Supporting Information to

Polyhydrogenated Graphene – Excited State Dynamics in Photo- and Electroactive 2D-Domains

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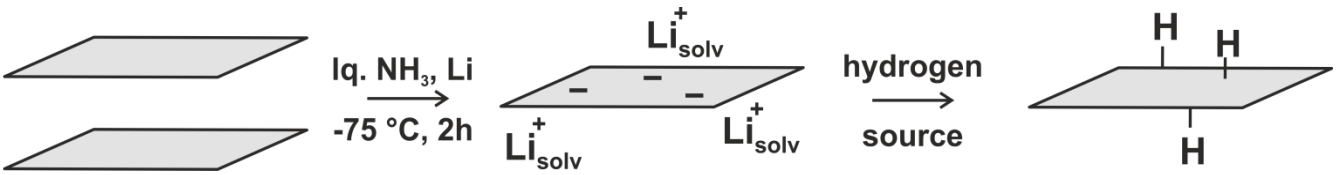
Experimental Details

1, **2** and **3** were synthesized according to previous published procedures starting from spherical graphite with ethanol (1), iso-propanol (2) and *tert*-butanol (3) as proton source. **4, 5** and **6** were synthesized according to previous published procedures with spherical graphite (4), pyrolytic graphite (5) and natural graphite (6) as starting material.[17]

For solid-state photoluminescence spectroscopy the pristine, dry samples were deposited on a glass slide. A home-made fiber optic connected to a fluorimeter was focused on the sample and adjusted such that maximum intensity was obtained. Dispersions of phGs were prepared by ultrasonication. To this end 0.1 mg phG were added to 5 mL of the respective solvent/surfactant solution and then treated in a bath type sonicator for 60 min. The effect of sonication was tested by monitoring the absorption and emission with varying sonication time. Centrifugation in common solvents lead to a quantitative precipitation of the dispersed phG. Therefore, prior to the spectroscopic measurements the solid material in the dispersions was allowed to settle under gravity for 15 min to ensure stable measurement conditions. For the solid-state transient-absorption investigations a dispersion of phG in chloroform was dropcast onto a glass slide and the solvent was evaporated under reduced pressure to give homogeneous thin films of phG. Dispersions of phG in the phosphate buffered PDI solutions were achieved by stepwise addition of phG and sonication under the aforementioned conditions.

Steady state absorption measurements were carried out with a Lambda 2 UV/Vis/NIR-spectrometer (Perkin Elmer) or a Cary 5000 UV/Vis/NIR-spectrometer (Varian). Steady state fluorescence emission measurements were performed with a FluoroMax®-3 (Horiba). All spectra were corrected for inner filter effects and for absorption intensity. Time-correlated single-photon counting was performed with a FluoroLog®-3 spectro-fluorometer (Horiba) in connection to a SuperK Exteme/Varia laser system for selective sample excitation. All spectra were corrected for the instrument response. Femtosecond transient absorption studies were carried out using a transient absorption pump/probe system (Clark-MXR Inc) in conjunction to a CPA-2101 femtosecond laser. Transmission electron microscopy was performed with a Zeiss Leo TEM 912 Omega at 80 kV acceleration voltage.

Mechanism



Scheme S1: Synthesis of polyhydrogenated graphene with ethanol (1), propan-2-ol (2), or *tert*-butanol (3) and water (4) as hydrogen source.

Materials

Table S1: Starting material parameters

material	grade	description	C / %	grain / µm	d_{bulk} / gcm^{-3}	pH	TGA Δm / %
4	Nat. Pas.	natural flake	---	1000	0.74	7.33	2.38
5	2012	Sri Lankan (natural pyrolitic)	>97	70-150	0.88	6.92	4.22
6	SGN18	natural spherical	99.99	20	0.92	7.12	0.54

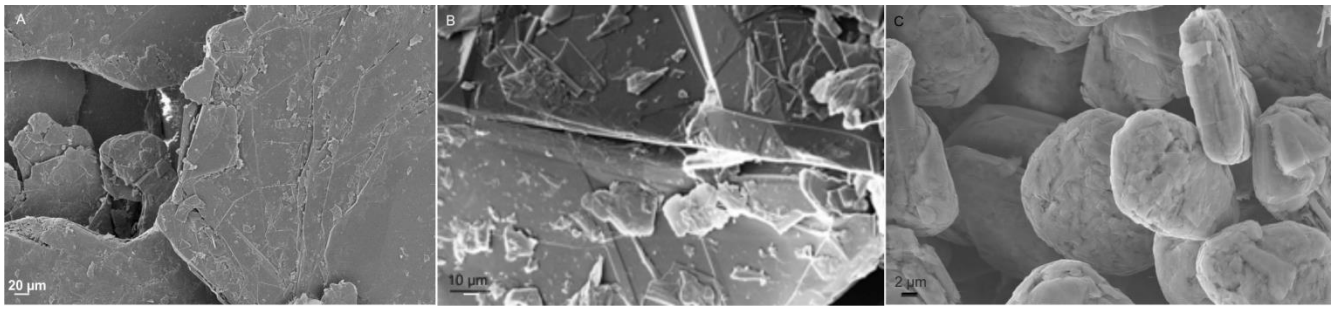


Figure S1: Representative SEM images of starting material: Nat. Pass. (**4**), 2012 (**5**) and SGN18 (**6**).

Thermogravimetric Analysis coupled with Mass Spectrometry

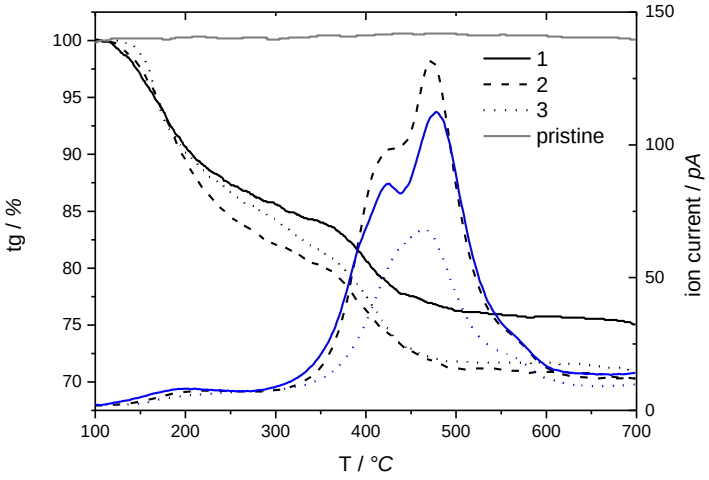


Figure S2: In black: thermogravimetric analysis (10K/min) coupled with mass spectrometry of **1** (solid), **2** (dashed) and **3** (dashed) black under He atmosphere. In blue: mass spectrometric profiles (m/z 2) of **1** (solid), **2** (dashed), and **3** (dashed.

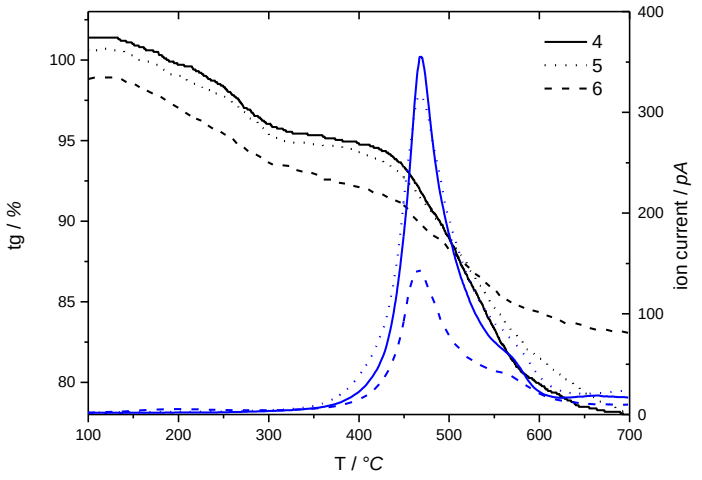


Figure S3: In black: thermogravimetric analysis (10K/min) coupled with mass spectrometry of **4** (solid), **5** (dotted), and **6** (dashed) black under He atmosphere. In blue: mass spectrometric profiles (m/z 2) of **4** (solid), **5** (dotted), and **6** (dashed).

Steady State Absorption Spectroscopy

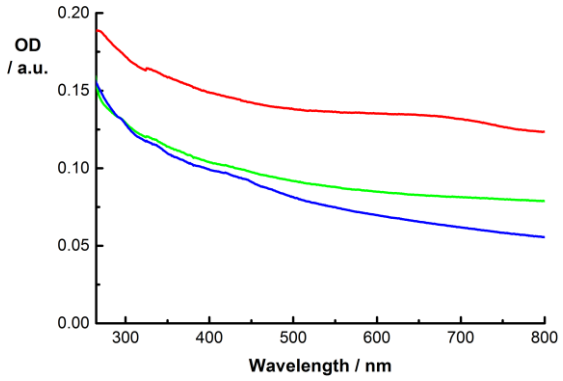


Figure S4: Steady state UV-vis absorption spectra of **4** (blue), **5** (green), and **6** (red) dispersed in DMF.

Time-Resolved Emission Spectroscopy

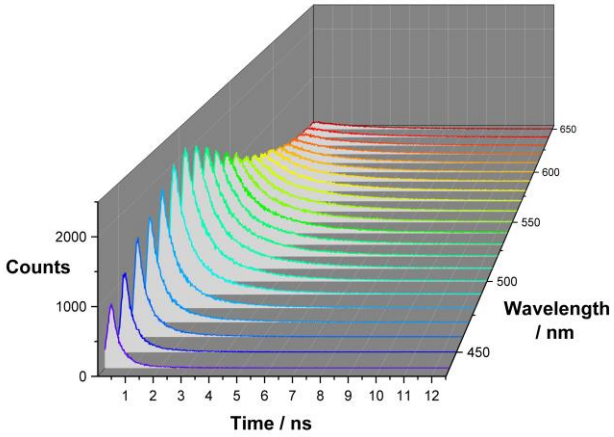


Figure S5: Time-resolved photoluminescence spectra of **4** in the solid state at room temperature upon 403 nm excitation.

Dispersions in different solvents

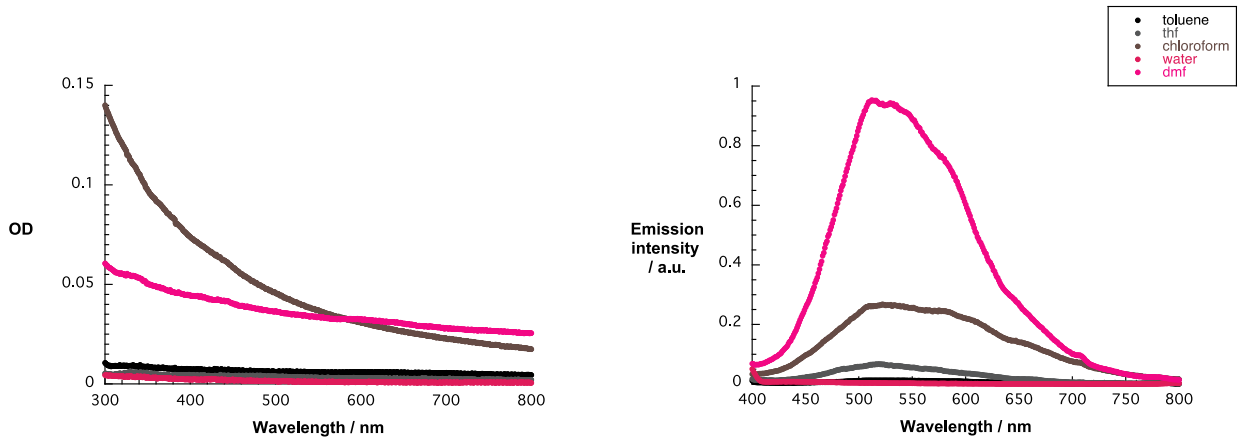


Figure S6: Left – absorption spectra of **4** dispersed in different solvents at room temperature. Right – photoluminescence spectra of **4** dispersed in different solvents upon 350 nm excitation.

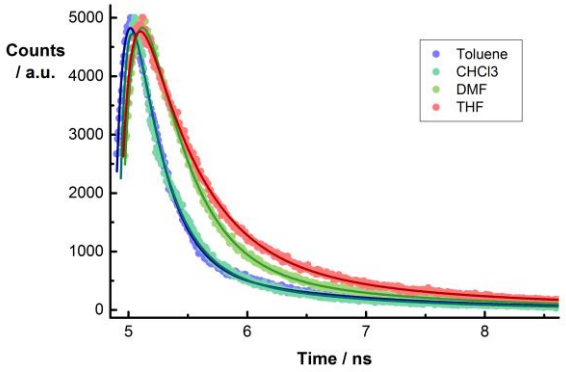


Figure S7: Photoluminescence-time profiles of **4** dispersed in different solvents recorded at 500 nm upon 435 nm excitation.

Table S2: Photoluminescence lifetimes of 4 dispersed in different solvents recorded at 500 nm upon 435 nm excitation.

	τ_1 / ns		τ_2 / ns	
toluene	**0.31**	**(90%)**	**1.97**	**(10%)**
THF	**0.55**	**(88%)**	**2.75**	**(12%)**
$CHCl_3$	**0.29**	**(88%)**	**1.56**	**(12%)**
DMF	**0.47**	**(93%)**	**2.84**	**(7%)**

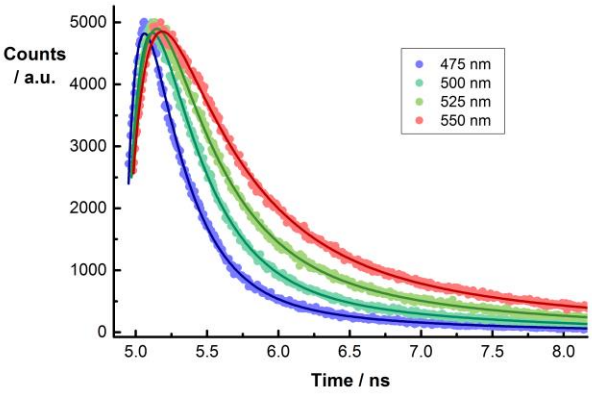


Figure S8: Photoluminescence time profiles of **4** dispersed in DMF recorded at different wavelengths upon 435 nm excitation.

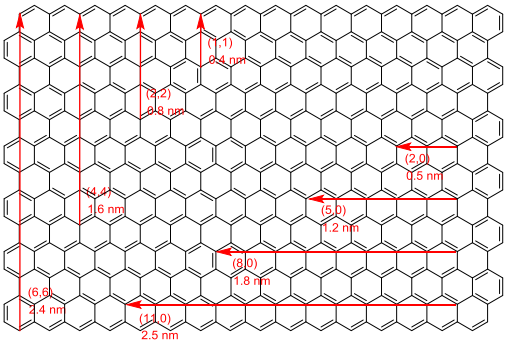


Figure S9: Illustration of a graphene sheet for the determination of the island sizes.

Femtosecond Transient Absorption Spectroscopy

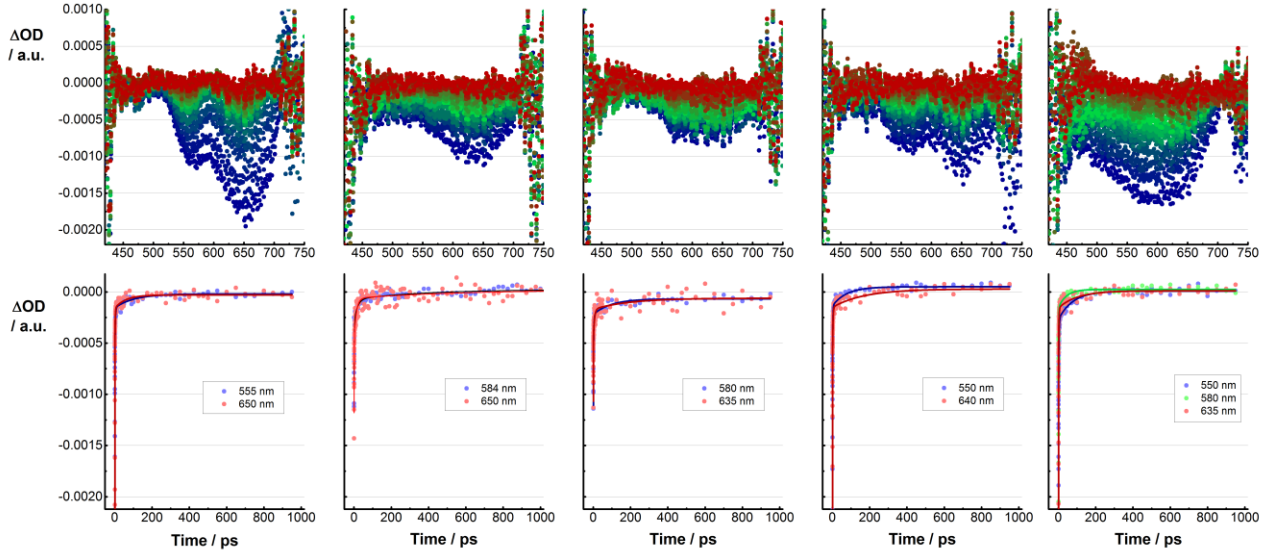


Figure 10: Upper part – differential absorption spectra obtained upon femtosecond pump probe experiments (387 nm) of five slides covered with **4** in the solid state with several time delays between 0 and 1000 ps at room temperature. Lower part – time absorption profiles of the spectra shown in the upper part at different wavelengths.

Table S3: Lifetimes obtained of 4 by femtosecond transient absorption spectroscopy upon 387 nm excitation.

slide	emission wavelength	τ_1 / ps		τ_2 / ps		τ_3 / ps	
slide1	585	**<0.3**	(14%)	**4.7**	(69%)	**120**	(17%)
	650	**<0.3**	(38%)	**5.4**	(50%)	**178**	(12%)
slide2	580	**<0.3**	(49%)	**2.8**	(35%)	**96**	(16%)
	635	**<0.3**	(60%)	**5.8**	(29%)	**194**	(11%)
slide3	550	**<0.3**	(74%)	**1.7**	(20%)	**77**	(6%)
	640	**<0.3**	(81%)	**2.2**	(14%)	**170**	(5%)
slide4	550	**<0.3**	(61%)	**1.9**	(30%)	**78**	(9%)
	580	**<0.3**	(77%)	**1.7**	(18%)	**92**	(5%)
	635	**<0.3**	(73%)	**2.0**	(20%)	**101**	(8%)
slide5	550	**<0.3**	(60%)	**2.3**	(29%)	**69**	(11%)
	650	**<0.3**	(66%)	**1.9**	(25%)	**98**	(9%)

Dispersion with an electroactive PDI based surfactant

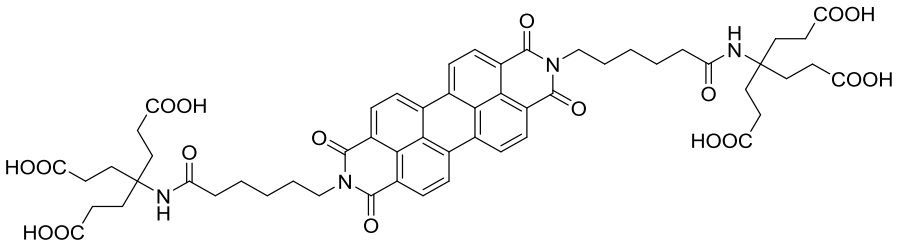


Figure S11: Molecular structure of $\mathbf{PDI}^{6-}$.

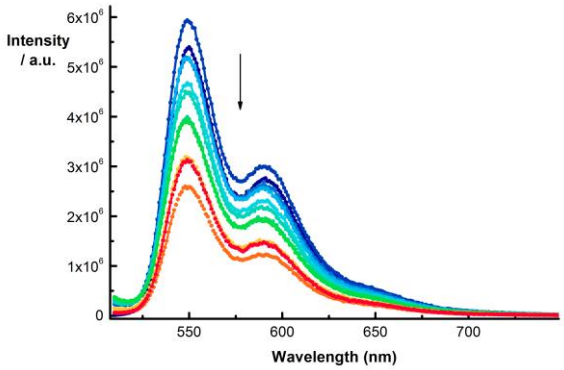


Figure S12: Steady state emission spectra of $\mathbf{PDI}^{6-}$ (blue) upon sequential addition of **4** (blue>cyan>green) and after centrifugation with 2, 10, and 20 kG (orange>red) in phosphate buffered H_2O upon 500 nm excitation at room temperature.

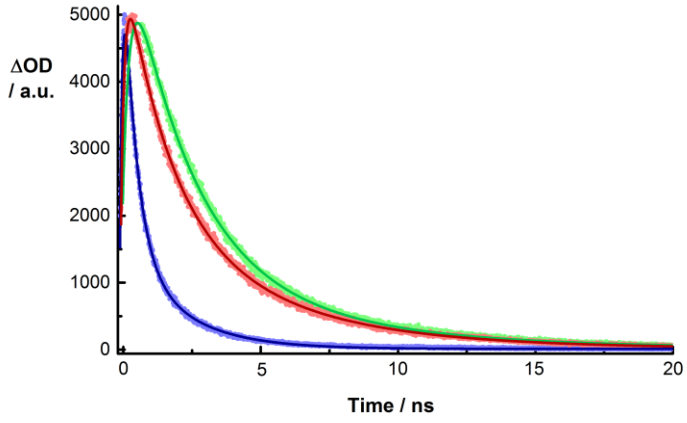


Figure S13: Photoluminescence time profiles of $\mathbf{PDI}^{6-}$ (green), $\mathbf{PDI}^{6-}$/**4** (red), and **4** (blue) in phosphate buffered H_2O recorded at 550 nm upon 500 nm excitation.

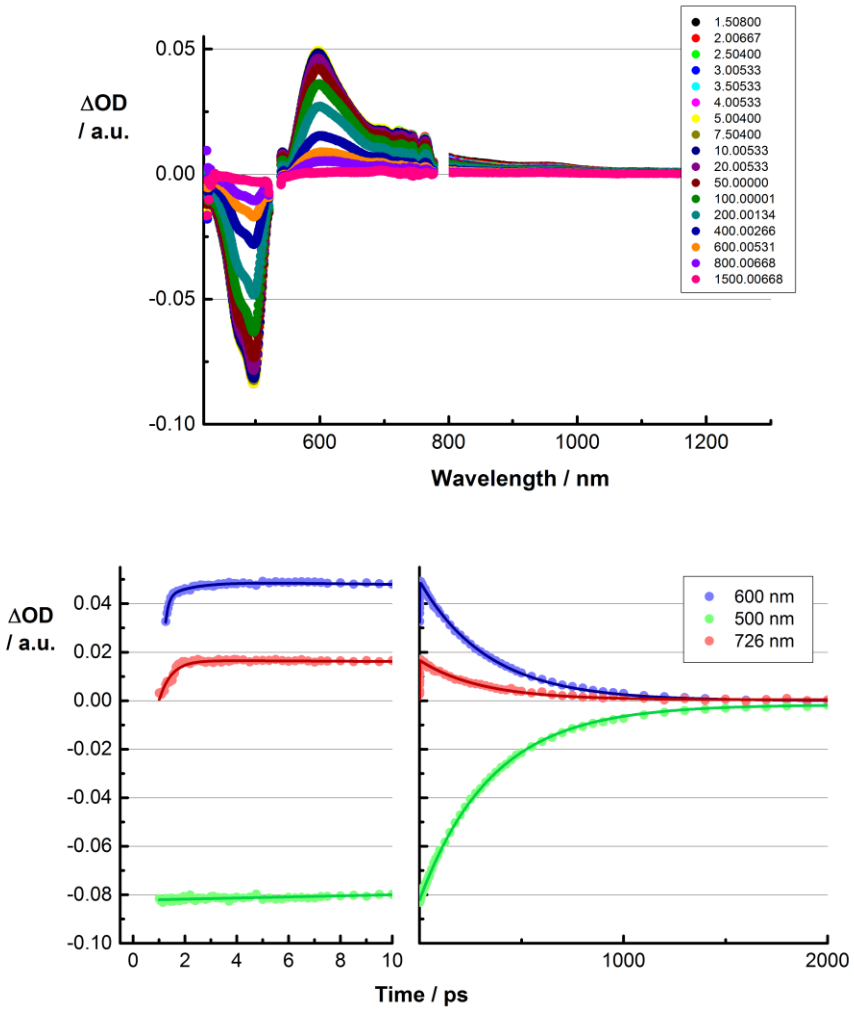


Figure S14: Upper part – differential absorption spectra obtained upon femtosecond pump probe experiments (530 nm) of **PDI**$^{6-}$ in phosphate buffered H_2O with several time delays between 0 and 5000 ps at room temperature. Lower part – time absorption profiles of the spectra shown in the upper part at 500 (green), 600 (blue), and 726 nm (red) monitoring the excited state decay.