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.
$^1$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$_2$ (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$_2$ with 0.1 M H$_2$SO$_4$ and 0.1 M KI according to the reaction

$$4H^+ + 2I^- + NO_2^- \rightarrow 2H_2O + 2NO + I_2$$

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.

\[ \text{NH}_2(CH_2)_3NH_2 \quad \text{PhMe} \quad \text{MeCN} \quad \Delta / 3 \text{d} \]

\[ \text{EtOH} / \text{Na}_2\text{CO}_3 \quad \Delta / 1 \text{h} \]

\[ \text{K}_2\text{CO}_3 / \text{KI} \quad \Delta / 1 \text{h} \]

\[ \text{H}_2\text{N}(\text{H}_2\text{C})_3\text{HN} \]

Scheme 1S

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

1,3-propylendiamine (1.7 ml, 20 mmol) and Na$_2$CO$_3$ (2.12 g, 20 mmol) were refluxed in 50 ml of ethanol for 15 min. 4-chloro-2-(trifluoromethyl)-1-nitrobenzene (600 μl, 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 C$_{10}$H$_{12}$F$_3$N$_3$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: [M+H]$^+$ 264.2 (100%).

$^1$H-NMR CD$_3$OD: δ 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 (NH$_2$CH$_2$CH$_2$CH$_2$NH, 2H, t, J = 7.0 Hz), 2.71 (NH$_2$CH$_2$CH$_2$CH$_2$NH, 2H, t, J = 7.1 Hz), 1.74 (NH$_2$CH$_2$CH$_2$CH$_2$NH, 2H, m)

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

Compound 3 (105 mg, 0.4 mmol), K$_2$CO$_3$ (96 mg, 0.7 mmol) and 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 C$_{25}$H$_{22}$F$_3$N$_3$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: [M+Na]$^+$ 476.3 (100%).

$^1$H-NMR CDCl$_3$-$d_1$: δ 1.89 (NHCH$_2$CH$_2$CH$_2$NH, 2H, m), 3.15
(AntrCH₂NHCH₃, 2H, t, J = 5.2 Hz), 3.27 (CH₂NHCH₆H₃NO₂CF₃, 2H, t, J = 5.1 Hz), 4.79 (AntrCH₂NH, 2H, s), 6.28 (1H, dd, J₁ = 9.2 Hz, J₂ = 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).