Supporting Information

Colorimetric Detection of Trace Water in Tetrahydrofuran Using N,N'-Substituted Oxoporphyrinogens

Shinsuke Ishihara, Jan Labuta, Tomáš Šikorský, Jaroslav V. Burda, Naoko Okamoto, Hideki Abe, Katsuhiko Ariga, and Jonathan P. Hill

Table of contents

- 1. Materials
- 2. Methods
 - 2.1 General Methods
 - 2.2 Synthesis
 - 2.3 H₂O Titration in UV-Vis spectroscopy
 - 2.4 H₂O Titration in ¹H-NMR spectroscopy
 - 2.5 Multiple equilibria binding model
- 3. Additional binding study data and sensitivity (UV-Vis and NMR)
 - 3.1 Binding properties of compound **1**
 - 3.2 Binding properties of compound 2
 - 3.3 Binding properties of compound 3
 - 3.4 Binding properties of compound **4**
 - 3.5 Binding properties of compound **5**
 - 3.6 Binding properties of compound **5** + BHT
 - 3.7 Binding properties of compound 6
 - 3.8 Binding properties of compound 7
- 4. DFT and TD-DFT methods and results
 - 4.1 DFT and TD-DFT methods
 - 4.2 Additional DFT and TD-DFT results: geometry, energy and UV-Vis spectra calculations
- 5. VT-experiment
- 6. Recycling of OxP
- 7. IR spectra
- 8. Calibration map for OxP 5 rapid determination of water amount (in ppm) in THF

1. Materials

Freshly purchased tetrahydrofuran (Super Dehydrated, Stabilizer Free, $H_2O < 0.001\%$, Wako Pure Chemical Industries, Ltd.) was taken by syringe under dry N₂, and used for UV-Vis spectroscopic measurements. Methyl 4-(bromomethyl)benzoate, 4-bromobenzyl bromide, *N*,*N*dimethylformamide, potassium carbonate (Tokyo Chemical Industry, Co., Ltd.) were used as received. THF-*d*₈ was obtained from Cambridge Isotope Laboratories, Inc. Water used for titration of H₂O into THF was distilled using an Autostill WG220 (Yamato) and deionized using a Milli-Q Lab (Millipore).

2. Methods

2.1 General Methods

All ¹H-NMR spectra were obtained at 25 °C (unless stated otherwise) using an AL300 BX spectrometer (JEOL, Tokyo, Japan). Mass spectra were measured using a Shimadzu-Kratos Axima CFR+ MALDI-TOF mass spectrometer with dithranol as matrix. Electronic absorption spectra were measured using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer at 25 °C (unless otherwise stated). Concentration of H₂O in tetrahydrofuran is defined in parts per million (ppm) per volume. IR spectra were measured using a Nicolet NEXUS 670 FT-IR spectrophotometer with samples deposited on CaF₂ substrate under dry N₂.

2.2 Synthesis

Preparation of OxPs **1** and **7** have been reported previously.^{S1} OxPs **2**, **3**, **6** were synthesized by *N*-alkylation of OxP **1** using the corresponding benzyl bromide.^{S1,S2}

N₂₁,N₂₃-Bis(4-bromobenzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene) porphyrinogen (OxP 2)

¹H-NMR (THF- d_8 , 300 MHz): $\delta = 9.81$ (s, 2H, NH), 7.65 (d, 4H, hemi-quinone-H), 7.28 (d, 4H, Ar-H), 7.18 (d, 4H, hemi-quinone-H), 7.00 (d, 4H, pyrrole β -H), 6.71 (d, 4H, Ar-H), 6.69 (s, 4H, pyrrole β -H), 4.52 (s, 4H, bezyl-CH₂), 1.34 (s, 36H, *tert*-butyl), 1.26 (s, 36H, *tert*-butyl) ppm. MALDI-TOF-MS: calcd for C₉₀H₁₀₂Br₂N₄O₄ 1462.62 m/z, found 1463.52 m/z [M+H]⁺.

$N_{21},N_{23}\mbox{-Bis}(4\mbox{-(methoxycarbonyl)benzyl})\mbox{-}5,10,15,20\mbox{-}(3,5\mbox{-}di\mbox{-}tert\mbox{-}butyl\mbox{-}4\mbox{-}oxo\mbox{-}2,5\mbox{-}cyclohexadienylidene)porphyrinogen (OxP 3)$

¹H-NMR (CDCl₃, 300 MHz): $\delta = 9.66$ (s, 2H, NH), 7.82 (d, 4H, Ar-H), 7.56 (s, 4H, hemiquinone-H), 7.03 (s, 4H, hemi-quinone-H), 6.89 (s, 4H, pyrrole β -H), 6.82 (d, 4H, Ar-H), 6.57 (s, 4H, pyrrole β -H), 4.56 (s, 4H, bezyl-CH₂), 3.84 (s, 6H, COOCH₃), 1.34 (s, 36H, *tert*-butyl), 1.21 (s, 36H, *tert*-butyl) ppm. MALDI-TOF-MS: calcd for C₉₄H₁₀₈N₄O₈ 1421.82 m/z, found 1423.31 m/z [M+H]⁺.

N_{21} , N_{22} , N_{23} , N_{24} -Tetrakis(4-(methoxycarbonyl)benzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen (OxP 6)

¹H-NMR (CDCl₃, 300 MHz): δ = 7.93 (d, 8H, Ar-H), 7.29 (s, 8H, hemi-quinone-H), 6.77 (d, 8H, Ar-H), 6.75 (s, 8H, pyrrole β -H), 4.64 (s, 8H, benzyl-CH₂), 3.93 (s, 12H, COOCH₃), 1.31 (s, 72H, *tert*-butyl) ppm. MALDI-TOF-MS: calcd for C₁₁₂H₁₂₄N₄O₁₂ 1717.92 m/z, found 1718.83 m/z [M+H]⁺.

N₂₁,N₂₃-Di-(4-carboxybenzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-

cyclohexadienylidene)porphyrinogen (OxP 4)

OxP 3 (20mg) was dissolved in THF (50 mL), and added to a mixture of methanol (10 mL) and KOH (100 mg) in H_2O (5 mL). The solution was refluxed for 24 hr then the mixture was allowed to cool to room temperature, and organic solvents were evaporated under reduced pressure. The purple powder was dissolved in dichloromethane, and washed with 0.1 M HCl aq. and distilled water twice. Dichloromethane was evaporated and the resulting solid was dried in vacuo overnight (Yield:

quantitative). ¹H-NMR (CDCl₃-CD₃OD, 300 MHz): $\delta = 7.85$ (d, 4H, Ar-H), 7.62 (s, 4H, hemiquinone-H), 7.13 (s, 4H, hemi-quinone-H), 6.95 (s, 4H, pyrrole β -H), 6.83 (d, 4H, Ar-H), 6.71 (s, 4H, pyrrole β -H), 4.56 (s, 4H, benzyl-CH₂), 1.23 (m, 72H, *tert*-butyl) ppm. MALDI-TOF-MS: calcd for C₉₂H₁₀₄N₄O₈ 1393.79 m/z, found 1394.94 m/z [M+H]⁺.

*N*₂₁,*N*₂₃-Bis(4-carboxybenzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene) porphyrinogen Disodium Salt (OxP 5)

OxP 4 (5 mg) was dissolved in THF (20 mL), and added to a mixture of methanol (5 mL) and NaOH (5 mg) in H₂O (2 mL). The mixture was stirred at room temperature, then solvents were evaporated under reduced pressure. The purple powder was washed with distilled water several times on a 0.22 µm PVDF filter. The residue was dissolved in THF, solvent was evaporated under reduced pressure and dried in vacuo overnight (Yield: quantitative). ¹H-NMR (CDCl₃ CD₃OD, 300 MHz): δ = 7.73 (d, 4H, Ar-H), 7.67 (s, 4H, hemi-quinone-H), 7.30 (s, 4H, hemi-quinone-H), 6.98 (s, 4H, pyrrole β -H), 6.75 (d, 4H, Ar-H), 6.61 (s, 4H, pyrrole β -H), 4.60 (s, 4H, bezyl-CH₂), 1.33 (s, 36H, *tert*-butyl), 1.25 (s, 36H, *tert*-butyl) ppm. MALDI-TOF-MS: calcd for C₉₂H₁₀₂N₄O₈Na₂ 1436.75 m/z, found 1395.10 m/z [M - 2Na + 3H]⁺.

2.3 H₂O Titration by UV-Vis spectroscopy.

To a THF solution of OxP $(3.5 \times 10^{-6} \text{ M}, 3 \text{ mL})$ in a 1cm quartz cell with screw cap, ultrapure water was added using a microsyringe. After shaking the solution, UV-Vis spectra were measured at 25 °C. In a range of H₂O = 0-400 ppm, stock solution (THF containing 1-2 vol.% of H₂O) was used for titration. Starting from H₂O > 400 ppm, water was added directly by micro-syringe.

2.4 H₂O Titration by ¹H-NMR spectroscopy.

To a THF- d_8 solution of OxP (7.0×10⁻⁴ M, 0.5 mL) in an NMR sample tube, ultrapure water was added using a microsyringe. After shaking the solution, ¹H-NMR spectra were measured at 25 °C. In a range of H₂O = 0-5000 ppm, stock solution (THF- d_8 containing 10 vol.% of H₂O) was used for titration. Starting from H₂O > 5000 ppm, water was added directly by micro-syringe.

2.5 Multiple equilibria binding model

The model of multiple equilibria binding (Ref. 11 in the main manuscript) has been adapted because the system of OxP and water appears to exhibit negative cooperativity (see Hill's plot below) and simple 1:1 stoichiometry binding models show significantly different equilibrium binding constants when calculated at different wavelengths in UV-Vis spectra. This indicates that more than two species (free OxP and OxP bound to 1 water molecule) are present in the system. Moreover, TD-DFT calculations illustrate the possibility of binding several water molecules in independent manner (as indicated by additivity of their interaction energy). However, the largest variations in electronic absorption spectra appear to originate from water binding to quinonoid carbonyl groups. The effect of THF as polar aprotic solvent (dipole moment 1.63 D) can also influence OxP's affinity to water binding. Therefore, in the multiple equilibria binding model the binding isotherm is constructed as the average number of water molecules per single OxP, i, and can be expressed using the following formula

$$\bar{i} = \frac{\sum_{i}^{n} i\beta_{i} [\mathbf{W}]_{t}^{i}}{1 + \sum_{i}^{n} \beta_{i} [\mathbf{W}]_{t}^{i}}$$
(S1)

where stepwise binding constants K_i are expressed in terms of overall binding constants $\beta_i = \prod_{j=1}^{i} K_j$,

 $[W]_t$ is total concentration of water in THF (approximation $[OxP] \leq [W]$ is used) and *n* describes the maximum number of water molecules bound to OxP.

The value of *n* is an important piece of information and is sometimes obvious from structural considerations. However, in the current case we have tried to keep *n* minimal (and also subject to least-squares fitting procedure). In order to obtain good fits (UV-Vis and/or NMR binding isotherms) the *n* value is always $n \le 3$. Then the UV-Vis binding isotherm $A([W]_t)$ takes the form

$$A([W]_{t}) = \frac{\Delta A \times \sum_{i}^{n} i\beta_{i} [W]_{t}^{i}}{1 + \sum_{i}^{n} \beta_{i} [W]_{t}^{i}} + B$$
(S2)

where ΔA (at a particular wavelength) is the average change in OxP's absorbance per one bound water molecule and *B* is the initial absorbance of free OxP (at particular wavelength).

The NMR binding isotherm $\delta([W]_t)$ takes the form

$$\delta([\mathbf{W}]_{t}) = \frac{\Delta \delta \times \sum_{i}^{n} i \beta_{i} [\mathbf{W}]_{t}^{i}}{1 + \sum_{i}^{n} \beta_{i} [\mathbf{W}]_{t}^{i}} + B_{\text{NMR}}$$
(S3)

where $\Delta \delta$ is the average change in OxP's NH resonance shift per bound water molecule and B_{NMR} is the initial chemical shift of free OxP's NH resonance.

Stepwise binding constants were evaluated for UV-Vis and NMR binding isotherms separately using the least-squares fitting procedure. UV-Vis results usually indicate $n \le 3$ and lower K_i than NMR results where $n \le 2$ (compounds **2** and **3**). TD-DFT calculations on **2** show that the maximum change in absorption spectrum originates from water bound to quinonoid C=O where more molecules can be bound than at pyrrolic NH. NMR is sensitive mainly to pyrrolic NH binding mode so that the *n* values obtained from each method differ.

3. Additional binding study data and sensitivity (UV-Vis and NMR)



3.1 Binding properties of compound 1 (*meso*-tetrakis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen)

Figure S1. (a) Experimental electronic absorption spectra of **1** in THF (initial $[1] = 3.9 \times 10^{-6}$ M, 1 cm cell, 25 °C) during titration with water. Inset shows magnification of the region about the isosbestic point. (b) Electronic absorption spectra corrected for dissolution during water titration (since dissolution is less then 10 % we assume a linear correction in absorbance). Inset shows magnified region around isosbestic point. (c) Hill's plot (θ is saturation, $[W]_t$ is total concentration of water in THF in units M) as obtained from dissolution-corrected spectra [Fig. (S1b)] indicating negative cooperativity. (d) Variation of absorption at 519 nm and 600 nm including binding isotherm (red curve) based on the multiple equilibria model (n = 2, $\Delta A_{600} = 0.027$ a.u., $B_{600} = 0.319$ a.u.). Blue line indicates initial sensitivity. (e) Hill's plot (NH resonance of **1**) as obtained from an NMR titration experiment in THF- d_8 (initial [**1**] = 8.7×10^{-4} M, dissolution correction was applied, 25 °C). (f) Chemical shift of NH resonance in response to water titration. Binding isotherm (red curve, multiple equilibria model) and initial sensitivity (blue line) are shown. In the inset the low water concentration region is magnified. (g) Binding constants and sensitivity as obtained from NMR titration experiment (n = 1, $\Delta \delta = 1.434$ ppm, $B_{\rm NMR} = 9.870$ ppm). ^aThe unit ppm/ppm describes NMR chemical shift change (ppm) divided by water concentration in THF- d_8 (ppm).



3.2 Binding properties of compound 2 (*N*₂₁,*N*₂₃-bis(4-bromobenzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen)

Figure S2. (a) Experimental electronic absorption spectra of 2 in THF (initial $[2] = 3.4 \times 10^{-6}$ M, 1 cm cell, 25 °C) during titration with water . Inset shows magnification of the region about the isosbestic point. (b) Electronic absorption spectra corrected for dissolution during water titration (since the dissolution is less then 10 % we assume a linear correction in absorbance). Inset shows a magnification of the region about the isosbestic point. (c), (d) Hill's plot (θ is saturation, [W]_t is total concentration of water in THF in units M) as obtained from dissolution-corrected spectra [Fig. (S2b)] indicating negative cooperativity. (e) Variation of absorption at 507 nm and 600 nm including binding isotherms (red curves) based on the multiple equilibria model (n = 3, $\Delta A_{507} = -0.042$ a.u., B_{507} = 0.484 a.u., ΔA_{600} = 0.052 a.u., B_{600} = 0.131 a.u.). Blue lines indicate initial sensitivity. (f) Hill's plot (NH resonance of 2) as obtained from NMR titration experiment in THF- d_8 (initial [2] = 7.0×10⁻⁴ M, dissolution correction was applied, 25 °C). (g) Chemical shift of NH resonance in response to water titration. Binding isotherm (red curve, multiple equilibria model) and initial sensitivity (blue line) are shown. In inset the low water concentration region is magnified. (h) Binding constants and sensitivity as obtained from an NMR titration experiment (n = 2, $\Delta \delta = 0.684$ ppm, $B_{\text{NMR}} = 9.508$ ppm). ^aThe unit ppm/ppm describes NMR chemical shift change (ppm) divided by water concentration in THF- d_8 (ppm).



3.3 Binding properties of compound 3 (*N*₂₁,*N*₂₃-bis(4-(methoxycarbonyl)benzyl)-5,10,15,20-(3,5-di*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen)

Figure S3. (a) Experimental electronic absorption spectra of **3** in THF (initial $[3] = 4.0 \times 10^{-6}$ M, 1 cm cell, 25 °C) during titration with water. Inset shows magnification of the region about the isosbestic point. (b) Electronic absorption spectra corrected for dissolution during water titration (since the dissolution is less then 10 % we assume linear correction in absorbance). Inset shows a magnification of the region about the isosbestic point. (c) Hill's plot (θ is saturation, $[W]_t$ is total concentration of water in THF in units M) as obtained from dissolution-corrected spectra (at 600 nm) [Fig. (S3b)] indicating negative cooperativity. (d) Variation of absorption at 507 nm and 600 nm including binding isotherm (red curve) based on the multiple equilibria model (n = 3, $\Delta A_{600} = 0.053$ a.u., $B_{600} = 0.174$ a.u.). Blue line indicates initial sensitivity. (e) Hill's plot (NH resonance of **3**) as obtained from NMR titration experiment in THF- d_8 (initial [**3**] = 7.1×10^{-4} M, dissolution correction was applied, 25 °C). (f) Chemical shift of NH resonance in response to water titration. Binding isotherm (red curve, multiple equilibria model) and initial sensitivity (blue line) are shown. In inset the low water concentration region is magnified. (g) Binding constants and sensitivity as obtained from NMR titration experiment (n = 2, $\Delta \delta = 0.666$ ppm, $B_{NMR} = 9.535$ ppm). ^aThe unit ppm/ppm describes NMR chemical shift change (ppm) divided by water concentration in THF- d_8 (ppm).





Figure S4. (a) Experimental electronic absorption spectra of **4** in THF (initial $[4] = 3.7 \times 10^{-6}$ M, 1 cm cell, 25 °C) during titration with water. Inset shows magnification of the region about the isosbestic point. (b) Electronic absorption spectra corrected due to dissolution during water titration (since the dissolution is less then 10 % we assume linear correction in absorbance). Inset shows a magnification of the region about the isosbestic point. (c), (d) Hill's plot (θ is saturation, [W]_t is total concentration of water in THF in units M) as obtained from dissolution-corrected spectra [Fig. (S4b)] indicating negative cooperativity. (e) Variation of absorption at 507 nm and 600 nm including binding isotherms (red curves) based on the multiple equilibria model (n = 3, $\Delta A_{507} = -0.020$ a.u., $B_{507} = 0.536$ a.u., $\Delta A_{600} = 0.039$ a.u., $B_{600} = 0.164$ a.u.). Blue lines indicate initial sensitivity.



3.5 Binding properties of compound 5 (*N*₂₁,*N*₂₃-bis(4-carboxybenzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen, disodium salt)

Figure S5. (a) Experimental electronic absorption spectra of **5** in THF (initial [**5**] = 3.5×10^{-6} M, 1 cm cell, 25 °C) during titration with water. Inset shows magnification of the region about the isosbestic point. (b) Electronic absorption spectra corrected for dissolution during water titration (since the dissolution is less then 10 % we assume linear correction in absorbance). Inset shows magnification of the region about the isosbestic point. (c), (d) Hill's plot (θ is saturation, [W]_t is total concentration of water in THF in units M) as obtained from dissolution-corrected spectra [Fig. (S5b)] indicating negative cooperativity. *Figures 2c,d in main manuscript show the dissolution-corrected binding isotherm. Additional data from the multiple equilibria binding model (n = 3, $\Delta A_{507} = -0.034$ a.u., $B_{507} = 0.494$ a.u., $\Delta A_{600} = 0.055$ a.u., $B_{600} = 0.168$ a.u.).

3.6 Binding properties of compound 5 + **BHT** (N_{21} , N_{23} -bis(4-carboxybenzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen, disodium salt, and 3,5-di-*tert*-butyl-4-hydroxytoluene)



Figure S6. (a) Experimental electronic absorption spectra of **5** in THF (initial [**5**] = 4.2×10^{-6} M, BHT stabilizer 600 ppm, 1 cm cell, 25 °C) during titration with water. Inset shows magnification of the region about the isosbestic point. (b) Electronic absorption spectra corrected for dissolution during water titration (since the dissolution is less then 10 % we assume linear correction in absorbance). Inset shows magnification of the region about the isosbestic point. (c), (d) Hill's plot (θ is saturation, [W]_t is total concentration of water in THF in units M) as obtained from dissolution-corrected spectra [Fig. (S6b)] indicating negative cooperativity. (e) Variation of absorption at 519 nm and 600 nm including binding isotherms (red curves) based on the multiple equilibria model (n = 3, $\Delta A_{519} = -0.027$ a.u., $B_{519} = 0.586$ a.u., $\Delta A_{600} = 0.043$ a.u., $B_{600} = 0.187$ a.u.). Blue lines indicate initial sensitivity.

3.7 Binding properties of compound 6 (*N*₂₁,*N*₂₂,*N*₂₃,*N*₂₄-tetrakis(4-(methoxycarbonyl)benzyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen)



Figure S7. (a) Experimental electronic absorption spectra of **6** in THF (initial [**6**] = 4.0×10^{-6} M, 1 cm cell, 25 °C) during titration with water. (b) Electronic absorption spectra corrected for dissolution during water titration (since the dissolution is less then 10 % we assume linear correction in absorbance). Note that no isosbestic point is present. (c) Variation of absorption at 507 nm and 600 nm including binding isotherms (red curves) based on the multiple equilibria model (n = 1, $\Delta A_{507} = 0.006$ a.u., $B_{507} = 0.571$ a.u., $\Delta A_{600} = 0.007$ a.u., $B_{600} = 0.055$ a.u.). Blue lines indicate initial sensitivity. Note that experimental error is comparable to acquired values of absorbance and compound **6** show only little response to water in general.

3.8 Binding properties of compound 7 (*N*₂₁,*N*₂₂-bis(naphth-2-ylmethyl)-5,10,15,20-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienylidene)porphyrinogen)



Figure S8. (a) Chemical structure of compound 7. (b) Experimental electronic absorption spectra of 7 in THF (initial [7] = 3.5×10^{-6} M, 1 cm cell, 25 °C) during titration with water. Inset shows a magnification of the region about the isosbestic point. (c) Electronic absorption spectra corrected for dissolution during water titration (since the dissolution is less then 10 % we assume linear correction in absorbance). Inset shows magnified region about the isosbestic point. (d), (e) Hill's plot (θ is saturation, [W]_t is total concentration of water in THF in units M) as obtained from dissolutioncorrected spectra [Fig. (S8c)] indicating negative cooperativity. (f) Variation of absorption at 507 nm and 600 nm including binding isotherms (red curves) based on the multiple equilibria model (n = 3, $\Delta A_{507} = -0.057$ a.u., $B_{507} = 0.495$ a.u., $\Delta A_{600} = 0.061$ a.u., $B_{600} = 0.146$ a.u.). Blue lines indicate initial sensitivity. (g) Binding constants and sensitivity as obtained from UV-Vis spectra.

4. DFT and TD-DFT methods and results

4.1 DFT and TD-DFT methods

Equilibrium geometries of all the studied molecules were calculated without any symmetry constraints, using the local meta-GGA M06-l functional from Truhlar's group^{S3} with Pople's 6-31G(d,p) basis set.^{S4} To ensure that calculated structures were local minima on the potential energy surface, frequency calculations were performed and no negative values were found. Interaction energies were computed at the same level of theory as geometry optimization, using correction scheme according to Boys and Bernardi to account for basis set superposition error.^{S5} Excitation energies of the 4 lowest singlet-singlet transitions at the optimized geometry were obtained with hybrid-meta-GGA functional M06-2X^{S6} from the same family and Pople's basis set augmented with diffusion function on all atoms, i.e. 6-31++G(d,p). Using the calculated result, the electronic absorption spectra were simulated using gauss- shaped curves with variance, sigma, of 50 – 70 nm and the area under curve proportional to transition probability. All computations were performed using the Gaussian 09 program-package (Revision A.02)^{S7} in the gas phase using a pruned (99,590) grid.^{S8}

4.2 Additional DFT and TD-DFT results: geometry, energy and UV-Vis spectra calculations

Table S1. Summary of energy, interaction energy and UV-Vis spectral data as calculated for all complexes of OxP 2 (bromine atoms at benzyl substituents have been replaced with hydrogen atoms to simplify the calculations) and water. Note the additivity in interaction energies.

	OxP-free		OxP-H ₂ Oª		OxP-1H ₂ O ^b		OxP-2H ₂ O ^b		OxP-4H ₂ O ^b		OxP-5H₂O°	
Energy / Hartree	-4011.852		-4088.294		-4088.274		-4164.698		-4317.542		-4393.985	
BSSE corrected energy / Hartree	-4011.852		-4088.288		-4088.270		-4164.689		-4317.526		-4393.963	
Energy of H ₂ O / Hartree	-76.411		-76.411		-76.411		-76.411		-76.411		-76.411	
Interaction energy / Hartree	0		-0.0259		-0.0078		-0.0156		-0.0301		-0.0563	
Interaction energy / kJ/mol	0		-68.0		-20.5		-41.0		-79.1		-147.7	
UV-Vis spectrum	wavelen ght / nm	relative intensity	wavelen ght / nm	relative intensity	wavelen ght / nm	relative intensity	wavelen ght / nm	relative intensity	wavelen ght / nm	relative intensity	wavelen ght / nm	relative intensity
State 1	560.6	0.004	559.4	0.011	564.2	0.002	566.0	0.005	573.6	0.003	571.7	0.010
State 2	514.3	1.951	518.4	1.984	517.5	1.964	519.7	1.977	526.4	2.015	530.1	2.045
State 3	495.3	1.191	485.9	1.106	498.1	1.220	500.7	1.255	507.4	1.301	496.6	1.230
State 4	452.2	0.021	449.8	0.009	455.1	0.007	454.7	0.060	447.7	0.000	445.3	0.025

^aWater bound to pyrrolic NH. ^bWater bound to quinonoid C=O groups. ^cOne water bound to pyrrolic NH and four water molecules bound to respective quinonoid C=O groups.



Figure S9. (a) Plot of calculated absorption wavelength based on structures from Table S1. (b) Top and side views of calculated hydrogen bonded structures $OxP-1H_2O$ and $OxP-2H_2O$ (in both, the water is bound to quinonoid C=O groups) based on DFT calculations (M06-L/6-31G(d,p), at 0 K in vacuum.). Bromine atoms at benzyl substituents have been replaced with hydrogen atoms to simplify calculations.



Figure S10. Electrostatic potential surfaces (ESP) of all calculated structures at electronic density $0.001 \ e/au^3$ (rainbow scale in Hartree, 1 Hartree = 627.51 kcal/mol).

5. VT-experiment



Figure S11. Temperature dependency of UV-Vis spectral changes of OxP 5 in THF containing different amounts of water. (a) in anhydrous THF, (b) in THF with 3700 ppm H₂O, and (c) in THF with 33000 ppm H₂O.

6. Recycling of OxP



Figure S12. (a) UV-Vis spectra of OxP **5** in repeated cycles of anhydrous THF and hydrated THF, showing that OxP can be reused. (b) Plots of Abs. at 507 nm and 600 nm in repeated cycles of anhydrous THF and hydrated THF.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is C The Royal Society of Chemistry 2012

7. IR spectra



Figure S13. IR spectra of OxP 4 and OxP 5 on CaF_2 substrate.

8. Calibration map for OxP 5 – fast determination of water amount (in ppm) in THF

A calibration curves can be derived in order to determine readily and accurately the amount of water in THF. OxP **5** has been adopted for this purpose since is show highest sensitivity and strongest affinity to water. The method is based on measurement of a single UV-Vis spectrum of water contaminated THF containing a sufficient concentration of OxP **5** (0.2 a.u. < max. absorbance at 507 nm < 1 a.u. equivalent to 1.4×10^{-6} M < [**5**] < 7.0×10^{-6} M) which need not be known exactly in advance. (Note: molar extinction coefficient of OxP **5** in anhydrous THF at spectral maximum 507 nm is $\varepsilon = 141150$ L mol⁻¹ cm⁻¹.) We can derive calibration curve from binding isotherm at 507 nm (isotherm at 600 nm is too strongly temperature dependent, see Fig. S11) and relation for isosbestic point at 535 nm considering that small deviation in OxP's concentration has a linear effect on absorbance change. Then the following equations can be constructed

$$A'_{507} = A_{507}(p)\frac{c'}{c_0}$$
(S4a)

$$A'_{535} = A_{535} \frac{c'}{c_0}$$
(S4b)

where A'_{507} and A'_{535} are absorbance (a.u.) at 507 nm and 535 nm (isosb. point), respectively, of the investigated sample containing an unknown quantity of water. $A_{507}(p)$ is binding isotherm as calculated from Eq. S2. and expressed in terms of independent variable p (instead of [W]_t), which is the amount of water in THF in ppm (in volume) units. A_{535} is absorbance at isosbestic point as obtained from titration experiment. c_0 is concentration of OxP **5** as determined in the titration experiment (see Fig. S5) and c' is concentration of OxP **5** in the investigated sample (which does not need to be precisely known). Eqs. S4 can be transformed into the form

$$\frac{A'_{507}}{A'_{535}} = \frac{A_{507}(p)}{A_{535}}$$
(S5)

where $r = \frac{A'_{507}}{A'_{535}}$ is the ratio of absorbances determined from investigated sample. In Eq. S5

qualitative independence of UV-Vis spectrum on OxP's concentration is anticipated, howerver, when calibration curve was subject to proof if was found that the dependence on OxP's concentration cannot be neglected. Therefore, two-parameter criteria were found in order to assess amount of water.

One parameter is ratio $r = \frac{A'_{507}}{A'_{535}}$ and second is A'_{535} . Two-dimensional map can be constructed based

on calibration curves measures at different pairs of r and A'_{535} (see Fig. S14). In the calibration map weak dependenci on A'_{535} can be seen but also high accuracy especially in low water concentration region (small p).



Figure S14. Calibration map (OxP 5) for determination of water concentration (in ppm) in THF at 25°C. Data points (lines) show dependence of *r* on A_{535} (in a.u.) at constant *p* (in ppm); circle (p < 10 ppm), square (p = 50 ppm), triangle (p = 200 ppm), diamond (p = 500 ppm), half-circle (p = 1000 ppm), half-square (p = 2000 ppm), half-triangle (p = 3000 ppm), half-diamond (p = 5000 ppm).

REFERENCES

S1. J. P. Hill, W. Schmitt, A. L. McCarty, K. Ariga and J. P. Hill, Eur. J. Org. Chem., 2005, 2893.

S2. J. P. Hill, I. J. Hewitt, C. E. Anson, A. K. Powell, A. L. McCarthy, P. Karr, M. Zandler, F. D'Souza, J. Org. Chem., 2004, 69, 5861.

S3. Y. Zhao and D. G. Truhlar, J. Chem. Phys., 2006, 125, 194101.

S4. R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 1971, 54, 724.

S5. S. F. Boys and F. Bernardi, Mol. Phys., 1970, 19, 553.

S6. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc., 2008, 120, 215.

S7. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S8. V. I. Lebedev and A. L. Skorokhodov, Russian Acad. Sci. Dokl. Math., 1992, 45, 587.