#### Supplementary Information

#### Photoinduced Architectural Transformation of Non-Covalent Fluorescent Photochromic Organic Nanoparticles by Amplified Fluorescence Photoswitching

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#### **1. SYNTHETIC PROCEDURES**

All reagents were purchased from Aldrich and Fisher-Scientific and used as received. Air-sensitive reactions were performed under argon using a vacuum line. Analytical TLC was performed on Kieselgel F-254 precoated plates. Visualization was done with UV lamp. Flash chromatography was carried out with silica gel 60 (230-400 mesh) from SDS. All reactions requiring an inert atmosphere were carried out using Schlenk techniques. Solvents were dried and distilled under argon using standard procedures. Compounds  $2^1$  and  $7^2$  were prepared according to literature procedure. High resolution mass spectra (HRMS) were recorded by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific), MALDI-TOF (Voyager DE-STR, Applied Biosystems) at CEISAM, Nantes, or using a ZabSpecTOF (LSIMS at 4 kV) spectrometer Bruker MicrO-Tof-Q II (Centre Régional de Mesures Physiques de l'Ouest, Rennes).

#### 1.1. Synthesis of fluorophore (F)

The targeted fluorophore (F) was synthesized following a five-step procedure, starting with the selective dibromination of benzodiathiazole 1 into 2 (Scheme 1).



**Scheme 1.** Synthetic pathway for fluorophore (**F**). i- Br<sub>2</sub>, HBr 40 %, rflx, 79 %. ii- -4-(diphenylamino) phenylboronic acid pinacol ester, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, ethanol, Na<sub>2</sub>CO<sub>3</sub> 2 M, 45 °C, 12 h, 70 %. iii- 4-formylphenylboronic acid, Pd(PPh<sub>3</sub>)<sub>4</sub>, ethanol, Na<sub>2</sub>CO<sub>3</sub> 2 M, 60 °C, 12 h, 85 %. iv- NBS, CHCl<sub>3</sub>, rflx, 4 h, 98 %. v- 4-*tert*-butylphenylboronic acid, toluene, ethanol, Na<sub>2</sub>CO<sub>3</sub> 2 M, rflx, 12 h, 62 %.

A notable modification of the literature procedure<sup>3</sup> was performed regarding the neutralization step, involving KOH treatment before bromine reduction with a saturated solution of sodium thiosulfate. Such basic treatment avoids formation of colloidal sulfur upon dismutation that would otherwise immediately

poison the catalyst in the following coupling reaction step. The next step conducted to the dissymetric compound **3** using a palladium-catalyzed Suzuki aromatic cross-coupling between **2** and the commercially available triarylamine boronate ester. Contrary to reports in literature,<sup>2</sup> keeping the temperature below 50 °C and stopping the reaction after 12 h revealed to be crucial to minimize the amount of symmetric compound resulting from a double coupling reaction. A second Suzuki coupling reaction with **3**, carried out at 70 °C, provided the bright red compound **4** in high yield. Synthesis of fluorophore **6** (**F**) was eventually achieved after quantitative bromination of **4** using N-bromosuccinimide in refluxing chloroform, followed by a third Suzuki aromatic coupling.

*Compound* **2**. To a solution of benzothiadiazole **1** (1.17g, 8.6.mmol, 1 eq.) in HBr (15 mL) was added a solution of Br<sub>2</sub> (4.1 g, 1.3 mL, 25.8 mmol, 3eq.) in HBr (20 mL). The mixture was refluxed for 6 h. After cooling at room temperature, the solution was alcalinized with KOH, then a solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added. After filtration and washing with water and water:ethanol 1:1, compound **2** was isolated as a pure white product (1.99 g, 6.8 mmol, 79 %). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 7.73 (s, 2H). HRMS: m/z (ESI<sup>+</sup>) 292.8380 ([M]<sup>+</sup>= C<sub>6</sub>H<sub>3</sub>N<sub>2</sub>SBr<sub>2</sub><sup>+</sup> calcd 292.8378).

*Compound 3.* To a solution of compound 2 (1.2 g, 4.1 mmol, 1.5 eq.) in toluene (24 mL) were added 4-(diphenylamino) phenylboronic acid pinacol ester (1.0 g, 2.7 mmol, 1 eq.), ethanol (16 mL), and a 2 mol. L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> aqueous solution (16 mL). The solution was deoxygenated with argon and Pd(PPh<sub>3</sub>)<sub>4</sub> (50 mg, 1.5 mol. % mol) was added. The reaction was carried out at 45°C overnight. CH<sub>2</sub>Cl<sub>2</sub> was added and the extracted organic layer was washed three times with water, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After solvent evaporation under vacuum, compound **3** was obtained as a bright orange-red compound after purification by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether from 0:100 to 20:80 as an eluent (601 mg, 70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 7.89 (d, <sup>3</sup>*J*(H-H) = 7.6 Hz, 1 H), 7.82 (d, <sup>3</sup>*J*(H-H) = 8.8 Hz, 2 H), 7.54 (d, <sup>3</sup>*J*(H-H) = 7.6 Hz, 1 H), 7.32 (m, 4 H), 7.21 (m, 6 H), 7.10 (tt, <sup>3</sup>*J*(H-H) = 7.2 Hz, <sup>4</sup>*J*(H-H) = 2.2 Hz, 2 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 154.0, 153.2, 148.5, 147.4, 133.5, 132.4, 130.0, 129.9, 129.5, 127.3, 125.1, 123.6, 122. 7, 112.2. LRMS: *m/z* (EI-TOF) 458.0, 460.0 ([M+1]<sup>+</sup> = C<sub>2</sub>4H<sub>16</sub>BrN<sub>3</sub>S<sup>+</sup> calcd 458.02, 460.02).

*Compound 4.* To a solution of compound **3** (0.53 g, 1.16 mmol, 1eq.) in toluene (9 mL) were added 4formylphenylboronic acid (190 mg, 1.27 mmol, 1.1 eq), ethanol (7 mL) and a 2 mol. L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> aqueous solution (7 mL). The mixture was deoxygenated with argon and Pd(PPh<sub>3</sub>)<sub>4</sub> (40 mg, 3 mol. %) was added. The reaction was carried out at 70°C for overnight. CH<sub>2</sub>Cl<sub>2</sub> was added and the extracted organic layer was washed three times with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After solvent evaporation under vacuum, the crude mixture was purified by column chromatography on silica gel using CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether from 0:100 to 20:80 as an eluent to provide compound **4** as an bright red solid (483 mg, 85 %).<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 10.12 (s, 1 H), 8.17 (d, <sup>3</sup>*J*(H-H) = 8.3 Hz, 2 H), 8.06

(d,  ${}^{3}J(\text{H-H}) = 8.5 \text{ Hz}, 2 \text{ H}), 7.90$  (d,  ${}^{3}J(\text{H-H}) = 8.8 \text{ Hz}, 2 \text{ H}), 7.86$  (d,  ${}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.80$  (d,  ${}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.31$  (t,  ${}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 4 \text{ H}), 7.21$  (m, 6H), 7.08 (t,  ${}^{3}J(\text{H-H}) = 7.3 \text{ Hz}, 2 \text{ H}).^{13}\text{C}$ NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 192.0, 154.1, 154.0, 148.5, 147.5, 143.5, 135.8, 134.2, 131.0, 130.4, 130.1, 129.9, 129.5, 129.2, 127.1, 125.2, 123.6, 122.7. MS: m/z (EI-TOF) 484.2 ([M+1]<sup>+</sup> = C<sub>31</sub>H<sub>21</sub>N<sub>3</sub>OS<sup>+</sup> calcd 484.14).

*Compound* **5**. To a solution of compound **4** (473 mg, 0.97 mmol, 1 eq.) in CHCl<sub>3</sub> (30 mL), was added N-bromosuccinimide (360 mg, 2.02 mmol, 2.05 eq.). The reaction mixture was refluxed for 4 h. After solvent removal under reduced pressure, acetonitrile was added to precipitate compound **5** as a pure bright red solid (623 mg, 98 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 10.11 (s, 1 H), 8.17 (d, <sup>3</sup>*J*(H-H) = 8.3 Hz, 1 H), 8.05 (d, <sup>3</sup>*J*(H-H) = 8.4 Hz, 1 H), 7.92 (d, <sup>3</sup>*J*(H-H) = 8.7 Hz, 1 H), 7.86 (d, <sup>3</sup>*J*(H-H) = 7.4 Hz, 1 H), 7.40 (d, <sup>3</sup>*J*(H-H) = 8.8 Hz, 2 H), 7.20 (d, <sup>3</sup>*J*(H-H) = 8.7 Hz, 1 H), 7.04 (d, <sup>3</sup>*J*(H-H) = 8.8 Hz, 2 H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 192.0, 154.1, 154.0, 147.5, 146.2, 143.4, 135.9, 133.8, 132.7, 131.7, 131.4, 130.4, 130.1, 129.9, 129.1, 127.4, 126.3, 123.5, 116.4. HRMS: *m/z* (ESI<sup>+</sup>) 638.9626 ([M]<sup>+</sup> = C<sub>31</sub>H<sub>19</sub>N<sub>3</sub>OSBr<sub>2</sub><sup>+</sup> calcd 638.9616).

Compound 6 (F). To a solution of compound 5 (623 mg, 0.97 mmol, 1 eq.) in toluene (14 mL) were added 4-tert-butylphenylboronic acid (442 mg, 2.48 mmol, 2.5 eq.), ethanol (10 mL) and a 2 mol. L<sup>-1</sup> Na<sub>2</sub>CO<sub>3</sub> aqueous solution of (10 mL). The mixture was deoxygenated with argon and Pd(PPh<sub>3</sub>)<sub>4</sub> (35 mg, 3 mol. %) was added. The reaction mixture was heated at reflux overnight. CH<sub>2</sub>Cl<sub>2</sub> was added and the extracted organic layer was washed three times with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After solvent removal under reduced pressure, the crude solid was purified by column chromatography on silica-gel using CH<sub>2</sub>Cl<sub>2</sub>:petroleum ether from 0:100 to 20:80 as an eluent to provide the targeted fluorescent compound 6 (F) as a bright red solid (450 mg, 62 %).  $T_g = 96$  °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 10.12 (s, 1H), 8.18 (d, <sup>3</sup>*J*(H-H) = 8.3 Hz, 1 H), 8.06 (d, <sup>3</sup>*J*(H-H) = 8.3 Hz, 1 H), 7.95 (d,  ${}^{3}J(\text{H-H}) = 8.7 \text{ Hz}, 1 \text{ H}), 7.87 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.81 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ (d, }{}^{3}J(\text{H-H}) = 7.4 \text{ Hz}, 1 \text{ H}), 7.55 \text{ Hz}, 1 \text{ H}), 7.55 \text{ Hz}, 1 \text{ H}), 7.55 \text{ Hz}, 1 \text{ H}), 7.5 \text{$ H) = 8.5 Hz, 4H), 7.48 (d,  ${}^{3}J$ (H-H) = 8.5 Hz, 2 H), 7.30 (t,  ${}^{3}J$ (H-H) = 8.5 Hz, 6 H), 1.38 (s, 18H).  ${}^{13}C$ NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 192.0, 154.2, 154.0, 150.1, 148.3, 146.4, 143.6, 137.8, 136.2, 135.8, 134.2, 131.1, 130.8, 130.3, 130.1, 129.9, 129.2, 128.0, 127.2, 126.5, 125.9, 125.2, 123.2, 34.6, 31.5. HRMS: m/z (ESI<sup>+</sup>) 747.3258 ([M]<sup>+</sup>= C<sub>51</sub>H<sub>45</sub>N<sub>3</sub>OS<sup>+</sup> calcd 747.3283). UV-vis (toluene),  $\lambda_{max}^{abs}$  ( $\varepsilon_{max}$ (L.mol<sup>-1</sup>.cm<sup>-1</sup>): 466 (1.80×10<sup>4</sup>), 339 (5.59×10<sup>4</sup>) nm. UV-vis (THF),  $\lambda_{max}^{abs}$  ( $\varepsilon_{max}$  (L.mol<sup>-1</sup>.cm<sup>-1</sup>): 459  $(2.27 \times 10^4)$ , 335  $(7.50 \times 10^4)$  nm.

#### **1.2** Synthesis of photochrome (P)



Scheme S2. Synthetic pathway for photochrome (P).

*Compound* **8***o* [(*o*)-(*P*)]. In a Schleck tube, precursor **7** (20 mg, 0.043mmol), 4-iodobenzoic acid (15 mg, 0.06 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (2 mg, 0.003 mmol) and CuI (1 mg, 0.005 mmol) were dried under vacuum for 30 min. Well-deoxygenated THF (20 mL) and Et<sub>3</sub>N (20 µL, 0.03 mmol) were subsequently added. The reaction mixture was left under stirring at room temperature for 14 h. The solvents were further evaporated under vacuum to obtain a crude product that was purified by column chromatography, using CH<sub>2</sub>Cl<sub>2</sub> with 3% MeOH as an eluent. Compound **20** was obtained as a pale yellow powder (25 mg, 60 %). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 297 K):  $\delta$  ppm 8.09 (d, <sup>3</sup>*J* = 8.0 Hz, 2H, *o*-C<sub>6</sub>H<sub>4</sub>COOH), 7.59 (s, <sup>3</sup>*J* = 8.0 Hz, 2H, *m*-C<sub>6</sub>H<sub>4</sub>COOH), 7.54 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 7.41-7.30 (m, 5H, C<sub>6</sub>H<sub>5</sub>+ CH<sub>Thio</sub>), 1.97 (s, 3H, CH<sub>3</sub>), 1.96 (s, 3H, CH<sub>3</sub>), 1.59 (br, 1H, OH). <sup>13</sup>C NMR (125.76 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  ppm 170.85 (CO), 144.37, 142.67, 141.47, 138.4, 132.45, 131.69, 132.47, 130.31, 129.17, 128.87, 128.15, 127.75, 125.66, 125.43, 122.32, 121.06, 93.21 (C=C), 85.08 (C=C), 14.72 (CH<sub>3</sub>), 14.67 (CH<sub>3</sub>). IR (KBr) (cm<sup>-1</sup>): 2202 (w, v<sub>C=C</sub>), 1681 (s, v<sub>C=O</sub>). HR-MS ESI(*m*/*z*): 587.0581 ([M]<sup>+</sup> = C<sub>30</sub>H<sub>18</sub>F<sub>6</sub>O<sub>2</sub>S<sub>2</sub><sup>+</sup> calcd 587.0580). UV–vis (THF),  $\lambda_{max}^{abs}$  ( $\varepsilon_{max}$  (L.mol<sup>-1</sup>.cm<sup>-1</sup>): 340 (2.10×10<sup>4</sup>), 318 (2.70×10<sup>4</sup>), 276 (2.70×10<sup>4</sup>).

*Data for* 8*c* [(*c*)-(*P*)]. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  ppm 8.10 (d, <sup>3</sup>*J* = 8.0 Hz, 2H, *o*-C<sub>6</sub>H<sub>4</sub>COOH), 7.60 (d, <sup>3</sup>*J* = 8.0 Hz, 2H, *m*-C<sub>6</sub>H<sub>4</sub>COOH), 7.59-7.57 (m, 2H, *m*-C<sub>6</sub>H<sub>5</sub>), 7.44-7.42 (m, 3H, *o*-C<sub>6</sub>H<sub>5</sub>+ *p*-C<sub>6</sub>H<sub>5</sub>), 6.68 (s, 1H, CH<sub>Thio</sub>), 6.54 (s, 1H, CH<sub>Thio</sub>), 2.21 (s, 3H, CH<sub>3</sub>), 2.20 (s, 3H, CH<sub>3</sub>), 1.63 (br, 1H, OH). UV–vis (THF),  $\lambda_{max}^{abs}$  ( $\varepsilon_{max}$  (L.mol<sup>-1</sup>.cm<sup>-1</sup>): 604 (1.18×10<sup>4</sup>), 322 (3.30×10<sup>4</sup>), 260 (2.87×10<sup>4</sup>).

#### 2. PHOTOPHYSICAL PROPERTIES OF FONS



Figure S1. Normalized absorption (bold line) and emission (dotted line,  $\lambda_{exc} = 450$  nm) spectra of (F) in toluene and THF solution, and as FONs in water.

#### 3. PHOTOSWITCHING STUDIES



Figure S2. A) Absorption spectra of (P) in THF solution upon irradiation at 340 nm (PSS1) and additional irradiation at 540 nm (PPS2A). B) Time-resolved absorbance evolution of (P) in THF solution at 604 nm corresponding to the (c) form maximum absorption in the visible after successive irradiation at 340 and 540 nm (purple curve: absorbance evolution; red curve: fit).



**Figure S3.** Evolution of the absorption spectra of aqueous **PON** dispersions upon irradiation at A) 340 nm, and B) 540 nm. Both irradiation powers were set at 50 mW.cm<sup>-2</sup>. Initial and final states were referenced as bold black and red curves respectively. Inset: absorbance evolution at 597 nm (maximum absorption wavelength of the closed forms) as a function of time. C) Absorption spectra of aqueous **PON** dispersions upon irradiation at 340 nm (PSS1) and additional irradiation at 540 nm (PPS2A).





Figure S4. Spectral evolutions of PFON dispersions in water, made from a stock solution containing a 1:1 (F):(P) molar ratio. Upon irradiation at 340 nm: A) Absorption spectra, B) emission spectra ( $\lambda_{exc} =$  450 nm). Upon irradiation at 488 nm after a first irradiation at 340 nm (50 mW.cm<sup>-2</sup> power for both irradiation wavelengths): C) absorption spectra, D) emission spectra ( $\lambda_{exc} =$  450 nm).



Figure S5. Spectral evolutions of PFON dispersions in water, made from a stock solution containing a 2:1 (F):(P) molar ratio. Upon irradiation at 340 nm: A) Absorption spectra, B) emission spectra ( $\lambda_{exc} =$  450 nm). Upon irradiation at 488 nm after a first irradiation at 340 nm (50 mW.cm<sup>-2</sup> power for both irradiation wavelengths): C) absorption spectra, D) emission spectra ( $\lambda_{exc} =$  450 nm).



Figure S6. Spectral evolutions of PFON dispersions in water, made from a stock solution containing a 5:1 (F):(P) molar ratio. Upon irradiation at 340 nm: A) Absorption spectra, B) emission spectra ( $\lambda_{exc} =$  450 nm). Upon irradiation at 488 nm after a first irradiation at 340 nm (50 mW.cm<sup>-2</sup> power for both irradiation wavelengths): C) absorption spectra, D) emission spectra ( $\lambda_{exc} =$  450 nm).



**Figure S7.** Absorption spectra of **PFON** dispersions in water in their initial state, after 340 nm irradiation (50 mW.cm<sup>-2</sup>) until reaching the photostationary state (PSS1), and further additional 488 nm irradiation (50 mW.cm<sup>-2</sup>) until reaching again the photostationary state (PSS2) to restore the initial state. A) **1:1 PFONs**, B) **2:1 PFONs**, C) **5:1 PFONs**.



**Figure S8.** Two independent series of TEM images of **PONs** deposited on holey carbon-coated copper grids: A) before, B) after irradiation at 340 nm once the photostationary state was reached. Partial disintegration of **PONs** was observed after phototransformation of (**P**) in their closed forms.



Figure S9. Spectral evolutions of mixed PON and FON dispersions in water in an equimolar ratio in terms of (P) and (F) contents. Upon irradiation at 340 nm: A) Absorption spectra, B) emission spectra ( $\lambda_{exc} = 450$  nm). Upon irradiation at 488 nm after a first irradiation at 340 nm: C) absorption spectra, D) emission spectra ( $\lambda_{exc} = 450$  nm). E) Change in the emission spectra before UV irradiation (plain down to the baseline), after UV irradiation at 340 nm (clear tint) followed by irradiation at 488 nm (hatched area) (50 mW.cm<sup>-2</sup> power for both irradiation wavelengths).



**Figure S10**. Spectral evolution of an equimolar solution of (**F**) and (**P**) dyes in THF ( $4.2 \times 10^{-6}$  mol.L<sup>-1</sup>) upon irradiation at 340 nm (50 mW.cm<sup>-2</sup>). A) Absorption spectra (inset: time evolution of the absorbance at 597 nm during irradiation). B) Emission spectra ( $\lambda_{exc} = 450$  nm).



**Figure S11.** Fluorescence intensity decay at 650 nm ( $\lambda_{exc} = 450$  nm) of aqueous dispersions of **FONs** (red spheres – red decays), **PON+FON** (red+white spheres – purple decays) and **1:1 PFON** (tainted red-white spheres – gold decays) before UV irradiation (dark colors) and after UV irradiation at 340 nm (50 mW.cm<sup>-2</sup>) (light colors).

#### **3.2.** LIST OF TABLES

Sample	$\lambda_{\max}^{abs}$ (nm)	$\lambda_{\max}^{em} (nm)^{a}$	${D}_{f}^{\mathrm{a,b}}$	$ au_s^{\mathrm{a,c}}$
(F) in toluene	466, 339	603	0.58	5.86
<b>(F)</b> in THF	459, 335	678	0.23	4.08
FON	476, 339	654	0.27	2.77 <sup>d</sup>
1:1 PFON	479, 333	648	0.11	2.35 <sup>d</sup>
1+1 PON+FON	478, 332	650	0.17	$2.66^{d}$

**Table S1.** Photophysical of (**F**) fluorophore in THF and toluene solution, and processed as **FON** and **PFON** aqueous dispersions.

<sup>a</sup>  $\lambda_{exc} = 450$  nm. <sup>b</sup> Determined from coumarin 540A as a fluorescence standard ( $\Phi_f = 0.38$ ). <sup>c</sup>  $\lambda_{em} = 650$  nm. <sup>d</sup> Amplitude-averaged lifetime.

**Table S2.** Photochemical properties of **(P)** photochrome in THF solution and processed as **PON** aqueous dispersion.

Sample X	$\lambda_{\max}^{abs}$ (nm)	${\it P}_{\scriptscriptstyle OC}$	$arPhi_{CO}$	ρ <sub>oc</sub>
(o)-(P)	340, 318, 276	0.69 <sup>a</sup>	0.018 <sup>a</sup>	0.92
<i>(c)</i> -( <b>P</b> )	604, 322, 260	-	0.013 <sup>b</sup>	-
(o)-PON	320, 270	n.a.	n.a.	0.66
(PSS)-PON	597, 319, 266	n.a.	n.a.	-

<sup>a</sup> Measured at  $\lambda_{obs} = 604$  nm upon irradiation at  $\lambda_{irr} = 340$  nm (P = 0.18 mW). <sup>b</sup> Measured at  $\lambda_{obs} = 604$  nm upon irradiation at  $\lambda_{irr} = 547$  nm (P = 6.9 mW).

**Table S3.** Photokinetics of **1:1, 2:1, 5:1 PFON** and **1+1 PON+FON** aqueous dispersions (rate constants for the time evolutions of the emission intensity at 650 nm and absorbance at 630 nm upon 340 nm irradiation and an additional 488 nm irradiation step until reaching the photostationary state for both steps),  $(o) \rightarrow (c)$  photoconversion yield  $\rho_{oc}^{NP}$ , and energy transfer efficiency  $\Phi_{ET}$  after UV irradiation (50 mW.cm<sup>-2</sup> power for each irradiation).

Rate constants <sup>a</sup>	after irradiation at 340 nm		after irradiation at 488 nm		oNP	Ф
	$k^{UV}(em^{650})$	$k^{UV}(abs^{630})$	$k^{VIS}(em^{650})$	$k^{VIS}(abs^{630})$	$P_{oc}$	(94)
	$(10^{-2} \text{ s}^{-1})$	$(10^{-2} \text{ s}^{-1})$	$(10^{-3} \text{ s}^{-1})$	$(10^{-3} \text{ s}^{-1})$	(70)	(70)
1:1 PFON	$81.2\pm2.1$	$13.3\pm0.4$	$9.0\pm1.4$	$22.4\pm8.1$	35	~100
<b>2:1 PFON</b>	$60.3\pm1.9$	$13.2\pm1.9$	$8.1\pm0.7$	$24.1\pm0.8$	43	99
5:1 PFON	$20.9 \pm 1.1$	$13.7\pm1.3$	$37.2\pm4.6$	$65.3\pm5.6$	91	82
1+1 PON+FON	$26.9 \pm 2.1$	$13.9\pm0.6$	$5.9\pm0.5$	$8.0\pm0.4$	72	73

<sup>a</sup> Monoexponential laws were used to model with high confidence the time spectral evolutions.

**Table S4.** DLS and  $\zeta$  zeta potential measurements of **1:1 PFON** aqueous dispersions before, after 340 nm irradiation and an additional 540 nm irradiation step until reaching the photostationary state for both steps, performed each with a 50 mW.cm<sup>-2</sup> power.

	$D_H$ (fractional co	(mV)		
	Intensity-weighted	Number-weighted	ς (Πν)	
initial state	66 ± 3 (0.25)	64 + 3(1)	-219 + 34	
lintial state	$240 \pm 9 \; (0.75)$	$04 \pm 5(1)$	$21.7 \pm 5.7$	
after irradiation at 340 nm	58 ± 3 (0.18)	$58 \pm 3 (0.18)$ $55 \pm 3 (1)$		
	$226 \pm 9 \ (0.82)$	55 - 5 (1)	22.7 - 510	
after irradiation at 540 nm	192 ± 29 (1)	129 ± 17 (1)	$-32.1 \pm 3.7$	

**Table S5.** Time constants  $\tau_i$ , fractional amplitudes  $\alpha_i$ , and amplitude-averaged lifetime  $\langle \tau_s \rangle$  for the fluorescence time decays ( $\lambda_{exc} = 450 \text{ nm}$ ,  $\lambda_{em} = 650 \text{ nm}$ ) of **FON**, **1:1 PFON** and **1+1 PON+FON** (equimolar ratio) dispersions in water before and after UV irradiation (50 mW.cm<sup>-2</sup>) until reaching the photostationary state.

Sample		$ au_i(lpha_i)(\mathrm{ns})^{\mathrm{a}}$	$< \tau_s > (ns)^a$
FON	before irradiation	7.28 (0.13), 2.75 (0.41), 0.64 (0.46)	2.77
FOR	after irradiation	6.99 (0.14), 2.52 (0.41), 0.56 (0.56)	2.25
1.1 <b>DEON</b>	before irradiation	6.66 (0.13), 2.65 (0.44), 0.65 (0.42)	2.35
1.11100	after irradiation	3.76 (0.07), 1.28 (0.35), 0.31 (0.58)	0.88
1+1 PON+FON	before irradiation	8.11 (0.14), 2.92 (0.43), 0.64 (0.43)	2.66
	after irradiation	6.33 (0.10), 2.42 (0.48), 0.59 (0.42)	1.95

<sup>a</sup> Fluorescence decays were modeled through a triexponential mathematical law.

$$I(t) = \sum_{i=1}^{3} \alpha_i \exp(-t/\tau_i)$$
 with the fractional amplitudes  $a_i = c$ 

$$= \alpha_i / \sum_j \alpha_j \qquad \langle \tau_S \rangle = \sum_{i=1}^3 a_i \tau_i$$

#### 4. **References**

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