Electronic supplementary information for

Photoisomerization-Induced Gel-to-Sol Transition and Concomitant Fluorescence Switching in a Transparent Supramolecular Gel of Cyanostilbene Derivative

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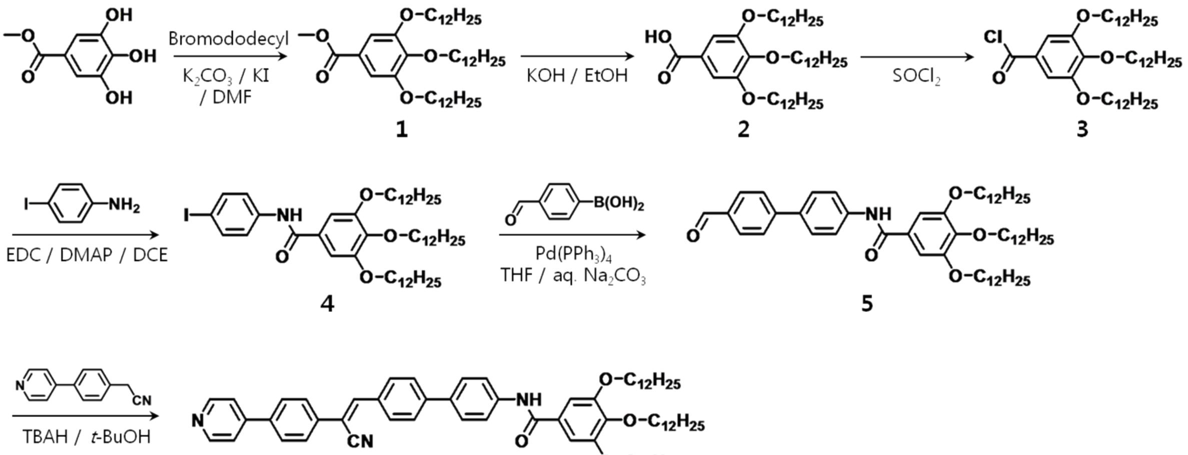
1. Synthetic details



Scheme S1. The synthesis of PyG.

Methyl 3,4,5-tridodecoxybenzoate (**1**). Anhydrous potassium carbonate (27.02g, 195.49 mmol) and a small amount of potassium iodide were added to a solution of methyl 3,4,5-trihydroxybenzoate (4.0g, 21.72 mmol) in DMF (100 mL), which was then stirred at 60 °C for 2h. 1-bromododecane (21.65g, 86.89 mmol) was then slowly added and the solution was heated at 60 °C for 8h. The solution was filtered to remove solids. Evaporation of the solvnet gave a solid, which was then dissolved in ethyl acetate. The resulting solution was washed with HCl and deionized water, dried over anhydrous Na_2SO_4, filtered and concentrated to dryness under vaccum. The product was purified by column chromatography with an eluent mixture of ethy acetate and hexane (1:5), followed by recrystallization from hot ethanol to obtain white solid (14.7g, yield 84%). ^1H NMR ($CDCl_3$, 300 MHz): δ [ppm]: 7.24 (s, 2H, Ar-H), 4.00 (m, 6H, OCH_2), 3.88 (s, 3H, OCH_2), 1.81-1.77 (m, 6H, CH_2), 1.45-1.24 (m, 54H, CH_2), 0.87 (t, 9H, CH_3).

3,4,5-tridodecyloxybenzoic acid (**2**). Potassium hydroxide (1.63g, 30 mmol) was added to a solution of compound **1** (10g, 15 mmol) in ethnol (200 mL). The mixture was heated at reflux for 8 h and the cooled to room temperature. The solution was diluted with deionized water and acidified by addition of 1M hydrochloric acid to pH 1. The precipitate was then filtered, washed with deionized water and diethyl ether, and dried under vaccum. Recrystallizatoin from hot ethnol gave white solid (xxg, 97%). ^1H NMR ($CDCl_3$, 300 MHz): δ [ppm]: 7.29 (s, 2H, Ar-H), 4.00 (m, 6H, OCH_2), 1.81-1.72 (m, 6H, CH_2), 1.45-1.24 (m, 54H, CH_2), 0.87 (t, 9H, CH_3)

3,4,5-tridodecyloxy-N-(4-iodopheny)benzamide (**4**). A suspension of compound 2 (5.0g, 7.41 mmol) in thionyl chloride (13.22g, 111.10 mmol) was stirred and refluxed for 4 h. Then thionyl chloride was evaporated under reduced pressure, and the resulting solid was dried under vaccum to give compound 3. A solution of compound 3 (5.1g, 7.35 mmol), EDC (1.26g, 8.10 mmol) and DMAP (0.63g, 5.15 mmol) in dichloroethane (200 mL) was stirred for 1h at room temperature. 4-iodoaniline (1.94g, 8.82 mmol) was added in the mixture solution. The reaction mixture was stirred for 1 day at room temperature, filtered and concentrated to afford a yellow oil, which was washed with deionized water and brine and then dried over anhydrous magnesium sulfate. The solution was removed under vaccum. The crude product was purified by column chromatography to provide the product as a white solid (5.74g, yield 88.5%). ^1H NMR ($CDCl_3$, 300 MHz): δ [ppm]: 7.68 (s, 1H, NH), 7.66 (d, 2H, Ar-H), 7.41 (d, 2H, Ar-H), 7.01 (s, 2H, Ar-H), 4.02 (m, 6H, OCH_2), 1.88–1.73 (m, 6H, CH_2), 1.47 (m, 6H, CH_2), 1.38–1.20 (m, 54H, CH_2), 0.88 (t, 9H, CH_3)

3,4,5-tridodecyloxy-N-(4'-formylbiphenyl-4-yl)benzamide (**5**). Compound 4 (4.0 g, 4.57 mmol) was reacted with 4-formylphenyl boronic acid (0.82g, 5.48 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.02g, 0.003 mmol) was dissolved in 60 mL of tetrahydrofuran. After addition of 20 mL of aqueous 2 N potassium carbonate solution, the reaction mixture was stirred at 85 °C and refluxed for 1 day. The cooled crude mixture was poured into 200 mL of water and extracted with ethyl acetate (150 mL), then dried over anhydrous magnesium sulfate. Finally, silica gel column chromatography gave the product as a white powder (3.46g, 4.05 mmol) in 89 % yield. ^{1}H NMR ($CDCl_3$, 300 MHz): δ [ppm]: 10.06 (s, 1H, Formyl), 7.95 (d, 2H, Ar-H), 7.81 (s, 1H, amide), 7.76 (d, 4H, Ar-H), 7.66 (d, 2H, Ar-H), 7.07 (s, 2H, Ar-H), 4.04 (m, 6H, OCH_2), 1.87–1.71 (m, 6H, CH_2), 1.49–1.27 (m, 54H, CH_2), 0.88 (t, 9H, CH_3)

(Z)-N-(4'-(2-cyano-2-(4-(pyridin-4-yl)phenyl)vinyl)biphenyl-4-yl)-3,4,5-tridodecyloxy benzamide (Compound 1, **PyG**). A mixture of 2-(4-(pyridin-4-yl)phenyl)acetonitrile (0.23 g, 1.17 mmol) and compound 5 (1.0 g, 1.17 mmol) in tert-butyl alcohol (30 mL) and THF (1 mL) was stirred at 50 °C for 1 h. Tetrabutylammonium hydroxide (TBAH) (1 M solution in methanol) (0.1 mL, 10 mol %) was slowly dropped into the mixture and stirred for 1 h. The yellow precipitate was collected by filtration and washed with methanol. Purification on a silica column chromatography afforded the product as a greenish-yellow powder (1.09g, 1.06 mmol) in 91% yield. mp: 153 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 8.82 – 8.59 (m, 2H), 8.02 (d, J = 8.5 Hz, 2H), 7.84 (d, J = 8.5 Hz, 2H), 7.79 – 7.62 (m, 10H), 7.55 (d, J = 6.1 Hz, 2H), 7.08 (s, 2H), 4.04 (dd, J = 14.7, 6.6 Hz, 6H), 1.94 – 1.67 (m, 6H), 1.49 – 1.27 (m, 49H), 0.90 – 0.86 (m, 10H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ [ppm]: 165.88, 153.55, 150.69, 147.31, 142.98, 142.40, 142.00, 139.03, 138.37, 135.98, 135.50, 132.53, 130.27, 129.96, 127.93, 127.88, 127.43, 126.90, 121.66, 120.72, 118.18, 110.58, 106.19, 73.83, 69.78, 32.15, 30.57, 29.96, 29.93, 29.87, 29.81, 29.64, 29.61, 29.59, 26.32, 22.92, 14.33; FAB-MS (m/z (%)) calcd: 1029.73; Found: 1030.74. Anal. calcd for $C_{69}H_{95}N_3O_3$: C 80.42; H 9.29; N 4.08; O 6.21. Found: C 80.15; H 9.34; N 4.03; O 6.53%.

(E)-N-(4'-(2-cyano-2-(4-(pyridin-4-yl)phenyl)vinyl)biphenyl-4-yl)-3,4,5-tridodecyloxy benzamide (**1-cis**). A cconcentrated solution of trans-PyG in THF was irradiated by UV light irradiation to give a mixture of trans- and cis-PyG. Purification on a silica column chromatography afforded the pure cis-PyG product as a powder in 30% yield. ^{1}H NMR ($CDCl_3$, 300 MHz) δ [ppm]: 8.69 (d, J = 6.1 Hz, 2H), 7.74 – 7.66 (m, 5H), 7.60 – 7.52 (m, 7H), 7.47 (d, J = 15.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.05 (s, 2H), 4.03 (q, J = 6.6 Hz, 6H), 1.93 – 1.67 (m, 6H), 1.48 (m, 6H), 1.26 (m, 48H), 0.88 (t, J = 6.6 Hz, 9H).

2. Measurements

Characterization: ^{1}H NMR spectra were recorded on a Bruker, Avance-300 (300 Mhz) and Avance-500 (500 MHz) in $CDCl_3$ solution. Mass spectra were measured using a JEOL, JMS-600W mass spectrometer. Elemental analysis was carried out using a CE instruments, EA1110 elemental analyzer. UV-visible absorption spectra were recorded on a Shimazu, UV-1650 PC spectrometer. Photoluminescence spectra were obtained using a Varian, Cary Eclipse Fluorescence spectrophotometer. The relative fluorescence quantum yield of compound 1 in solution was measured using quinine sulfate in 0.1 M H_2SO_4 solution as a standard reference (5×10^{-6} mol L^{-1}, $\Phi_f = 0.54$). The absolute photoluminescence quantum efficiency of the doped PMMA film was measured using an integrating sphere (Lasphere Co., 600 diameter). Time-resolved fluorescence lifetime experiments were performed by the time-correlated single photon counting (TCSPC) technique with a FluoTime200 spectrometer (Pico- Quant) equipped with a PicoHarp300 TCSPC board (Pico-Quant) and a PMA182 photomultiplier (PicoQuant). The excitation source was a 377 nm picosecond pulsed diode laser (PicoQuant, LDH375) driven by a PDL800-D driver (Pico-Quant) with fwhm80ps. The decay time fitting procedure was carried out with the IRF by using the vFit program (CDP, Russia). SAXS measurements were performed using Ni-filtered CuK_α radiation (λ=0.154184 nm) on a Nanostar instrument (Bruker, Germany) equipped with a 2D area detector, operating at 40 kV and 35 mA, with a sample-to-detector distance of 22 cm ($1<q<10$ nm^{-1}, $q=4\pi\sin\theta/\lambda$). FE-SEM images were acquired on a JEOL, JSM-6330F microscope. AFM measurements were performed in the Nanowizard scanning probe microscope (version 1.3) of JPK instruments, and the images were obtained in the contact mode using a soft cantilever. T_{gel} was determined by the ball dropping experiment. A ball (~90mg) was carefully placed on top of the gel and the temperature was slowly raised with a rate of 1.0 °C/min. The gel temperature was determined as the temperature at which gel was unable to bear the ball and it dropped down.

3. The DFT calculation of the trans and the cis isomer of compound **1**.

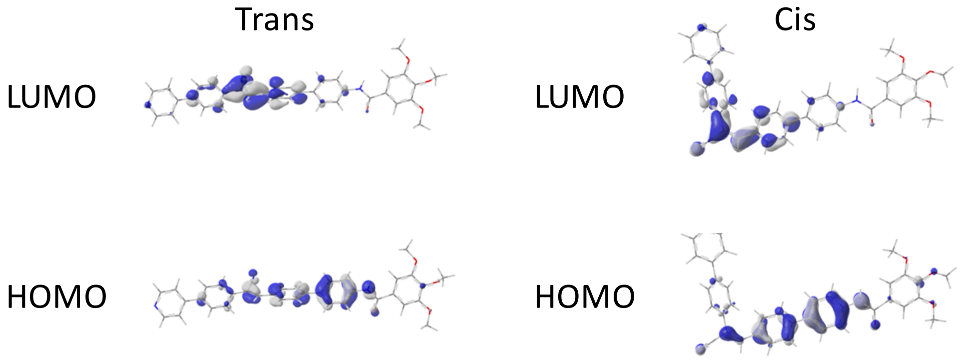


Figure S1. The DFT calculation results of the trans and cis isomer of compound **1** (Gaussian 09: TDDFT B3LYP/6-31G(d,p)); Their optimized conformations and the electron populations in the HOMO and LUMO energy levels.

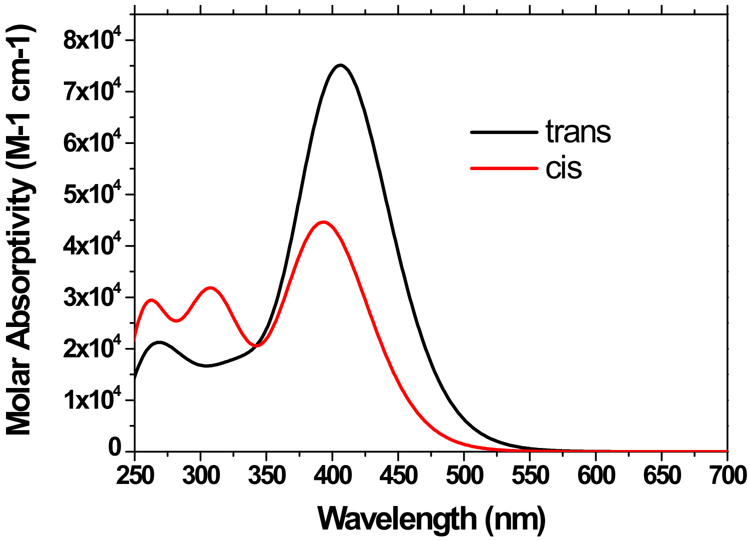


Figure S2. The DFT calculation results of the trans and cis isomer of compound **1** (Gaussian 09: TDDFT B3LYP/6-31G(d,p)); Their absorption spectra in gas phase. The calculated results are similar to the experimental data in terms of the absorption band shape and the spectral difference in trans and cis isomer, even though the calculated wavelength is not identical to the corresponding experimental ones.

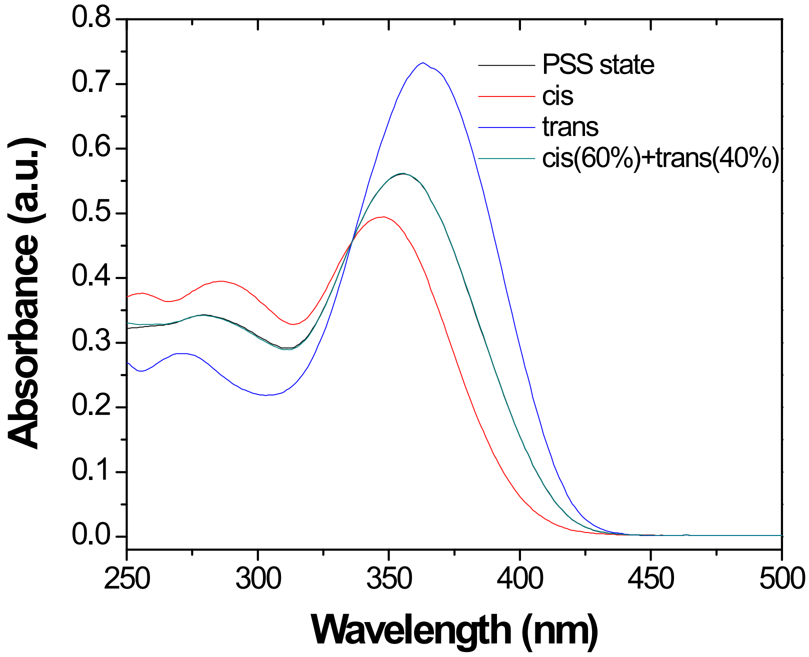


Figure S3. The absorption spectra of compound **1** in chloroform solution in the pure trans, the pure cis, the photostationary state, and the estimated absorption spectra from the mixture of cis (60%) and trans (40%) isomer.

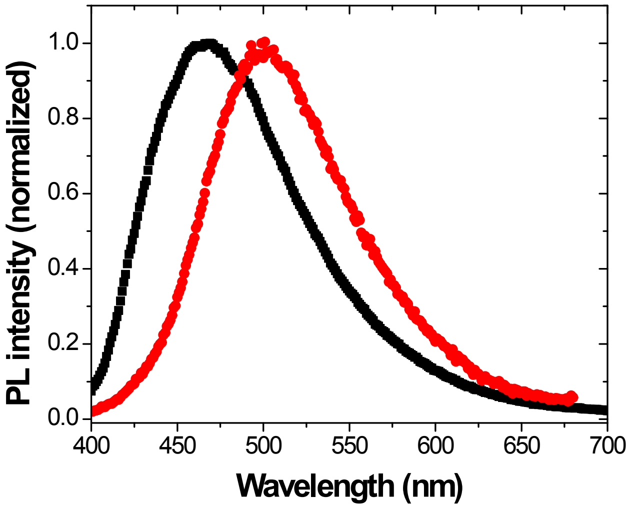


Figure S4. The fluorescence spectra of PMMA film doped with 2 wt% (black) and 23.3 wt% (red) of the compound **1**.

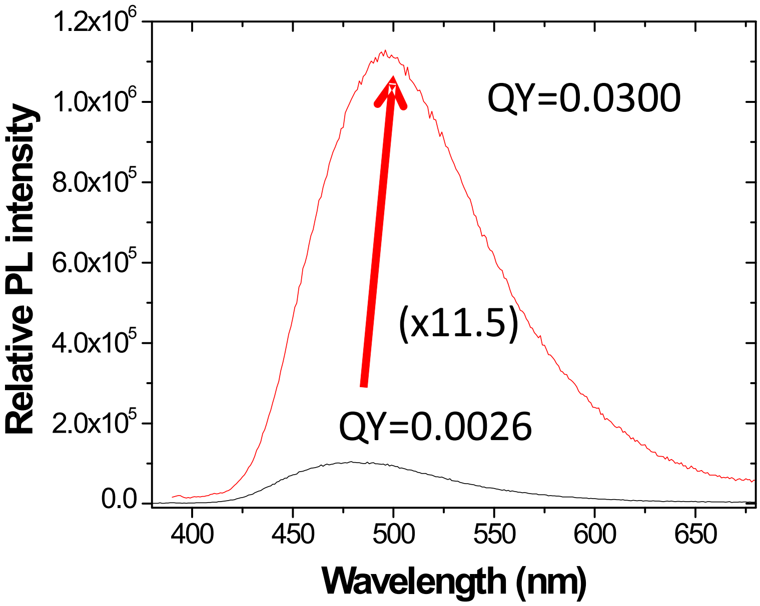


Figure S5. The relative fluorescence spectra of compound **1** in THF (black) and THF : H_2O (= 20 : 80) (red). ($2x10^{-5}$ M concentration)

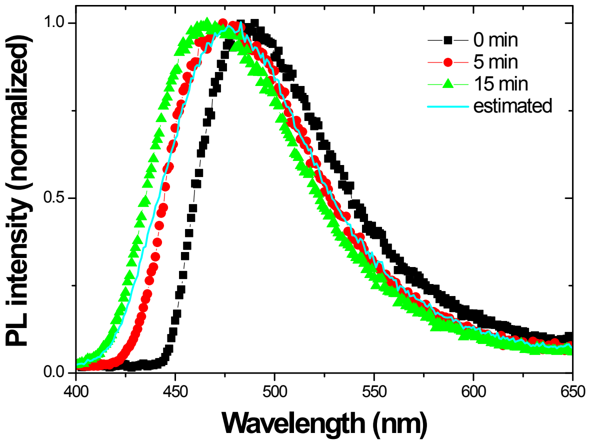


Figure S6. Fluorescence spectra of the gel (0.25 wt%) in cyclohexane depending on the irradiation time using the blue LED. The estimated line was obtained by the sum of the monomer emission (70%) and the aggregates-emission (30%). This composition ratio is also similar to that obtained from ^{1}H-NMR results

Table S1. Fluorescence quantum yields, lifetimes, and kinetic constants in THF, nanoparticle and PMMA film (23.3 wt% doping) of compound 1

	τ_{av} [ns]	τ_i (amplitude a_i) [ns]	Φ_F	k_r [ns^{-1}]	k_{nr} [ns^{-1}]
THF solution	-	-	0.003	-	-
Nanoparticle (THF:water=1:4)	2.693	6.14(0.06) 1.90(0.35) 0.65 (0.59)	0.030	0.0111	0.3602
PMMA film (23.3wt% doping)	2.652	6.43 (0.03) 2.31 (0.21) 0.43(0.76)	0.270	0.1018	0.2753

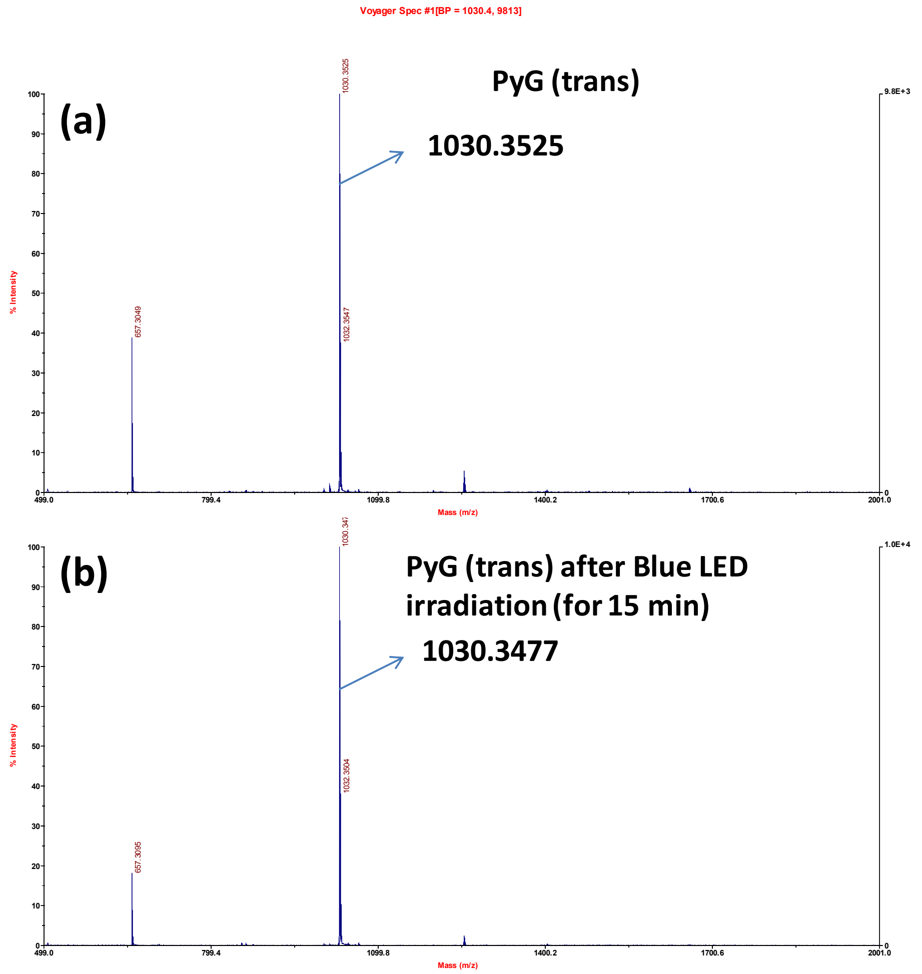


Figure S7. The MALDI-TOF results of the compound **1** before and after the light irradiation.

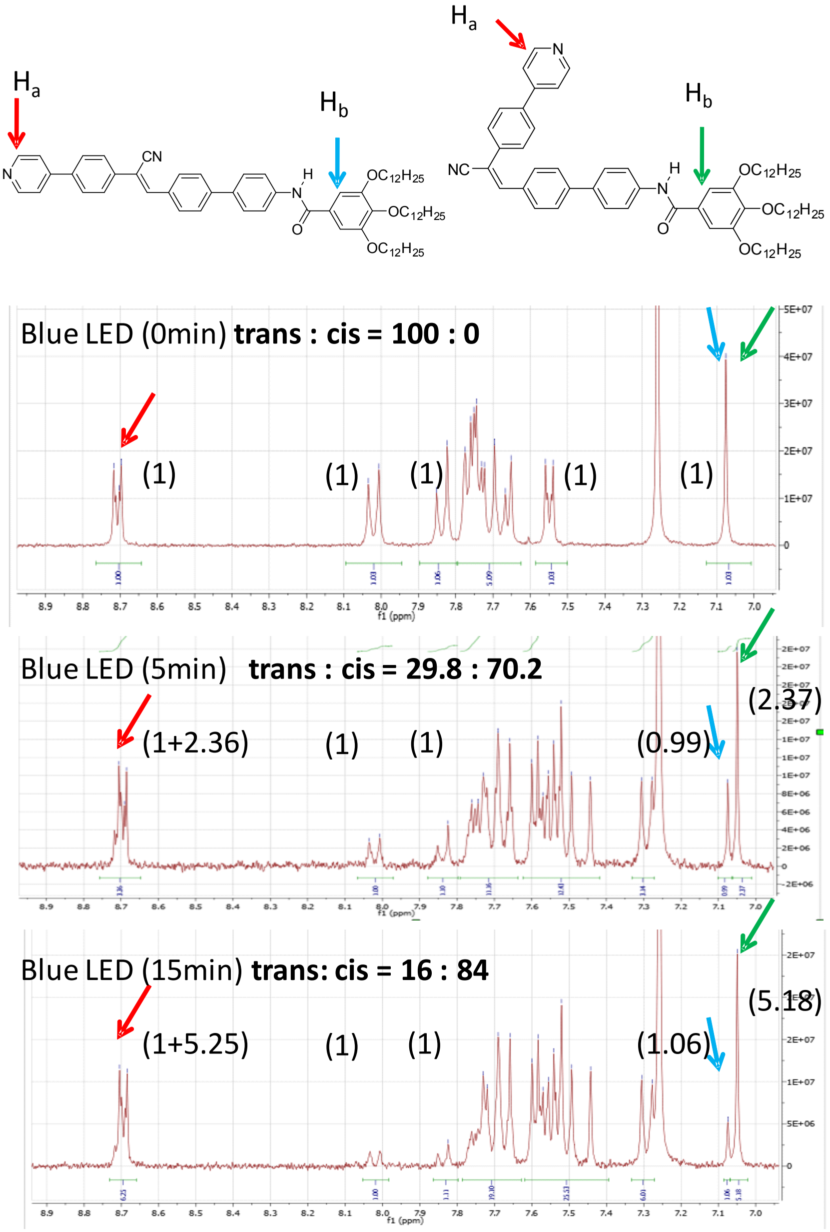


Figure S8. The partial ^{1}H NMR spectra of compound **1** (in CDCl$_3$) according to the exposure time of the blue LED (0, 5 and 15 min). The red arrows indicated the H$_a$ proton of the pyridine ring for trans and cis isomers. The blue and green arrow indicated the H$_b$ proton of the tridodecyloxyl-substituted benzene for trans and cis isomer, respectively.