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ELECTRONIC SUPPLEMENTARY INFORMATION of

All-optical switching in dye-doped DNA nanofibers

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Section S1. Synthetic route and technical details of PY-*p*CN compound synthesis, DNA-CTMA functionalization and biofibers preparation

PY-*p*CN. The synthesis route of (*E*)-4-(2-(1-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)vinyl)benzonitrile (PY-*p*CN) was performed by the following steps, presented also in Fig. 1c. At first 4-(bromomethyl)benzonitrile was synthesized. 4-methylbenzonitrile (25 g, 0.21 mol) was dissolved in 150 cm^3 of CCl_4. Equimolar amount of N-Bromosuccinimide (NBS) and 0.3 g of azobisisobutyronitrile (AIBN) were added. The reaction mixture was refluxed for five hours and after cooling to 40°C it was filtered and the used solvent left to evaporate. The residue was chromatographed on silica gel with dichloromethane as eluent. Afterwards, only the first fraction was collected. The yield of this step of synthesis was 25 g (57 %). According to the following procedure, the final compound PY-*p*CN was obtained. The 4-(bromomethyl)benzonitrile from the abovementioned first step of synthesis (in quantity 0.4 g, 2 mmol) and triphenylphosphine (0.524 g, 2 mmol) were dissolved and boiled in dry benzene overnight. The resulting salt was filtered, washed with hot benzene and used without further purification. To the suspension of phosphonium salt in dry tetrahydrofuran (THF, 25 cm^3), under inert atmosphere at room temperature, sodium ethanolate (0.108 g, 2 mmol) was added. The mixture color became deep red and afterwards the solution was stirred for further 30 minutes. Subsequently the solution of 1-phenyl-4,5-dihydro-1*H*-pyrazole-3-carbaldehyde (0.348 g, 2 mmol) in dry THF (10 cm^3) was added drop wise and it was stirred overnight at temperature equal to 50°C. Then the solvent was evaporated and dichloromethane was added to the orange residue until it became homogenous. The final product was purified on silica gel with dichloromethane as eluent. Finally, it was crystallized from heptane. The reaction yield was 0.325 g (59.5 %).

The PY-*p*CN structure was confirmed by ^{1}H NMR and infrared spectroscopy. ^{1}H NMR analysis of PY-*p*CN compound was performed by using a Bruker Avance III (300 MHz) apparatus. ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.61 (m, 2H), 7.47 (m, 2H), 7.29 (m, 2H), 7.05 (m, 2H), 6.87 (m, 1H), 6.66 (m, 1H), 3.90 (t, 1H), 3.69 (t, 1H), 3.12 (t, 1H), 2.91 (s, 1H), 2.56 (t, 1H).

Fourier-transform infrared (FTIR) spectra were recorded in range 4000-400cm^{-1} using KBr discs on a Bruker Vertex 70 spectrometer. A complete list of the characteristic vibrations coming from the functional groups for this compound is presented below:

IR (KBr) ν(cm^{-1}): 3065, 2969, 2926, 2866, 2225, 1646, 1598, 1533, 1503, 1475, 1455, 1417, 1400, 1366, 1349, 1311, 1297, 1283, 1242, 1223, 1208, 1172, 1146, 1125, 1067, 1033, 1017, 999, 974, 964, 956, 948, 882, 865, 816, 775, 753, 697, 692, 664, 586, 554, 531, 506, 468, 431.

In FTIR spectra, all of the vibrations characteristic for the investigated pyrazoline derivative (such as: C-H aromatic, C-H aliphatic, C-N, C=N) were observed. Few characteristic vibrations should be distinguished, i.e. for the -C=C- group vibration localized close to 1646 cm^{-1} or for the nitrile one (-C≡N) around 2225 cm^{-1}.

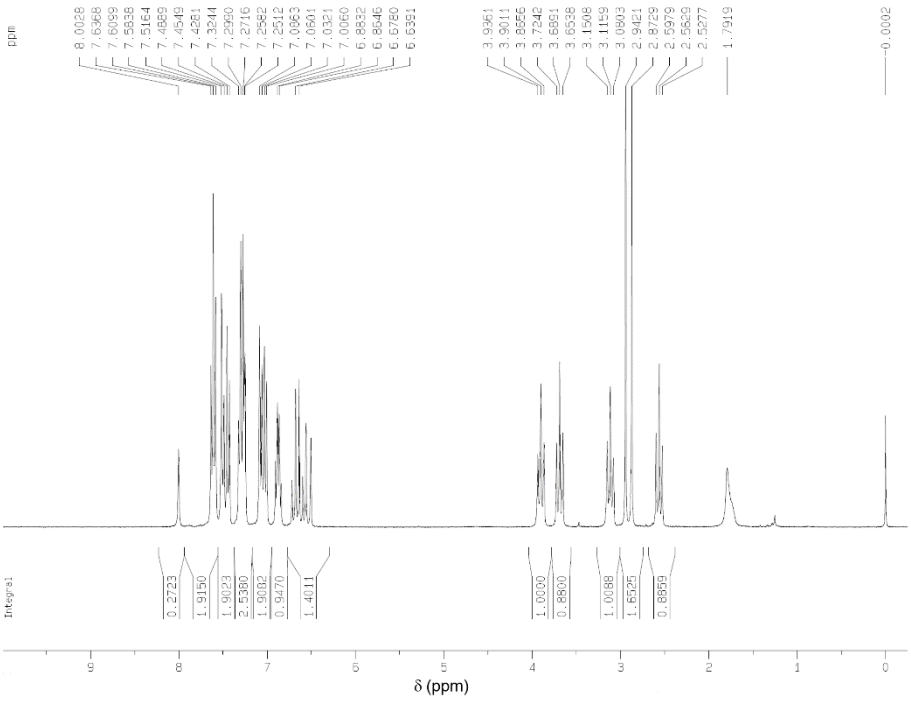

Figure S1. ^{1}H NMR spectrum of PY-*p*CN ($CDCl_3$, 300 MHz).

The photoluminescence (PL) spectrum of PY-*p*CN is shown in Figure S2. The spectrum was measured by using Hitachi F-4500 FL spectrophotometer. Applied scan speed was set at: 240 nm/min.

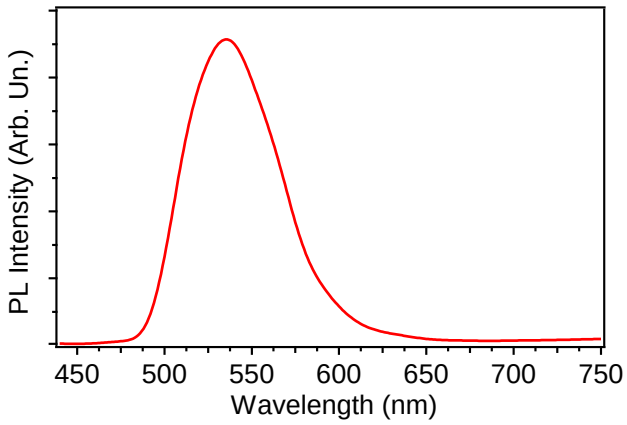

Figure S2. Photoluminescensce spectrum of PY-*p*CN.

DNA-CTMA. DNA functionalization by cetyltrimetylammonium chloride (CTMA) surfactant was carried out according to the methodology presented by Heckman and described in the literature.[S1] At the beginning the proper mass of DNA was weighted m_{DNA} = 0.67 g and then dissolved in 200 mL of deionized water. The solution was warmed up (T = 40 °C) and stirred till the moment when no parts of biopolymeric matrix were visible. The same portion of CTMA surfactant was taken and dissolved in deionized water with final concentration equal to c_{CTMA} = 4 g/dm^3. The latter solution was added drop wise to water mixture with DNA, forming in this way DNA-CTMA precipitate. The reaction mixture was stirred for two hours at room temperature and the final heterogeneous mixture was filtered through cellulose filter. The used filter was rinsed with deionized water to ensure that there is no undissolved or not reacted free CTMA left in pellet. Precipitate collected from the filter was dried in oven for 24 h at higher temperature (T = 40 °C) to evaporate the solvent.

Section S2. Electrospun nanofiber size distribution

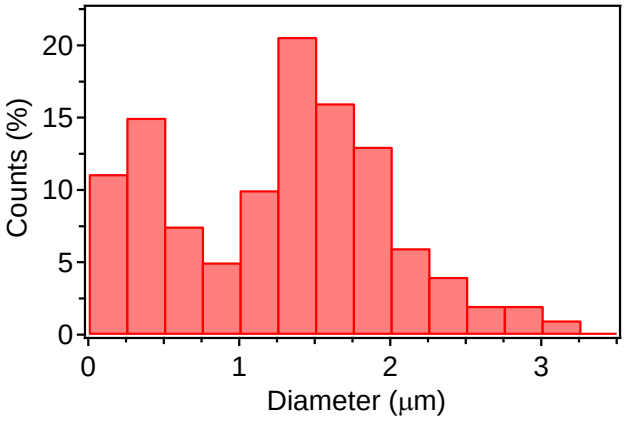

Figure S3. Distribution of the diameters of the DNA-CTMA electrospun nanofibers doped with PY-*p*CN.

Section S3. All-optical switching measurements

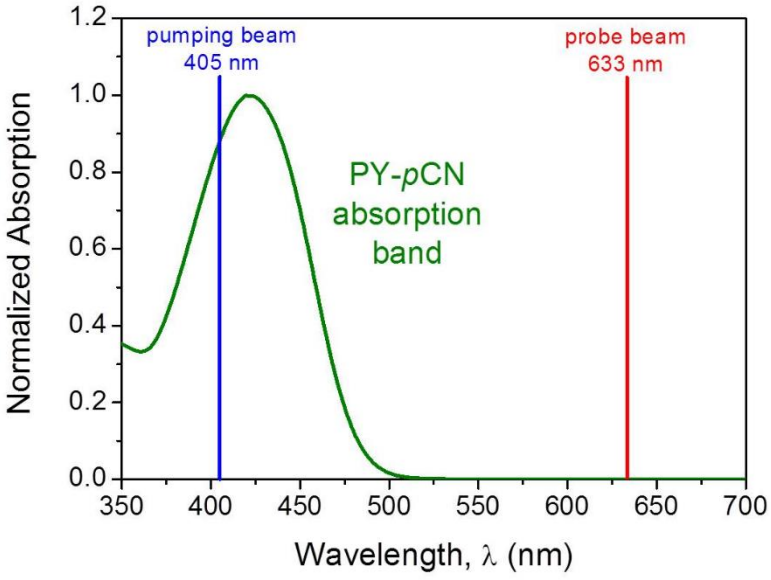

Figure S4. PY-*p*CN absorption in solid state and used pump/probe laser lines.

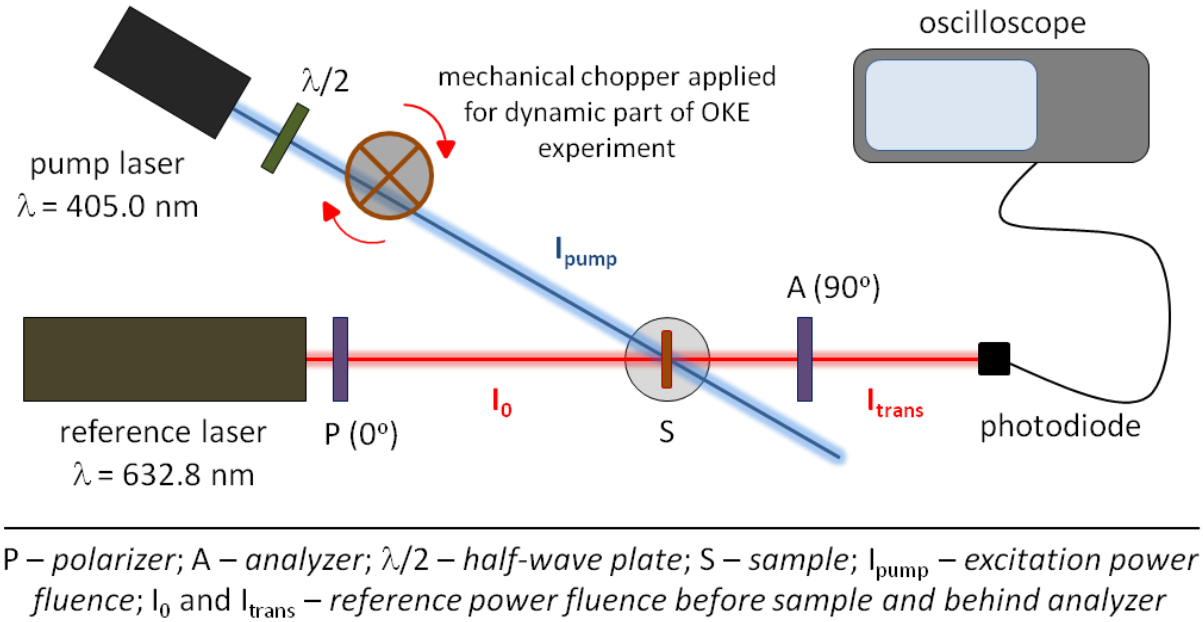

Figure S5. Scheme of the used experimental set-up.

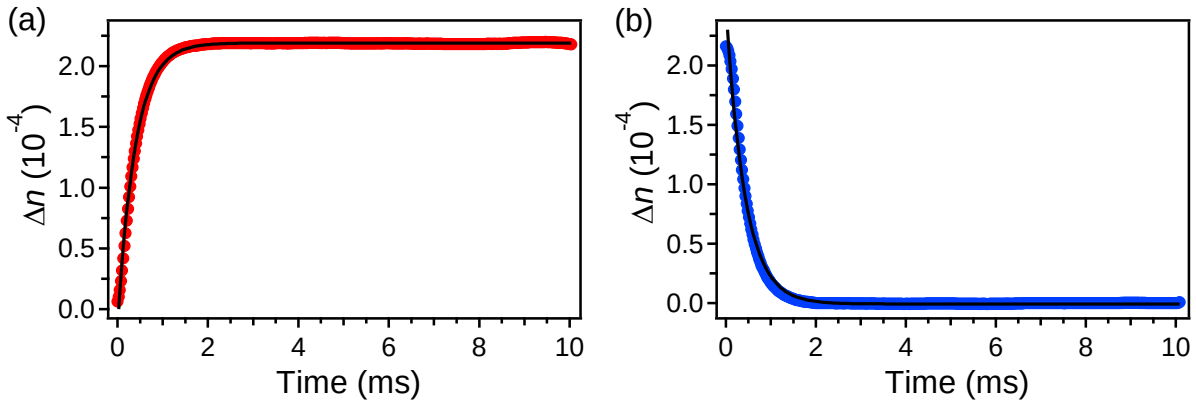

Figure S6. Exemplary behaviour of the increase (a) and decay (b) of signals in long-term photo-ordering for PY-*p*CN/DNA-CTMA fibers. τ_{inc} and τ_{dec}, characteristic times for signal increase and decay, are 0.39 ms and 0.42 ms, respectively. The continuous lines are fit to the data by single exponential function. Excitation intensity from the pump beam: 750 mW/cm^2.

References

S1 E. M. Heckman, J. A. Hagen, P. P. Yaney, J. G. Grote and F. K. Hopkins, *Appl. Phys. Lett.,* 2005, **87**, 211115.