Supporting information for

Fluorometric, water-based sensor for the detection of nerve gas G mimics DMMP, DCP and DCNP.

Andreas Wild, Andreas Winter, Martin D. Hager, Ulrich S. Schubert*

Laboratory of Organic and Macromolecular Chemistry (IOMC), Friedrich-Schiller-University Jena, Humboldtstr. 10, D-07743 Jena, Germany.

Jena Center for Soft Matter (JCSM), Friedrich-Schiller-University Jena, Humboldtstr. 10, D-07743 Jena, Germany.

Dutch Polymer Institute (DPI), P.O. Box 902, 5600 AX Eindhoven, The Netherlands.

Experimental

Materials. Solvents were dried and distilled according to standard procedures. If not otherwise specified solvents or solutions were degassed by bubbling with argon one hour prior to use. 4 and 6 were synthesized according to literature procedures.1,2

Instrumentation. Preparative size exclusion chromatography (SEC) was carried out on Bio-Rad S-X1 beads (size exclusion 600-14,000 g/mol), swollen in toluene. MALDI-TOF mass spectra were measured on a Voyager-DE PRO biospectrometry workstation (Applied Biosystems) time-of-flight mass spectrometer with dithranol as matrix. UV-Vis spectra were recorded on a Perkin Elmer Lambda 45, emission spectra on a Jasco FP6500. Measurements were carried out using 10^{-6} M solutions of the respective solvents (spectroscopy grade) in 1 cm cuvettes at 25 °C. Absolute quantum yields were determined by using a Hamamatsu C 10027 Photonic Multi-Channel Analyzer. Size exclusion chromatograms (SEC) were recorded with a Shimadzu system equipped with a SCL-A10 system controller, a LC-10AD pump, a RID-10A refractive-index detector, a SPD-10A UV-detector at 254 nm and a PL gel 5 mm Mixed-D column at 50 °C utilizing a chloroform/NEt3/2-propanol (94:4:2 ratio) mixture as eluent at a flow rate of 1 mL/min. The molar masses were calculated against linear PEG standards.

Titration. To a solution of 8 or 9 in water (c = 5.8 \times 10^{-7} M) an aqueous analyte solution (c = 0.116 mM) was added and the corresponding emission spectra (\lambda_{ex} = 400 nm) measured. pH 7.0 buffered solutions were prepared using 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer.

Synthesis of 2. To a solution of H_2IO_6 (14.6 g, 64 mmol) in methanol (120 mL) was added iodine (31.7 g, 125 mmol) and the solution was stirred for 10 minutes. Subsequently 1,4-dimethoxybenzene (I) (13.8 g, 100 mmol) was added and the mixture heated at reflux for 3 h. The resulting solution was poured into a solution of sodium sulfite in water (250 mL). The precipitate was collected and washed with methanol to obtain 2 as a white product (35.5 g, 91 mmol, 91%). ^1H NMR (250 MHz, CDCl3) \delta 7.20 (s, 2H), 3.83 (s, 6H, -OCH3). ^13C NMR (62.9 MHz, CDCl3) \delta 153.28, 121.56, 85.46, 57.19.
MALDI-TOF MS (dithranol): \( m/z = 390.86 \) (100%, \([M+H]^+\)). Anal. Calcd for C₈H₁₀N₂: C, 24.64%; H, 2.07%; I, 65.09%. Found: C, 24.61%; H, 2.23%; I, 64.83.

**Synthesis of 3.** A solution of 2 (7.80 g, 20 mmol) in 90 mL of anhydrous dichloromethane was degassed by bubbling with argon for one hour and cooled to –78 °C. Subsequently, BBr₃ (3.98 mL, 42 mmol) was added drop wise. The mixture was allowed to warm to room temperature and stirred overnight. Water was carefully added and the formed precipitate collected by filtration. After crystallization from ethanol-water mixture 3 was obtained as slightly orange solid (5.9 g, 16.4 mmol, 82%). ¹H NMR (250 MHz, acetone-d₆) \( \delta \) 8.78 (s, 2H, -OH), 7.29 (s, 2H). ¹³C NMR (62.9 MHz, acetone-d₆) \( \delta \) 151.59, 124.90, 84.20. Anal. Calcd for C₈H₁₀N₂: C, 19.91%; H, 1.11; I, 70.13%. Found: C, 20.03%; H, 1.29%; I, 69.87.

**Synthesis of 5.** 3 (362 mg, 1 mmol), 4 (4.6 g, 2.2 mmol), K₂CO₃ (1.4 g, 10 mol) and 18-crown-6 (106 mg, 0.4 mmol) were dissolved in dried acetone and stirred under reflux for 48 h. Subsequently, the solvent was evaporated, and the residue extracted with dichloromethane and water. The organic phases were dried and the solvent removed in vacuo. The crude product was precipitated several times in dichloromethane/diethyl ether mixtures (1/3). 5 was obtained as a white powder (3.6 g, 0.85 mmol, 85%). ¹H NMR (300 MHz, CD₂Cl₂) \( \delta \) 7.20 (s, 2H), 4.03 (m, 4H, -CH₂-O), 3.77 (m, 4H, -CH₂-O), 3.65 – 3.35 (m, PEG backbone), 3.27 (s, 6H, -OCH₃). Anal. Calcd: C, 51.57%; H, 8.47%; I, 5.99%. Found: C, 51.73%; H, 8.57%; I, 5.71%.

**Synthesis of 7.** 5 (1.6 g, 0.4 mmol) and 4’-(4-ethynylphenyl)-2,2’:6’,2”-terpyridine (6) (283 mg, 0.85 mmol) were dissolved in THF (20 mL) and NEt₃ (10 mL). Subsequently, tetrakis(triphenylphosphine)palladium (98 mg, 0.08 mmol) and CuI (15 mg, 0.08 mmol) were added and the solution was stirred for 24 h at 30 °C. The solvent was evaporated, the residue dissolved in chloroform and washed with NH₄Claq and water. The crude product was purified by passing through a short Al₂O₃ column, preparative size exclusion chromatography and precipitation into diethyl ether. 4 was obtained as a yellow powder (1.4 g, 0.30 mmol, 76%). ¹H NMR (300 MHz, CD₂Cl₂) \( \delta \) 8.83 (s, 4H, H₃`,5`) , 8.78 (m, 4H, H₆`,6``), 8.75 (m, 4H, H₃a,b), 7.96 (m, 6H, H₄a,b, Ha,b), 7.77 (m, 2H, H₅a,b), 7.43 (m, 4H, H₅`,5``), 7.18 (s, 2H), 4.29 (m, 4H, -CH₂-O), 3.98 (m, 4H, -CH₂-O), 3.85 (m, 4H, -CH₂-O), 3.70 – 3.51 (m, PEG backbone), 3.36 (s, 6H, -OCH₃). Anal. Calcd: C, 58.90%; H, 8.32%; N, 1.81%. Found: C, 59.32%; H, 8.11%; N, 1.52%.

**Synthesis of 8.** To the bisterypyridine monomer 7 (466 mg, 0.1 mmol) in N-methylpyrrolidone (NMP, 7 mL), zinc(II) acetate (22 mg, 0.1 mmol) in NMP (2 mL) was added. The resulting solution was stirred at 100 °C for 12 h. Subsequently, the solution was poured into diethyl ether (50 mL), and the resulting metallo-polymer was filtered off and washed with diethyl ether (20 mL) and toluene (5 mL). Finally, the polymer was dried under vacuum to obtain 13 as yellow solid (44 mg, 0.01 mmol) in methanol (1 mL), zinc(II) acetate (4.4 mg, 0.02 mmol) in methanol (0.5 mL) was added. The resulting solution was stirred for 1 h. Subsequently, the solution was precipitated into pentane/diethyl ether (10/1 mL), and the resulting mixture was filtered. Finally, the complex was dried under vacuum to obtain 13 as yellow solid (44 mg,
0.009 mmol, 88%). $^1$H NMR (300 MHz, CD$_3$OD) δ 8.66 – 8.33 (m), 8.20 – 8.03 (m), 7.98 – 7.75 (m), 7.69 – 7.46 (m), 7.13 – 6.96 (m), 4.33 – 4.19 (m, -CH$_2$-O), 4.06 (s, -CH$_2$-O), 3.87 – 3.37 (m, PEG backbone), 3.36 (s, -OCH$_3$), 1.67 (s, OAc). Anal. Calcd: C, 56.51%; H, 7.96%; N, 1.68%. Found: C, 56.72%; H, 7.71; N, 1.43%.

![Figure S1](image1.png)

**Figure S1.** $^1$H NMR (CD$_3$OD, 400 MHz) titration of 7 using Zn(OAc)$_2$.

![Figure S2](image2.png)

**Figure S2.** Absorption and emission spectra (10$^{-6}$ M) of a) 7, b) 8 and c) 9 in dichloromethane (blue) and water (red).
Figure S3. $^1$H NMR (CD$_2$Cl$_2$, 300 MHz) of 8 upon addition of one equivalent NaOH.

Figure S4. Schematic representation of the proposed mechanisms of DMMP and DCP detection with 8 and 9.

The proposed mechanism for the DMMP and DCP detection by 8 and 9 is schematically depicted in Figure S4. The addition of 1 equivalent of sodium hydroxide to the Zn$^{II}$-terpyridine polymer 8 results in partially depolymerization, as visible in the $^1$H NMR (Figure S3). Subsequently, the accessibility and Lewis acidity of the Zn$^{II}$ ion is much higher, since it is complexed only weakly by one terpyridine ligand. For that reason, the addition of DMMP led to a notably increased emission intensity (Figure 7a). In analogy to 8, also 9 was applied as sensor material. The structure of 9 resembles 8, after addition of NaOH, and therefore also the sensing behavior is similar.

Since zinc(II) terpyridine complexes are effective hydrolysis catalysts for DMMP, a possible mechanism for increased emission could be a DMMP hydrolysis, followed by an attack of the hydrolysis product, enabling a decomplexation of Zn$^{II}$. However, the halve-life times in comparable systems are at least 10 h, and the emission change in our system occurs in seconds, so only a minor part can be hydrolysed. According to the shift in emission wavelength the most probable mechanism for the increased emission intensity would be a decomplexation of the Zn$^{II}$. However, the evidences given in literature like TLC or MS are not applicable, since the Zn$^{II}$ terpyridine complex is very weak and will
cleave under the applied conditions. Also a $^1$H NMR experiment with DMMP and a Zn$^{II}$ terpyridine complex gave no hint for decomplexation like it was observable for the addition of sodium hydroxide. In addition, the photo-induced electron transfer (PET) is often discussed as potential quenching mechanism. Here the LUMO of the complex (acceptor) lies in the energy gap between the HOMO and LUMO of the chromophore (donor), enabling a non-radiative deactivation of the excited chromophore. The coordination of DMMP potentially induces the removal of this energy level between the HOMO and LUMO of the chromophore, resulting in increased emission.

Figure S5. a) Relative emission ($I_a$) vs. concentration (DMMP) plot fitted to Equation 1. b) Relative emission ($I_B$) vs. concentration (DMMP) plot fitted to Equation 1

Figure S6. I) $8$ ($10^{-6}$ M); II) $8$, NaOH (both $10^{-6}$ M); III) $8$ ($10^{-5}$ M), ammonium polysulfide, reflux, FeCl$_3$, filtration. All pictures were taken after the addition of the respective amount of analyte required for the point-of-equivalence (pictures of rows a and b were taken under irradiation at $\lambda_{ex} = 365$ nm).
**Figure S7.** a) Emission spectra of 9. b) Emission spectra of 8. c) Emission spectra of 7. d) Emission spectra of 8 buffered to pH = 7.0. All in water, c = 5.8 × 10^{-7} M, λ_ex = 400 nm, upon addition of DCP (water, c = 0.116 mM).

To exclude a potential N-protonation upon DCP hydrolysis, the reaction of 8 with DCP was accomplished again in a buffered solution (pH = 7.0, Figure S7d). Here the quenching was, owing to the prevented N-protonation, marginal less efficient. Nevertheless, similar observation as for the not buffered solution (Figure S7b) could be found, underlining the robustness of the detection system.

**Figure S8.** Absorption spectra (10^{-6} M) of 8 (red) and 8 upon addition of DCP (10^{-6} M) (black) in water.
However, when a DCP solution was prepared and stored for about one hour at buffered pH 7, hydrolysis occurred. The so-produced phosphate is not able to phosphorylate the nitrogen atoms and consequently the emission increases upon addition to 8 or 9.

![Emission spectra of 8, buffered to pH = 7.0, in water, c = 5.8 \times 10^{-7} M, \lambda_{ex} = 400 nm, upon addition of DCNP (water, c = 0.116 mM).](image)

**Figure S9.** Emission spectra of 8, buffered to pH = 7.0, in water, c = 5.8 \times 10^{-7} M, \lambda_{ex} = 400 nm, upon addition of DCNP (water, c = 0.116 mM).