69	0.40	0.15
6b	2	0.33	0.26	0.51	$4.4\ 10^{-2}$
	4	0.31	0.28	0.51	$4.4\ 10^{-2}$
	8	0.32	0.20	0.50	$3.3\ 10^{-2}$
	16	0.29	0.17	0.44	$2.2\ 10^{-2}$
G6b	2	0.30	2.69	0.46	0.37
	4	0.20	1.63	0.38	0.13
	8	0.18	1.65	0.33	0.10
	16	0.18	1.38	0.33	$8.1\ 10^{-2}$

[a]V_{oc} is open-circuit voltage. [b]I_{sc} is short-circuit current. [c]FF is fill factor. [d]η is efficiency.

Table S2. Performance of the DSSCs using TiO_2-S electrodes soaked with the different porphyrins and nanographene / porphyrin hybrids in THF/water (1:1 v/v) suspensions.

Dye	Soaking time (h)	V_{oc} [a] (V)	I_{sc} [b] (mA/cm^2)	FF [c] (%)	η [d] (%)
7a	2	0.03	0.005	0.44	0.6 10^{-4}
	4	0.04	0.005	0.60	1.1 10^{-4}
	8	0.06	0.006	0.56	2.4 10^{-4}
	16	0.06	0.009	0.56	3.3 10^{-4}
G7a	2	0.14	0.002	0.72	2.4 10^{-4}
	4	0.20	0.007	0.51	7.0 10^{-4}
	8	0.19	0.010	0.53	1.0 10^{-3}
	16	0.26	0.024	0.48	3.1 10^{-3}
7b	2	0.06	0.006	0.56	2.2 10^{-4}
	4	0.06	0.003	0.57	1.0 10^{-4}
	8	0.10	0.005	0.34	1.7 10^{-4}
	16	0.25	0.013	0.51	1.7 10^{-3}
G7b	2	-	-	-	-
	4	0.08	0.006	0.43	2.3 10^{-4}
	8	0.10	0.011	0.43	4.7 10^{-4}
	16	0.18	0.031	0.45	2.5 10^{-3}
6a	2	0.07	0.008	0.44	2.4 10^{-4}
	4	0.09	0.011	0.42	3.7 10^{-4}
	8	0.10	0.016	0.33	5.6 10^{-4}
	16	0.31	0.034	0.50	5.3 10^{-3}
G6a	2	0.09	0.011	0.48	4.6 10^{-4}
	4	0.27	0.014	0.53	2.0 10^{-3}
	8	0.29	0.024	0.51	3.4 10^{-3}
	16	0.30	0.043	0.46	6.0 10^{-3}
6b	2	0.08	0.005	0.39	1.4 10^{-4}
	4	0.19	0.006	0.50	8.4 10^{-4}
	8	0.12	0.006	0.38	2.6 10^{-4}
	16	0.27	0.022	0.54	3.3 10^{-3}
G6b	2	0.26	0.024	0.51	3.2 10^{-3}
	4	0.26	0.029	0.51	3.8 10^{-3}
	8	0.29	0.029	0.51	4.3 10^{-3}
	16	0.30	0.031	0.46	4.3 10^{-3}

[a] V_{oc} is open-circuit voltage. [b] I_{sc} is short-circuit current. [c] FF is fill factor. [d] η is efficiency.