

**Supplementary Information**

**Amplified nitric oxide photorelease in the DNA proximity**

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**Chemicals.**

All chemicals were purchased by Sigma-Aldrich and used as received. All solvents used were spectrophotometric grade.

**Instrumentation.**

<sup>1</sup>H NMR spectra were recorded on a VARIAN INOVA 200 spectrometer, using TMS as internal standard. ESI-MS spectra were recorded on an Agilent 1100 Series ESI/MSD spectrometer. Experimental conditions were as follows: capillary voltage, 3.5 KV; fragmentor, 100 V; source temperature, 350 °C; drying gas, N<sub>2</sub> (10 L/min), carrier solvent, methanol (0.4 mL/min). The samples were dissolved in a mixture methanol:acetonitrile.

UV/vis absorption spectra were recorded with a Jasco V 560 spectrophotometer. Fluorescence emission spectra were recorded with a Spex Fluorolog-2 (mod. F-111) spectrofluorimeter.

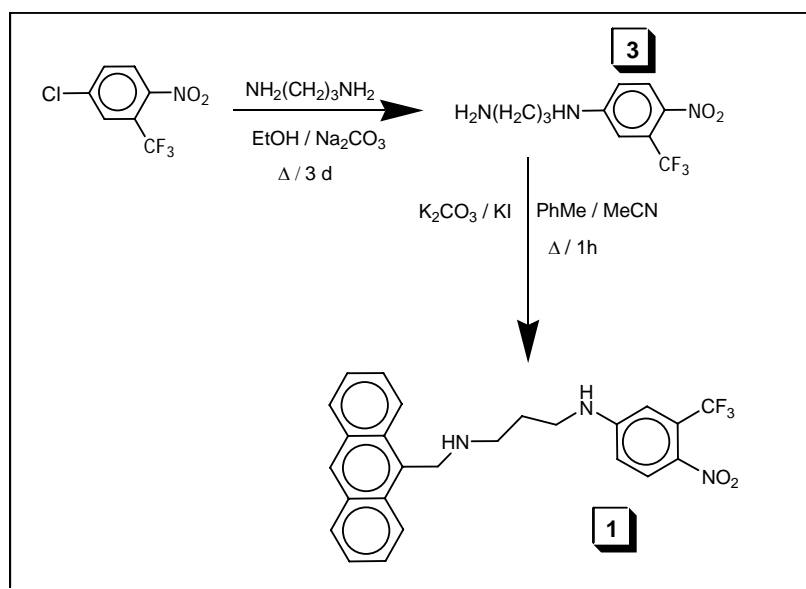
*NO measurements.*

NO release was measured with a World Precision Instrument, ISO-NO meter, equipped with a data acquisition system, and based on direct amperometric detection of NO with short response time (< 5 s) and sensitivity range 1 nM – 20 μM. The analog signal was digitalized with a four-channel recording system and transferred to a PC. The sensor was accurately calibrated by mixing standard solutions of NaNO<sub>2</sub> with 0.1 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M KI according to the reaction <sup>1S</sup>:  $4\text{H}^+ + 2\text{I}^- + \text{NO}_2^- \rightarrow 2\text{H}_2\text{O} + 2\text{NO} + \text{I}_2$

Irradiation was performed in a thermostated quartz cell (1 cm pathlength, 3 ml capacity) by using the monochromatic radiations of a fluorimeter Fluorolog-2 (mod. F-111) as light sources. NO measurements were carried out with the electrode positioned outside the light path in order to avoid false NO signal due to photoelectric interference on the ISO-NO electrode.

### Synthetic procedures.

*N*-(3-((anthracen-9-yl)methylamino)propyl)-3-(trifluoromethyl)-4-nitrobenzenamine (**1**) was synthesized in a two step synthesis as reported in Scheme 1S. Syntheses were carried out under a low intensity level of visible light.



Scheme 1S

#### *N*-(3-aminopropyl)-3-(trifluoromethyl)-4-nitrobenzenamine (**3**).

1,3-propyldiamine (1.7 ml, 20 mmol) and  $\text{Na}_2\text{CO}_3$  (2.12 g, 20 mmol) were refluxed in 50 ml of ethanol for 15 min. 4-chloro-2-(trifluoromethyl)-1-nitrobenzene (600  $\mu\text{l}$ , 4 mmol) was then added and the mixture was kept under continuous stirring for 3 days. After cooling down to ambient temperature the resulting suspension was filtered. The organic solution was concentrated under reduced pressure and purified by column chromatography (methanol 100%) to give **3** (yield 45 %) as a yellow powder. Anal. Calcd (%) for  $\text{C}_{10}\text{H}_{12}\text{F}_3\text{N}_3\text{O}_2$ : C, 45.63; H, 4.60; N, 15.96; found: C, 44.33; H, 4.92; N, 16.54. ESI-MS  $m/z$ :  $[\text{M}+\text{H}]^+$  264.2 (100%).  $^1\text{H-NMR}$   $\text{CD}_3\text{OD}$ :  $\delta$  7.93 (1H, d,  $J = 9.2$  Hz), 6.90 (1H, d,  $J = 2.6$  Hz), 6.69 (1H, dd,  $J_1 = 9.2$  Hz,  $J_2 = 2.6$  Hz), 3.19 ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$ , 2H, t,  $J = 7.0$  Hz), 2.71 ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$ , 2H, t,  $J = 7.1$  Hz), 1.74 ( $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$ , 2H, m)

#### *N*-(3-((anthracen-9-yl)methylamino)propyl)-3-(trifluoromethyl)-4-nitrobenzenamine (**1**)

Compound **3** (105 mg, 0.4 mmol),  $\text{K}_2\text{CO}_3$  (96 mg, 0.7 mmol) and  $\text{KI}$  (33 mg, 0.2 mmol) were refluxed for 15 min in a mixture toluene/acetonitrile. 9-chloromethyl anthracene (90 mg, 0.4 mmol) was then added and the mixture was kept under continuous stirring for 1 h. After cooling down to ambient temperature the resulting suspension was filtered. The organic solution was concentrated under reduced pressure and purified by column chromatography (chloroform:methanol, 99:1 + 2% triethanolamine) to give **1** (yield 60 %) as a yellow powder. Anal. Calcd (%) for  $\text{C}_{25}\text{H}_{22}\text{F}_3\text{N}_3\text{O}_2$ : C, 66.22; H, 4.89; N, 9.27; found: C, 65.01; H, 5.05; N, 9.89. ESI-MS  $m/z$ :  $[\text{M}+\text{Na}]^+$  476.3 (100%).  $^1\text{H-NMR}$   $\text{CDCl}_3-d_1$ :  $\delta$  1.89 ( $\text{NHCH}_2\text{CH}_2\text{CH}_2\text{NH}$ , 2H, m), 3.15

(AntrCH<sub>2</sub>NHCH<sub>2</sub>, 2H, t, J = 5.2 Hz), 3.27 (CH<sub>2</sub>NHC<sub>6</sub>H<sub>3</sub>NO<sub>2</sub>CF<sub>3</sub>, 2H, t, J = 5.1 Hz), 4.79 (AntrCH<sub>2</sub>NH, 2H, s), 6.28 (1H, dd, J<sub>1</sub> = 9.2 Hz, J<sub>2</sub> = 2.2 Hz), 6.49 (1H, d, J = 2.2 Hz), 6.90 (NH, 1H, s broad), 7.52 (4H, m), 7.90 (1H, d, J = 9.2 Hz), 8.042 (2H, d, J = 8.5 Hz), 8.305 (2H, d, J = 8.5 Hz), 8.46 (1H, d, J = 9.2 Hz).

(1S). D. W. Godwin, D. Che, D. M. O'Malley and Q. Zhou, *J. Neurosci. Methods*. 1997, **73**, 91.