# **Supporting information**

# Ultrafast Dye Regeneration in a Core-shell NiO-Dye-TiO<sub>2</sub>

# **Mesoporous Film**

Lei Tian<sup>1,†</sup>, Jens Föhlinger<sup>1,†</sup>, Palas Baran Pati<sup>1</sup>, Zhibin Zhang<sup>2</sup>, Junzhong Lin<sup>3</sup>, Wenxing Yang<sup>1</sup>, Malin Johansson<sup>1</sup>, Tomas Kubart<sup>2</sup>, Junliang Sun<sup>3</sup>, Gerrit Boschloo<sup>1</sup>, Leif Hammarström<sup>1,\*</sup>, Haining Tian<sup>1,\*</sup>

1 Department of Chemistry-Ångström Lab., Uppsala University, Sweden

2 Department of Engineering Sciences, Uppsala University, Sweden

3 Department of Materials and Environmental Chemistry, Stockholm University, Sweden

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# **Experimental Details**

### Synthesis

Chemicals and solvents were purchased from Aldrich and used without further purification unless specified. All the organic reactions were performed under inert atmosphere of nitrogen, and the synthesized materials were dried under vacuum. <sup>1</sup>H NMR spectra of the compounds were measured on a JEOL Eclipse+400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane by appropriate referencing to the deuterated solvent residual signals. High resolution mass spectral analyses (HRMS) were performed on high resolution and FTMS+pNSI mass spectrometer (OrbitrapXL). Synthetic route is depicted in the Scheme 1. Compound 1<sup>1</sup> and compound 2<sup>2-3</sup> were synthesized by following the routes reported in literatures.

Compound 3: A double Suzuki coupling was performed in one step, in which compound 1 (286 mg, 0.5 mmol), compound 2 (304 mg, 0.5 mmol) and 2,5-dibromothiophene (242 mg, 1.0 mmol) were added in 3 necked round bottom flux fitted with refluxing condenser. 40 mL THF was added to the reagents mixture. The resulting mixture was carefully degassed, and a Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst (60 mg, 5 mol%) and 2 M aqueous sodium carbonate solution (3 mL) were added subsequently. Then, the reaction mixture was carefully degassed again and stirred under a refluxing condition for 24 h. The reaction mixture was cooled and poured into the water. The organic layer was extracted by using dichloromethane. The combined organic phases were dried with anhydrous MgSO<sub>4</sub>, and the solvent was removed by rotary evaporator. The crude product was purified by using chromatography with PE : EtOAc (8 : 2, v/v) as the gradient eluent to afford 350 mg (35% yield) of the purple product. <sup>1</sup>H NMR (400 MHz, Acetone-d<sub>6</sub>)  $\delta$ ppm; 8.79 – 8.71 (m, 4H), 8.60 (m, 2H), 8.49 (d, J = 8 Hz, 1H), 7.95 – 7.91 (m, 4H), 7.88 (d, J = 4 Hz, 1H), 7.82 (d, J = 8 Hz, 2H), 7.78 (d, J = 8 Hz, 1H), 7.67 (d, J = 4 Hz, 1H), 7.50 (d, J = 4 Hz, 1H), 7.5 4 Hz, 1H), 7.45 (m, 1H), 7.35 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H), 7.22 – 7.17 (m, 4H), 2.82-2.88 (m, 2H), 1.16 (s, 6H), 1.15 (S, 6H). <sup>13</sup>C NMR (100 MHz, Acetone-d<sub>6</sub>) δ ppm; 165.4, 164.0, 150.4, 146.0, 145.7, 145.0, 140.2, 137.6, 137.3, 135.4, 132.6, 132.1, 131.1, 131.0, 130.6, 130.4, 129.5, 129.5, 129.1, 129.0, 128.8, 128.6, 127.5, 127.1, 126.9, 126.6, 126.2, 124.3, 124.1, 123.7, 123.5, 122.9, 121.13, 121.10, 120.6, 120.4, 80.9, 29.8, 28.3, 24.1. HRMS ES (m/z): calcd for [C<sub>66</sub>H<sub>58</sub>N<sub>2</sub>O<sub>6</sub>S+H]<sup>+</sup>, 1007.4094; found, 1007.4097.

**PB6**: Trifluoroacetic acid (31.4 mL, 0.4 mmol) was added to a solution of compound **3** (150 mg, 0.15 mmol) in dry DCM (5 ml). The mixture was stirred at room temperature for 12 h. The reaction mixture was neutralized using triethylamine. After being extracted with DCM, the organic phase was dried over anhydrous MgSO<sub>4</sub>. The crude product was purified by column chromatography using PE: EtOAc (3:1, v/v) as the gradient eluent to gain a purple product (115 mg, 85%).<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  ppm; 8.67-8.74 (m, 4H), 8.61 (d, *J* = 4 Hz, 1H), 8.59 (d, *J* = 4 Hz, 1H), 8.47 (d, *J* = 8 Hz, 1H), 7.92-7.96 (m, 3H), 7.88 (d, *J* = 8 Hz, 1H), 7.81 (d, *J* = 8 Hz, 1H), 7.70-7.75 (m, 3H), 7.55 (d, *J* = 4 Hz, 1H), 7.40 (d, *J* = 4 Hz, 1H), 7.37 (d, *J* = 8 Hz, 1H), 7.27 (d, *J* = 8 Hz, 2H), 7.20-7.24 (m, 2H), 7.14-7,17 (m, 4H), 2.75-2.84 (m, 2H), 1.12 (s, 6H), 1.14 (s, 6H). HRMS ES (m/z): calcd for [C<sub>58</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub>S-H]<sup>-</sup>, 893.2685; found, 893.2680



eme 1. Synthetic pathway of **PB6**; (i) 2,5-dibromothiophene, Pd(PPh<sub>3</sub>)<sub>4</sub>, dry THF, Na<sub>2</sub>CO<sub>3</sub>, 35%; (ii) Trifluoroacetic acid, DCM, 85%.







Figure S2. <sup>13</sup>C NMR of Compound **3**.



Figure S3. <sup>1</sup>H NMR of **PB6**.

#### Preparation of the mesoporous core shell NiO-Dye TiO2 film

NiO blocking layer: A 60 nm compact NiO blocking layer (BL NiO) was sputtered onto the pre-cleaned conducting fluorine-doped tin oxide (FTO) glass by reactive magnetron sputtering in Lesker CMS-18 ultra-high vacuum deposition system with a base pressure below  $10^{-5}$  Pa pumped by a cryopump (CTI CryoTorr 8). A Ni target with a thickness and diameter of 3 and 100 mm respectively, was mounted on a magnetron source Torus 4 HV with a standard strength magnetic system. The deposition was carried out in an atmosphere of Ar (100 sccm) and O<sub>2</sub> (3.5 sccm) at a constant total pressure of 1.3 Pa (10 mtorr) using radiofrequency discharge at a power of 150 W. The magnetron source was tilted with an angle of  $16^{\circ}$  in a confocal configuration with target-to-substrate distance of approximately 180 mm. Substrates, FTO glasses, were placed on a rotating substrate holder and no heating was employed. The NiO thickness was varied by the deposition time.

Mesoporous NiO (MP NiO) layer: MP NiO was performed on the top surface of BL NiO by two-time successive doctor-blading method with the guidance of previously reported NiO preparation method<sup>4</sup>. The film was sintered under 450 °C for 30 min after each time of doctor-blading. The thickness of the MP NiO layer resulted was 1.2  $\mu$ m, which was confirmed by with Scanning Electron Microscopy (SEM) measurement on cross-section.

Sensitization of dye: The NiO film was dipped into 0.2 mM PB6 of DCM solution overnight, following by flushing with methanol to obliterate away the excess of non-bonding molecule of



Scheme S1. The orientation between semiconductors and dyes in the previous studies combining p- and n-type materials<sup>5-7</sup>. Only those molecules that donor part absorbed onto  $TiO_2$  and acceptor part of dye is nearby the NiO could finish efficient charge separation in a single molecule, as the dye molecule shown in this scheme.



Scheme S2. Schematic of the preparation of the mesoporous core shell NiO-Dye  $TiO_2$  film 1) sputtering a NiO blocking layer on the FTO glass, 2) doctor-blading a mesoporous NiO film, 3) sensitization of the NiO film, 4) burying the dye in Atomic Layer Deposited  $TiO_2$ .

Atom layer deposition (ALD) of  $TiO_2$ : A 18 nm  $TiO_2$  layer (based on the deposition result on a flat silicon wafer) was carried out on a Picosun R200 ALD system. The precursors for  $TiO_2$  deposition were titanium chloride and H<sub>2</sub>O which were pulsed with 0.1 s. The excess of precursor were purged away by 15 s N<sub>2</sub> flow, respectively. The deposition of  $TiO_2$  was performed under 100 °C. The GPC was confirmed by ellipsometry after deposition on a flat silicon wafer, and 0.327 Å /cycle was obtained.

### SEM and TEM measurements

The SEM images were taken by a Leo 1550 FEG microscope (Zeiss, Oberjochen, Germany) equipped with 80 mm<sup>2</sup> Silicon Drift EDX detector and TEM images were taken by JEM-2100F

#### microscope.

#### Electrochemistry measurements

Cyclic voltammetry (CV) measurements were performed by utilizing AUTOLAB potentiostat with three-electrode configuration. NiO-PB6 or TiO<sub>2</sub>-PB6 electrode was applied as working electrode for reduction or oxidation of PB6, respectively. The reference electrode was Ag/AgNO<sub>3</sub> soaked in 1.0 mM AgNO<sub>3</sub> of acetonitrile solution. A Pt mash was used as counter electrode. 0.1 M Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in dichloromethane (DCM) was carried out as supporting electrolyte. In general cyclic voltammetry test, a scanning rate of 50 mV/s was applied in both positive and negative scanning. Ferrocene was used as an internal redox standard and all the potentials converted into the Normal Hydrogen Electrode (NHE). Spectraelectrochemistry for PB6<sup>-</sup> anion and PB6<sup>+</sup> cation were performed on NiO-PB6 or TiO<sub>2</sub>-PB6, respectively, by using a "HT-PEC" holder (Dyenamo AB). All the measurements were carried out by purging with solvent saturated argon.

### Steady-State Spectroscopy

Steady-state absorption and fluorescence emission spectra were tested by Varian Cary 50 and Horiba Jobin Yvon Fluorolog, respectively.

### Time-correlated single photon counting (TCSPC)

Time-correlated single photon counting (TCSPC) was carried out by a picosecond diode laser (EPL 470) of 470.4 nm as excitation light. A cut-off filter (OG 570 nm) was used to block the scattered excitation light during the measurement. TAC (Ortec 566, 50 ns) was read by DAQ-1 MCA computer card using 4096 channels and collected with Horiba Jobin Yvon DataStation 2.3.

### Photo-reduced absorption spectra (PIA)

PIA measurements were performed using a home-built system based on the pump-probe technique. A square-wave-modulated green laser (530) nm was utilized to excite the sample with a frequency 9.33 Hz, and a 20-W tungsten-halogen lamp was used as white probe light. The transmitted light will pass through monochoromator and detected with a Si photodiode by transformation light into photo current. The current was amplified firstly and subsequently fed to a lock-in amplifier (Stanford Research Systems models 830 and 570, respectively). The excitation laser intensity was controlled by adjusting the modulation voltage.

#### Fs transient absorption spectroscopy

The femtosecond to picosecond TAS set-up has been described previously<sup>8</sup>. Shortly, the excitation light (560 nm with a pulse energy of 300 nJ/pulse) was generated by a TOPAS. White light probe pulses were generated focusing the 800 nm fundamental of the amplifier on a moving CaF2 crystal. All fs-TA measurements were conducted in air. The region around the pump-wavelength (ca. 550–570 nm) is uncertain due to scattered pump-light. In the TA experiments, several scans averaging over 1000 pulses each were recorded. Comparing the TA data from each scan, changes were observed. Data were analysed with a home written Matlab routine. Several Kinetic traces ( $\Delta A$  vs. t) are fitted to a sum of exponential decays

 $\Delta A = \sum_i c_i(\lambda) \cdot \exp\left((t-t_0)/\tau_i\right))$ 

 $\vec{t}_i$  convoluted with a Gaussian shaped response. The lifetimes for each component  $(\tau_i)$  were determined using a global fitting procedure using several wavelengths at the same time. The corresponding amplitudes  $({}^{c_i}(\lambda))$  for each trace are presented in the decay associated spectra. The time dependent fs-TAS spectra were corrected for the spectral chirp which was obtained by having the time zero  $(t_0)$  as a free parameter during the fitting.

# Results

The Uv-vis absorption of PB6 and its stability test after ALD.



Figure S4. Uv-vis steady state absorption of PB6 and NiO film, (a) in DCM solution; (b) NiO film without sensitized PB6 (black line), after PB6 sensitization on NiO (red line), and after ALD  $TiO_2$  on NiO-PB6 film (blue line).

## TEM image of NiO-PB6-TiO<sub>2</sub> film



Figure S5. The magnified TEM image of NiO-PB6-TiO<sub>2</sub>. Crystallized NiO nanoparticle coated by amorphous TiO<sub>2</sub> layer.



## Calculation of the energy diagram

Figure S6. Cyclic voltammetry (CV) of NiO-PB6 reduction (a) and TiO<sub>2</sub>-PB6 oxidation (b) with a scanning rate 50 mV/s in 0.1 M TBAPF6 in DCM solution Differential pulse voltammetry (DPV) of NiO-PB6 reduction (c) and TiO<sub>2</sub>-PB6 oxidation (d) in 0.1 M TBAPF6 in DCM solution. Cyclic voltammetry (CV) of 2 mM PB6 in DCM solution with a scanning rate 50 mV/s in 0.1 M TBAPF6, (e) reduction; (f) oxidation.



Figure S7. The steady state spectra of PB6 in  $ZrO_2$ -PB6-Ti $O_2$  film. Uv-vis absorption spectrum (black line); fluorescence emission spectrum (red line). The  $ZrO_2$  film absorption was subtracted.

Table S1.  $E_{0-0}$  was calculated by the crossing section (631 nm) of absorption and emission spectra;  $E_{1/2}(s^+/s)$  and  $E_{1/2}(s/s^-)$  was estimated from DPV of oxidation and reduction, respectively. The electrochemistry property of excited PB6 was calculated by following equations, i.e.  $E_{1/2}(s^+/s^*) = E_{1/2}(s^+/s) - E_{0-0}$  and  $E_{1/2}(s^*/s^-) = E_{1/2}(s/s^-) + E_{0-0}$ .

Dye	E <sub>0-0</sub> (eV)	E <sub>1/2</sub> (s <sup>+</sup> /s) (V)	E <sub>1/2</sub> (s/s⁻) (V)	E <sub>1/2</sub> (s+ /s*) (V)	E <sub>1/2</sub> (s* /s⁻) (V)
PB6	1.96	1.13	-0.93	-0.83	1.03

## Photoluminescence (PL)



Figure S8. Time correlated single photon counting (TCSPC) measurements of the PL decay under 470.4 nm pulsed laser light excitation. The red lines are fitting curves based on reconvolution, the PL lifetime were inserted for each sample.

	$e_{\rm HI}$ /%	$\tau_{HI}/ps$	$e_{\rm EI}$ /%	$\tau_{\rm EI}/ps$
NiO- PB6	98%	35	-	-
ZrO <sub>2</sub> - PB6- TiO <sub>2</sub>	-	-	70	656
TiO <sub>2</sub> - PB6	-	-	65	789

Table S2. The hole injection efficiency  $(e_{HI})$ , hole injection time  $(\tau_{HI})$ , electron injection efficiency  $(e_{EI})$  and electron injection time  $(e_{EI})$  were calculated based on the TCSPC data.



Figure S9. The steady state emission normalized by the absorption intensity of PB6. The emission data at 682 nm was utilized for calculation of steady state fluorescence quantum yield ( $\Phi_{em,SS}$ ).

Table S3. Fluorescence quantum yield comparison calculated from steady state emission and the TCSPC lifetime.  $R_{fast}$  is the ratio of the tentative fast quenching process to the overall fluorescence quenching.

		$\tau_{TCSPC}(ps)$	$\Phi_{\text{em,TCSPC}}$	R <sub>fast</sub>	$e_{\rm HI}/\!\%$	$e_{EI}$ /%
	$\Psi_{em,SS}$				(ss)	(ss)
ZrO <sub>2</sub> -PB6	100%	1500	100%	0%	0	0
ZrO <sub>2</sub> -PB6-TiO <sub>2</sub>	7,30%	460	31%	76%	93	-
TiO <sub>2</sub> -PB6	8,50%	520	35%	75%	92	-
NiO-PB6	0,10%	34,4	2%	96%	-	99.9
NiO-PB6-TiO <sub>2</sub>	0,12%	54,3	4%	97%	-	99.9

By comparing the steady state fluorescence quantum yields from the steady state PL ( $\Phi_{em,SS}$ ) and the ones calculated from the lifetime change of the TCSPC decay ( $\Phi_{em,TCSPC}$ ), it is notable that  $\Phi_{em,SS}$  is much smaller than  $\Phi_{em,TCSPC}$ . Note that the fluorescence quantum yield of the ZrO<sub>2</sub>-PB6 sample (no quenching semiconductor) was arbitrarily set to 100%. A quenching process being faster than the time resolution of the TCSPC setup (~ 30 ps) can explain this behavior.

The fraction this additional quenching process  $(R_{fast})$  can be estimated by

$$R_{fast} = 1 - \frac{\phi_{em, SS}}{\phi_{em, TCSPC}} \tag{1}$$

Here  $\Phi_{em,SS}$  is the fluorescence quantum yield from steady state measurements, and  $\Phi_{em,TCSPC}$  is the quantum yield calculated from the change in decay rates from the TCSPC measurements. The assumption that all quenching is due to hole/electron injection is made. This assumption is likely to be valid due to the fast hole/electron injection kinetics observed in the fs-TAS. Please note that the steady state fluorescence quantum yield measurements have some uncertainty due to heterogeneity and different scattering properties. However, the order of magnitude of these measurements is expected to be correct.

Spectroelectrochemistry



Figure S10. Bulk electrolysis of reduction PB6 were performed on NiO-PB6. The electrolyte was in 0.1 M TBAPF6 in dichloromethane (DCM) solution. (a) in-situ absorption measurement; (b) the difference absorption of PB6 after/before bulk electrolysis.

#### Fs transient absorption



Figure S11. fs transient absorption of ZrO<sub>2</sub>-PB6 after 560 nm excitation. Upper left: kinetic traces and best fit by three exponentials, upper right: Spectra at different time delays, left down: residuals, right down: decay associated spectra, i.e. the wavelength dependent coefficients of the three exponential components.



Figure S12. fs transient absorption of NiO-PB6 after 560 nm excitation. Upper left: kinetic traces and best fit by three exponentials and an offset, upper right: Spectra at different time delays, left down: residuals, right down: decay associated spectra, i.e. the wavelength dependent coefficients of the three exponential components and an offset.



Figure S13. fs transient absorption of  $ZrO_2$ -PB6-TiO<sub>2</sub> after 560 nm excitation. Upper left: kinetic traces and best fit by three exponentials and an offset, upper right: Spectra at different time delays, left down: residuals, right down: decay associated spectra, i.e. the wavelength dependent coefficients of the three exponential components and an offset.

The fs-TAS experiment on a  $ZrO_2$ -PB6-TiO<sub>2</sub> sample showed a similar Stark effect as that found in NiO-PB6-TiO<sub>2</sub> but with a much weaker signal. No reduced PB6 absorption peak was found. One possible explanation is that no hole can be injected into the valence band of  $ZrO_2^9$  (3.9 eV vs NHE compared to oxidation potential of excited PB6, 1.3 V vs NHE). Instead, the positive charge is localized on the triphenylamine moiety (donor part of PB6) upon dye excitation. After electron injection into TiO<sub>2</sub> (as discussed in main text (Figure 3)), a weaker or less oriented electrical field is formed compared to NiO<sup>+</sup>-PB6-TiO<sub>2</sub><sup>-</sup>.



Figure S14. fs transient absorption of NiO-PB6-TiO<sub>2</sub> after 560 nm excitation. Upper left: kinetic traces and best fit by three exponentials and an offset, left down: residuals, right: decay associated spectra, i.e. the wavelength dependent coefficients of the three exponential components and an offset.



Figure S15. Comparison of the normalized average transient absorption spectrum for the NiO-PB6-TiO<sub>2</sub> sample from 370 ps to 1900 ps and the  $1^{st}$  order differential steady state absorption spectrum of the film.

The obsorption difference caused by Stark effect was described by the equation<sup>10-11</sup>

$$\Delta A = -\frac{dA}{d\nu} \times \frac{\lambda^2}{c} \times \frac{\Delta \vec{\mu} \cdot \Delta \vec{E}}{h}$$
(2)

Where dA/d v is the 1<sup>st</sup> order differential steady state absorption;  $\lambda$  is wavelength;  $\Delta \vec{\mu}$  and  $\Delta \vec{E}$  are the difference of dipole moment and difference electric field before/after charge separation; h is Planck constant; c is the velocity of light.



Figure S16. Normalized spectra of the different samples at 0.6 ps after excitation at 560 nm. The  $ZrO_2$ -PB6 sample shows the excited state spectrum of PB6. Both NiO samples show a peak around 630 nm indicating the reduced state of the PB6. Both samples after ALD of TiO<sub>2</sub> show a spectrum assigned to the Stark effect.

Figure S16 shows the difference of the TA spectra at 0.6 ps for the different samples. The  $ZrO_2$ -PB6 is the reference spectrum of the excited PB6 and the NiO-PB6 for the reduced state. When deposing TiO<sub>2</sub> on the films, there is a shift of the ground state bleach due to the growing in of the Stark-effect signal which is taking place at the sub-picosecond time scale. Between  $ZrO_2$ -  $PB6-TiO_2$  and  $NiO-PB6-TiO_2$  is the shoulder at 650 nm attributed to the reduced PB6 which is only present in the NiO sample



Figure S17. Normalized traces of the kinetics in the different samples at 520 nm and 700 nm.



Figure S18. Normalized PIA spectra of the sample ZrO<sub>2</sub>-PB6.



Figure S19. Normalized PIA spectra of the samples  $ZrO_2$ -PB6-TiO<sub>2</sub> and  $ZrO_2$ -PB6-Al<sub>2</sub>O<sub>3</sub> - TiO<sub>2</sub>.



Figure S20. The EDX element mapping analysis of NiO-PB6-TiO<sub>2</sub> films in different sensitization time: (a) PB6 sensitized overnight (images from Figure 2e); (b) PB6 sensitized for 5 min; (c) PB6 sensitized in 0 min and the corresponding Uv-vis absorption spectra (d).

The sample without dye (Figure 20c) showed better  $TiO_2$  penetration than those with dye (Figure 20a and b); it is because that the bare NiO film has better hydrophilic surface (more –OH units) than that of the films with hydrophobic dye. The hydrophilic surface is good for water pentation during ALD. However, in the presence of a dye, the different dye coverage did not show significant difference in  $TiO_2$  penetration.

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