# Supporting Information

# Solid-Supported Zn(II)Porphyrin Tweezers as Optical Sensors for Diamines

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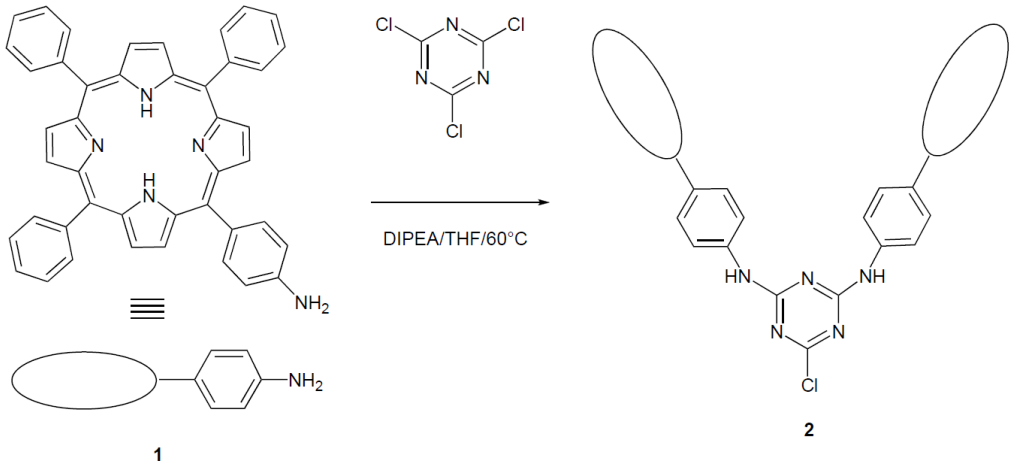
## Experimental Section

**Materials and Instrumentations**: Amino-functionalised TentaGel beads (dry diameter: 320 μm, loading: 0.21 mmol/g $NH_2$) were purchased from Rapp-Polymere (Germany). All the reagents were purchased from Sigma-Aldrich Company and were used without further purification. Anhydrous solvents Sure/Seal$^{TM}$ (Sigma-Aldrich) were used as for all the reactions. Amino-porphyrin **1** was synthesized according a previously reported procedure.[1] Controlled-Pore Glass (CPG) (120-200 mesh, pore size 700 Å, purchased from Fluka) were aminated with γ-aminopropyltriethoxysilane in toluene according the procedure reported in the literature.[2] The corresponding loading in amino-groups was $8.6x10^{-3}$ mmol/g as determined by following a reported protocol.[3] Single-bead UV-Vis analyses were performed on AvaSpec-2048 Fiber Optic Spectrometer (GHT Photonics, Italy) optically coupled to a confocal microscope (Olympus mod. CX41RF) by custom-made adapters. A custom modified web-cam replacing a microscope ocular allowed capturing digital images of the beads under observation. This apparatus permitted the registration of the UV–vis absorption spectrum of a single bead of resin. Polyamide coated fused silica capillaries used for the inlet and outlet of the flow-cells were from Supelco (ID: 0.25 mm; OD: 0.375 mm). Square glass capillaries (ID: 0.4 mm) were from Composite Metal Services Ltd. (UK). Solutions were delivered to the flow-cells by a syringe pump (KD-Scientific, Mod. KDS200) equipped with 5 mL gastight Hamilton syringes. The connection between tubing and syringes was realized with female Luer to female 10-32 adapters in conjunction with 10-32 finger tight fittings for 1/16 inch OD tubing (Upchurch).

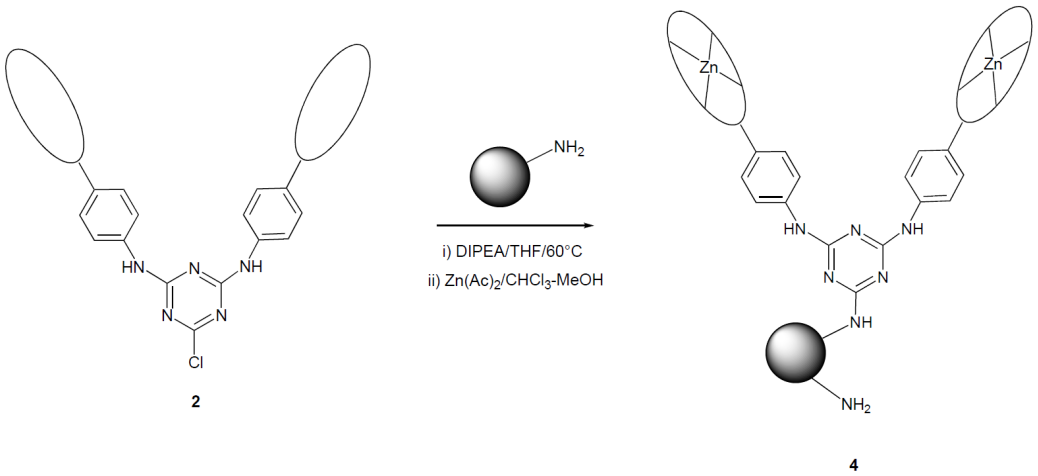
**Synthesis of compound 2**




1 2

The synthesis of compound **2** was already reported.[4] Briefly: a solution of amino-porphyrin **1** (10 mg, 16 µmol) in THF (1.0 mL) was cooled down at 0°C then cyanuric chloride (2.9 mg, 16 µmol) and DIPEA (2.5 mg, 19 µmol) were added. After 10 minutes stirring the solution was left to reach room temperature. When the reaction was complete as witnessed by TLC analysis (silica-gel, eluent:petroleum ether/ethyl acetate 3:2 v/v), another equivalent of amino-porphyrin **1** (10 mg, 16 µmol) was added together with 1.2 equivalents of DIPEA, and the reaction was left under stirring at 60°C with occasional monitoring by TLC analysis as above. The formation of the monochloro derivative **2** was confirmed by ESI-MS: 1371.5 ($[MH]^{+}$), 686.3 ($[MH_2]^{2+}$), 457.8 ($[MH_3]^{3+}$), 343.6 ($[MH_4]^{4+}$). Compound **2** was used without further purification for TentaGel-$NH_2$ functionalization.

## Preparation of material 4




100 mg of TentaGel beads (corresponding to 0.021 mmol $NH_2$ groups) were swollen in THF (1 mL) for 1h. The solvent was then removed with a pipette and the beads were allowed to equilibrate in a solution containing DIPEA (18 µL, 0.021 mmol) in THF (1mL). After 30 minutes the solution was removed and replaced with a THF solution of dimer **2** (17 µL, 0.21 µmol, 1.0 mol % with respect to the TentaGel amino groups) in 1 mL of THF. The reaction was heated at 80°C for 1 h resulting in a discoloration of the porphyrin solution and the formation of red beads. This material was recovered by filtration and washed extensively with THF. Metalation was carried out at 50°C in a mixture of $CHCl_3$ (2 mL) and a saturated solution of zinc acetate in $CH_3OH$ (0.5 mL) for 1 h. Single-bead UV-vis analysis of **Material 4** in free and as Zn(II) complex in DCM is reported in Figure S1, whereas the corresponding Zn(II) complex is reported in Figure 1A) of the paper.

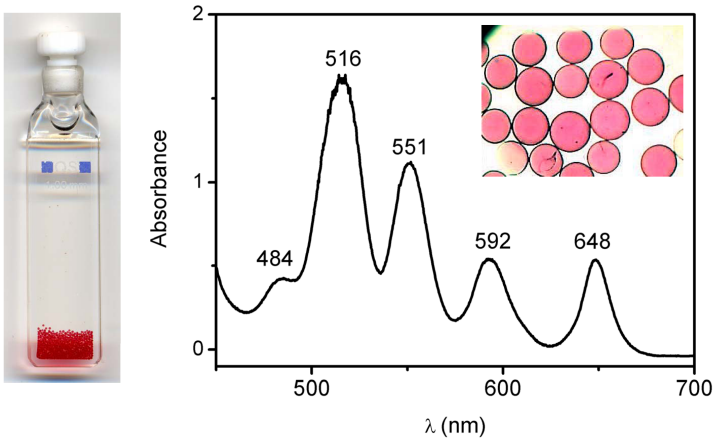
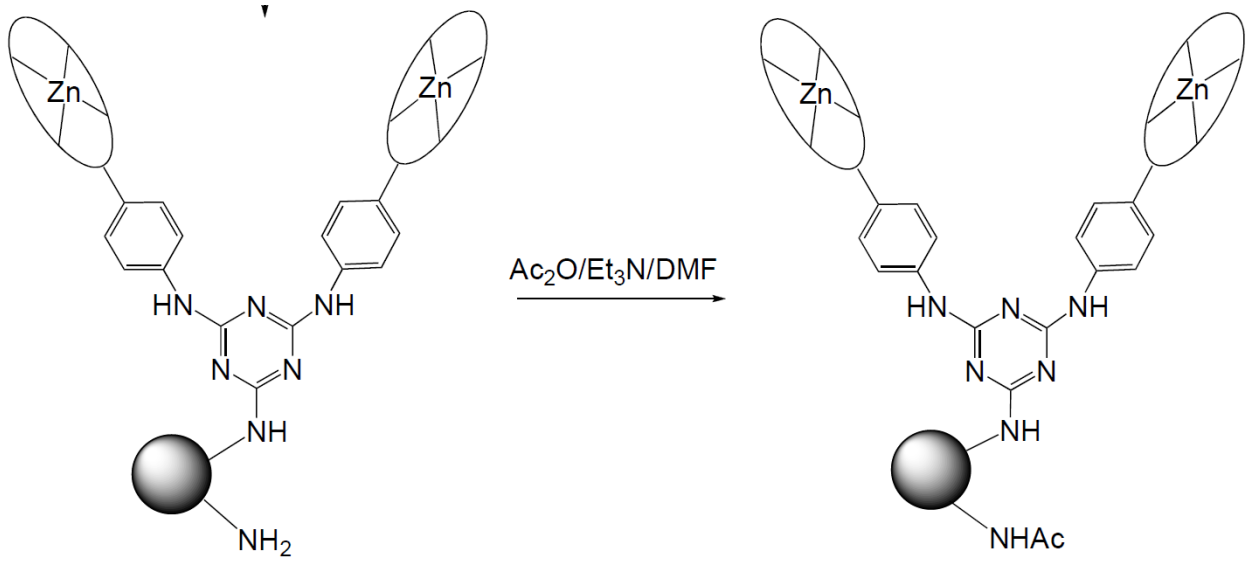



**Figure S1**: Single-bead UV-Vis spectrum of **Material 4** (free-base form) in DCM

**Preparation of material 5**




**4** **5**

Capping of the residual amino groups of **Material 4** was carried out by treatment with a mixture of triethylamine:acetic anydride:DMF (1:1:3 ratio in volume, 1 mL) at room temperature. After 30 minutes the solution was removed and replaced with the same amount of the fresh mixture. After further 30 minutes the beads were washed by using the following solvent sequence: DMF, MeOH, DCM, DMF, MeOH, DCM and $CHCl_3$. Metal insertion was carried out at 50°C in a mixture of $CHCl_3$ (2 mL) and a saturated solution of zinc acetate in $CH_3OH$ (0.5 mL) for 1 h. The single-bead of UV-vis spectrum of this material is reported in Figure 1B) of the paper.

**Flow-analysis of cadaverine with Material 5**

The flow-cell was constructed according the scheme reported in Figure S2. A functionalized bead and an unfunctionalized bead (for zeroing purposes) were introduced in a square glass capillary. The inlet and outlet fused silica capillaries coated with polyamide fitted in the square capillary and were pushed within in order to lock the two beads then they were glued to the capillary using a two components epoxy resin. To improve the mechanical stability of the flow-cell, this ensemble was in turn epoxy-glued to a microscope slide.

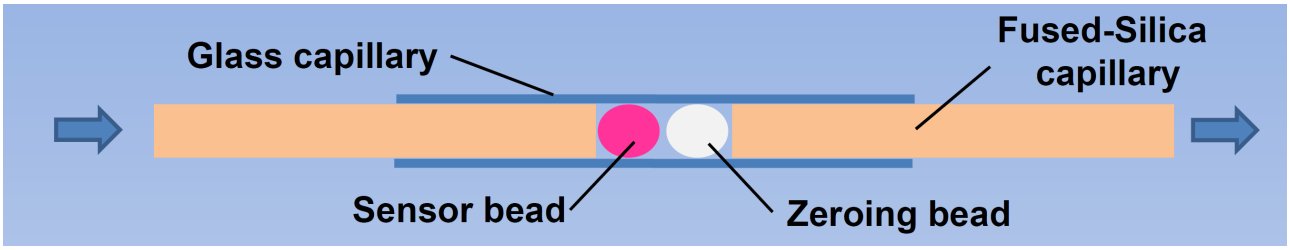



**Figure S2**: Flow-cell assembly scheme.

**Flow-analysis of cadaverine with Zn(II)-porphyrin tweezer supported onto CPG**

The CPG were characterized with the system shown in Figure S3. A miniaturized well was drilled on PMMA and filled with CPG. The well was optically coupled to the common end of an optical fiber bifurcated bundle. The two branches of the bundle were connected with a halogen lamp (Zeiss) and an Ocean Optics UV-vis spectrophotometer, respectively. The light coming from the source was scattered by the CPG and the portion of the light which was coupled back to the optical fiber bundle was modulated by the absorption properties of the CPG. A peristaltic pump allowed to deliver cadaverine solutions (in phosphate buffer at pH 7.4) to the miniaturized well. The inlet and outlet were made by two fused-silica glass capillaries having an internal diameter of 300 µm.

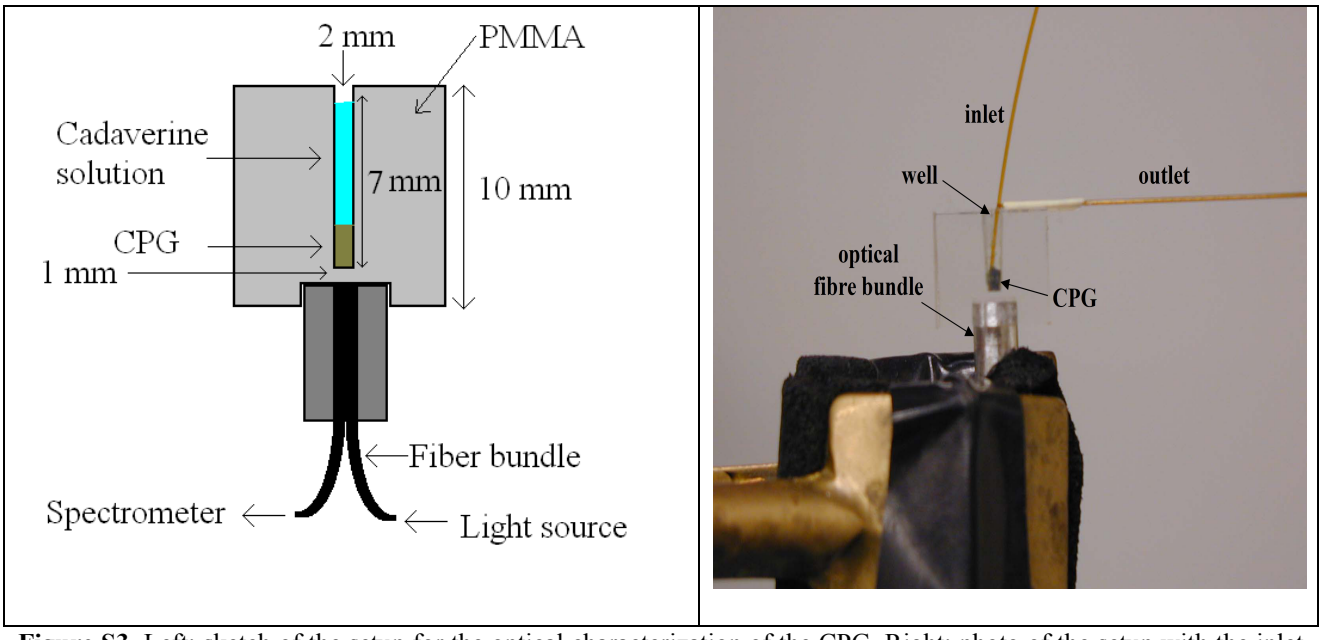



**Figure S3**. Left: sketch of the setup for the optical characterization of the CPG. Right: photo of the setup with the inlet and outlet for the cadaverine solutions, constituted by two glass capillaries.

**References**

1. W.J. Kruper, T.A. Chamberlin, M. Kochanny and K. Lang, *J. Org. Chem*. 1989, **54**, 2753-2756.

2. M. Bacci, F. Baldini and S. Bracci, *Appl. Spectr.*, 1991, **45**, 1508-1515.

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4. T. Carofiglio, A. Varotto and U. Tonellato, *J. Org. Chem*. 2004, **69**, 8121-8124.