Recovery and recycling of homogeneous catalysts: silica as temporary or permanent support

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Phosphorus Ligand Imaging with Two-Photon Fluorescence Spectroscopy: The way open for Rational Catalyst Immobilization

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Abstract. The advantages of homogeneous transition catalysts are to some extend damped by the necessity to separate, and if possible recycle, the catalyst from the solution. Immobilization of catalysts on a solid support is a frequently used strategy, but the general drawback is a lower catalyst activity and selectivity. We now report a new strategy to monitor catalyst immobilization by imaging with two-photon fluorescence microscopy at sub-micrometer level. To this end a diphosphine ligand with intrinsic fluorescent properties, which gives rise to active and selective rhodium hydroformylation catalysts was immobilized on a glass surface using traditional methods. The imaging of the immobilized ligand uncovered clustering of the ligands and therefore of the catalyst particles, explaining part of the deterioration of the catalyst performance compared to the homogeneous phase system. Based on these results a simple new immobilization process was developed that did not give rise to clustering and the supported rhodium catalysts gave activities and selectivities that are close to the homogeneous catalyst, with the advantage that separation and recycling can be done by simple filtration processes.

Catalyst recovery is an important topic in the area of homogeneous catalysis since the product-catalyst separation is one of the main obstacles towards application of these classes of catalysts. So far, several strategies for catalyst recycling have been explored, but a general strategy remains elusive. A widely studied approach to facilitate catalyst-product separation is the attachment of homogeneous catalysts to polymeric organic, inorganic, hybrid, or dendrimeric supports. Inorganic materials have shown to be particularly suited as solid support for homogeneous catalysts because of their physical strength and chemical inertness and many of such immobilized catalytic systems have been reported. A common drawback, however, remains the generally lower activity and selectivity compared to the homogeneous counterpart. It is known that the properties of the solid support affects the catalytic reaction to a certain extend. Surprisingly, an in-depth investigation of the effect of the immobilization process on the
performance of the catalyst appears to be lacking. To gain more insight into the immobilization of transition metal catalysts we set out to design a method for the detection of diphosphine ligands on surfaces. The ligand studied acts as a fluorescence probe and the detection is achieved by two-photon excitation fluorescence microscopy. In principle, this allows the immobilization product to be imaged with high spatial resolution (down to single molecules). Here we report our results of the first study of the immobilization process employing an intrinsically fluorescent ligand imaged on a submicrometer level and the venue toward rational catalyst design.

Two-photon excitation fluorescence microscopy has shown an astonishing potential, but application has been mainly restricted for imaging biological samples. Two-photon absorption is a process where two photons are absorbed simultaneously, exciting e.g. a molecule to a higher-lying electronic state, with the energy increase being equal to the sum of the photon energies. Such a process only occurs at a very high flux of photons, restricting the excitation to a very small focal volume, with no appreciable off-focal fluorescence. The two-photon selection rule yields low background fluorescence and hence high contrast in the images can be produced.

![Scheme 1](image)

**Scheme 1.** Immobilization of nixantphos 2 on glass coverslips and silica for imaging and catalysis with the aim of correlating the immobilization process to the catalysis results.
Organic materials that show strong two-photon absorption (TPA) have attracted considerable attention owing to its growing applications in various fields such as photonics and nanotechnology. Fundamental efforts have been focused to establish the structure-property relationship of the chromophore and the TPA cross-section ($\delta$, the probability of a transition to a given state). Molecules with large TPA cross-sections often consist of electron donor(s) and/or acceptor(s) connected to a $\pi$-conjugate system in a symmetrical (or quadrupolar, D-\(\pi\)-A-\(\pi\)-D or A-\(\pi\)-D-\(\pi\)-A) or asymmetrical (or dipolar, D-\(\pi\)-A) substitution arrangement.

Our attention, part of a broader effort to study the immobilization of transition metal catalysts, was directed towards the well known class of xanthene-based phosphorous ligands known as xantphos. These ligands have outstanding catalytic properties in various transition metal catalyzed reactions (e.g., Rh-catalyzed hydroformylation), their facile coordination behavior to various metals and high stability and ease of modification. In addition, besides the exceptional catalytic behavior, some members of the xantphos family, e.g., nixantphos (1, see scheme 1) display strong fluorescence. Within the molecular structure of nixantphos we identified the A-\(\pi\)-D-\(\pi\)-A pattern (A = phosphine, D = nitrogen) in an atypical V-shape. This initiated us to study the photophysical properties of 1 and particularly the possibility to use the immobilized ligand as two-photon excitation probe to study the immobilization process. For this purpose, N-functionalized nixantphos 2 was immobilized on glass coverslips and on activated silica allowing us to study the immobilization process spectroscopically and to correlate the results to the catalytic properties of the immobilized catalyst.

Ligand 1 possesses many useful chemical and spectroscopic characteristics, among which a well defined linear absorption spectrum. The spectrum exhibits strong absorption at 280 nm ($\varepsilon = 1.7 \times 10^4$ M$^{-1}$ cm$^{-1}$) and weaker absorption at 340 nm ($\varepsilon = 7.7 \times 10^3$ M$^{-1}$ cm$^{-1}$, see Figure 1). In addition, 1 shows a high fluorescence quantum yield ($\Phi_{em} = 428$ nm, $\Phi = 0.33$) and short lifetime of emission ($\tau = 1.4$ ns) yielding excellent properties for a fluorophore probe.
Since TPA occurs only upon simultaneous absorption of two photons, it requires a very high photon flux, obtained by focusing a strong, pulsed near infrared laser. Initial two-photon excitation experiments revealed that ligand 1 displays a strong fluorescence upon excitation at 720 nm. The recorded spectrum is virtually identical to the one-photon-induced emission spectrum (see Figure 1). To ensure that the recorded fluorescence is indeed the result of TPA, the excitation power was varied and the emission intensity measured (see supporting information). A quadratic relationship between emission intensity and excitation power was found, confirming the two-photon process. The two-photon excitation (TPE) spectrum was obtained by changing the excitation wavelength (at constant power) from 780 to 690 nm, and measuring the emission intensity at 428 nm. The shape is identical to that of the absorption spectrum at half the wavelength. By comparison with fluorescein,13 the TPE cross-section could be determined. The value of ~1.4 GM at 690 nm is modest, but with the fluorescence quantum yield of 0.33 it is adequate for imaging.

The immobilization strategy of choice is to introduce a trimethoxysilane moiety, which is known to attach covalently and specifically to silanol groups present on the glass surface or silica support. According to the standard immobilization process (method A), clean borosilicate microscope coverslips were immersed in a refluxing toluene solution of ligand 2 at 0.1 mM concentration. After 18 hrs, capping agent (n-propyl(trimethoxy)silane) was added to ensure all silanol-groups are silylated. The coverslips were cleaned in a sonicator twice with fresh toluene and once with methanol to remove all non-bonded fluorophore, dried under vacuum and stored under argon. The static water contact angle of the glass
coverslips shows a significant increase of ~19° indicating coverage of the surface by the hydrophobic phosphorous ligand.

Two-photon scanning images recorded on the cover slip with immobilized 2 shows besides uniformly dispersed ligand also more intense fluorescence spots (Figure 2, left). Analysis of these fluorescence spots confirms that the two-photon fluorescence spectra are identical to those of the parent compound 1. The recorded fluorescence lifetimes (0.8 ns) are significantly shorter, which are ascribed to self-quenching or concentration quenching. Furthermore, the intense spots are photobleached upon irradiation verifying that these spots are higher concentration immobilized ligand. Clearly, the standard immobilization process does not yield a homogeneous distribution of the ligand but also larger clusters of ligands. Such a high concentration of catalyst is anticipated to affect the catalytic results (vide infra).

Figure 2. Two-photon scanning images (65 x 65 µm) of nixantphos immobilized on microscope coverslips prepared by direct addition of 2 (left), and coverslips prepared by dropwise-diluted addition of 2 and propyl(trimethoxy)silane (right, see supporting information for details).

The clustering of ligands is attributed to pre-polymerization of the methoxy silane groups prior to immobilization. In order to achieve homogenously distributed ligands on the support, a mixture of 2 and \( n \)-propyl(trimethoxy)silane in a toluene solution was added slowly to a refluxing toluene solution containing the glass coverslips (method B). After the washing cycles the glass coverslips were studied. Images of the glass coverslips subjected to the new immobilization procedure do not display intense fluorescence spots (Figure 2, right). Analysis of the fluorescence lifetime images show a typical lifetime equal to the lifetime of compound 1. The two-photon fluorescence spectra taken at arbitrary points are identical to the emission spectra shown in figure 1 (see supporting information).

To evaluate if the new immobilization strategy indeed translates in improved performance of supported catalysts we immobilized nixantphos ligand 2 on silica (size 200-400 µm; 60 Å) using the two different
immobilization techniques (method A and B). The corresponding immobilized Rh-catalysts were applied in the industrially important hydroformylation reaction (Scheme 2) and the immobilized catalyst was separated after the reaction by simple filtration. In the case of the improved immobilization catalyst (method B), the catalytic material was reused in ten consecutive batch reactions.

Immobilized transition metal catalysts often display activities that are one order of magnitude lower than their homogeneous counterparts, frequently accompanied with lower selectivities. Indeed, compared to the homogeneous phase reaction (Table 1, entries 1 and 2) the silica-immobilized catalyst prepared according to method A clearly shows deteriorated activity (entry 3, 15 times lower activity) and a lower chemo- and regioselectivity (ratio linear/branched, l/b = 19.0). Although the immobilization on the glass surface and porous silica surfaces may not be identical, it is likely that the clustering observed on the glass coverslips also occurs on the silica, contributing to the lower catalytic performance. From the vast amount of literature concerning the hydroformylation reaction it is well established that a high concentration of catalyst promotes the formation of inactive dirhodium complexes with bridging carbonyls. Although the formation of this dormant state is reversible in nature, the number of active catalyst species will be reduced by cluster formation on silica and hence the reaction rate is decreased by this process. Furthermore, a high density of active catalyst species on a porous surface can also lead to a local depletion of substrates (CO, H₂, alkene), generally leading to isomerization side reactions and potentially initiating catalyst decomposition (such as formation of metal clusters) degrading the outcome of the hydroformylation reaction. Indeed, when these immobilized rhodium catalyst are applied in previous studies, higher syn-gas pressures (typically 50 bar) are required compared to the homogeneous phase reaction.

Scheme 2. Hydroformylation of 1-octene by rhodium catalyst to give the linear and the branched aldehyde.

Interestingly, the catalyst supported according to method B, with the ligands more homogenously distributed, indeed showed much better performance in the hydroformylation of 1-octene. At 80 °C and 50 bars of syngas about 80% conversion of the 1-octene was obtained with a l/b regioselectivity of around 36, indicating that both the activity and the selectivity was better than that obtained with the catalyst
prepared by method A (entries 3 and 4-6, table 1). In the first run we observed also the formation of 1-nonanol, a hydrogenation side reaction reducing the amount of linear aldehyde formed. Previously, we suppressed this side reaction by adding 2-propanol as co-solvent and hence subsequent recycle runs were therefore performed in the presence of 2-propanol, restoring the high chemoselectivity. The turnover frequencies obtained with catalyst B are increased by at least 8 times compared to catalyst A, and are half of that of the homogeneous phase (entry 1). The new catalyst material also shows excellent performance when the pressure of the syngas is reduced to 20 bars (entries 4-7), conditions that were previously shown to be incompatible with catalyst A and most other immobilized hydroformylation catalysts systems as the isomerization reaction dominates. Under these conditions, the catalyst B appears very active with TOFs comparable to the homogenous catalyst (130 and 149, respectively) while the chemo- and regioselectivity are identical (94% linear aldehyde and l/b = 55). In these catalytic cycles the reaction was run to nearly full conversion without affecting the catalytic performance in subsequent runs and rhodium analyses by means of ICP-OES measurements of each of the ten reaction solutions show no detectable amounts of rhodium (< 3 ppb). Lowering the reaction temperature to 60 °C only slows down the reaction while the selectivity is maintained according the to syngas pressure (entries 10 and 11). These experiments show that we now have an immobilized hydroformylation catalyst which gives similar activity and selectivity with respect of the homogeneous phase reaction and is sufficiently stable for numerous recycling experiments.

Table 1. Rhodium-catalysed hydroformylation of 1-octene[^a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Material</th>
<th>P (bar) T (°C)</th>
<th>Conversion[^b] (%)</th>
<th>Linear (%)</th>
<th>l/b</th>
<th>TOF[^c]</th>
<th>Cumulative TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>homog.</td>
<td>50/80</td>
<td>33.3[^d]</td>
<td>92.9</td>
<td>40.8</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>homog.</td>
<td>20/80</td>
<td>53.5[^d]</td>
<td>85.5</td>
<td>34.0</td>
<td>149</td>
<td></td>
</tr>
<tr>
<td>3[^e]</td>
<td>Support A</td>
<td>50/80</td>
<td>84.0</td>
<td>82.6</td>
<td>37.4</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Support B (1)</td>
<td>50/80</td>
<td>85.1</td>
<td>87.1</td>
<td>38.0</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>5[^f]</td>
<td>Support B (2)</td>
<td>50/80</td>
<td>85.1</td>
<td>87.1</td>
<td>38.0</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>6[^f]</td>
<td>Support B (3)</td>
<td>50/80</td>
<td>95.1</td>
<td>91.8</td>
<td>45.1</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>7[^f]</td>
<td>Support B (4)</td>
<td>50/80</td>
<td>96.6</td>
<td>94.0</td>
<td>54.1</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>8[^f]</td>
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<td>50/80</td>
<td>95.1</td>
<td>93.2</td>
<td>53.1</td>
<td>130</td>
<td></td>
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<tr>
<td>9[^f]</td>
<td>Support B (6)</td>
<td>50/80</td>
<td>96.6</td>
<td>93.1</td>
<td>57.3</td>
<td>130</td>
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<tr>
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<td>Support B (7)</td>
<td>50/80</td>
<td>95.7</td>
<td>92.3</td>
<td>37.5</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>11[^f]</td>
<td>Support B (8)</td>
<td>50/80</td>
<td>95.7</td>
<td>92.3</td>
<td>37.5</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>12[^f]</td>
<td>Support B (9)</td>
<td>50/80</td>
<td>95.0</td>
<td>91.3</td>
<td>39.9</td>
<td>115</td>
<td></td>
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<tr>
<td>13[^f]</td>
<td>Support B (10)</td>
<td>50/80</td>
<td>94.3</td>
<td>91.2</td>
<td>39.8</td>
<td>115</td>
<td></td>
</tr>
</tbody>
</table>

[^a]: Catalysis performed under CO/H₂ pressure in a 1/1 mixture in 13 mL toluene as solvent, 1 mL 1-octene as substrate and 1 mL n-decane as internal standard. [^b]: Conversions were calculated after 23 hours. Samples were analyzed by means of GC analyses. [^c]: Turnover frequencies were calculated as (mol product)(mol catalyst)⁻¹(hour)⁻¹ at 20-40% conversion, variations in TOF stem from differences in conversion and product distributions (full table is given in supporting info). [^d]: Conversion was calculated after 2 hours. [^e]: data taken from ref 11b. [^f]: 1 mL propanol and 12 mL toluene as solvent was used.
In conclusion, we demonstrate that ligand immobilization can be monitored by means of two-photon fluorescence microscopy, using nixantphos ligand 1 as the appropriate fluorophore for imaging purposes and as ligand for the rhodium catalyzed hydroformylation. The scanning images obtained with the fluorescence microscopic technique reveal clustering of ligands when these are immobilized under standard conditions, while an optimized ligand optimization procedure using slow addition of a diluted solution of 2 shows homogeneous distribution of ligand on support. The difference clearly translates to better catalyst performance as the immobilized hydroformylation catalyst using the new procedure give much higher activity and selectivity than that obtained via the standard procedures. We believe that the new immobilization strategy will be applicable to a wide range of catalysts, and depending on the mechanism and conditions applied these catalysts may benefit from the reported methodologies. In addition, also other ligands or transition metal catalysts that have appropriate fluorescence properties could be used as probes for catalyst imaging, further developing this important field in catalysis. In the end, this new powerful imaging tool allows rational catalyst immobilization, generating heterogeneous catalyst that compete homogeneous analogues but can be separated and recycled easily.

**Experimental Section**

General procedure for the immobilization of 2. Method A of immobilization has been published elsewhere.\textsuperscript{11}

General procedure for the immobilization of 2. Method B. A 1:1 mixture of N-(3-(trimethoxysilyl)propyl) nixantphos (250 mg - 0.35 mmol) and dimethoxydimethylsilane (50 µL - 0.35 mmol), in 20 mL of toluene, was added dropwise (addition rate: 0.05 mL/min) to a suspension of 2 g of commercially available silica gel (200-400 m particle size; 60 Å pore size, pretreated at 180 °C under reduced pressure), in 50 mL of toluene. The slurry was rotated (not stirred to avoid damage to the silica particles) and kept under
reflux for 18 hours. Then, an excess of dimethoxydimethysilane (2 mL – 14 mmol) was added, and the mixture was refluxed for another 18 hours. The slurry was cooled down to room temperature and the silica supported material was washed several times with hot toluene and methanol to remove the unsupported compounds. The material was then dried under reduced pressure and stored under argon atmosphere.
References


[16] The capping agent used in immobilization of 2 on glass surfaces was n-propyl(trimethoxys)ilane, while the immobilization reaction performed on silica dimethyldimethoxy)ilane was used.
Phosphorus Ligand Imaging with Two-Photon Fluorescence Spectroscopy: The way open for Rational Catalyst Immobilization

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Supporting Information

General procedures:
Unless stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were distilled under an atmosphere of nitrogen as follows: THF and hexane from sodium benzophenone ketyl, toluene from sodium and dichloromethane from CaH₂.

N-(3-trimethoxysilane-n-propyl)-4,5-bis(diphenylphosphino)-phenoazine was synthesized according to literature procedure.¹ n-Propyl(trimethoxy)silane was purchased from ABCR GmbH & Co and used without further purification. Dimethoxy(dimethyl)silane was purchased from Sigma-Aldrich and used without further purification.

Silica gel (200-400 µm; 60 Å) was purchased from Screening Devices B.V. and pretreated under vacuum at 180 °C for 24 hours prior its use. n-Decane and 1-octene were purchased from Sigma-Aldrich and purified over neutral alumina (purchased from MERCK KGaA).

Contact angles were measured using a home-built contact angle goniometer and the contact angles were determined using the program ImageJ 1.41o (Wyane Rasband, National Institute of Health, USA).

NMR and mass spectroscopy:
NMR spectra (¹H, ³¹P{¹H} and ¹³C{¹H}) were measured on Varian Mercury 300 MHz or Varian INOVA 500 MHz spectrometers. Chemical shifts are denoted in ppm, using the solvent itself as internal standard. High-resolution fast atom bombardment mass
spectrometry (HRMS FAB) measurements were carried out on a JEOL JMS SX/SX 102A spectrometer.

**Rhodium analyses:**
Rh-Analyses were performed on an ICP-OES, PerkinElmer Optima 3000XL with detection limit of 1.4 µg/l (1.4 ppb) and determination limit of 4.2 µg/l (4.2 ppb).

**Steady-state absorption:**
Electronic absorption spectra were recorded on a single beam HP 8453 diode array spectrophotometer with a spectral range from 190 to 1100 nm and a spectral resolution of about 2 nm. The spectra were recorded in rectangular 1.0 cm quartz cuvettes. Photographs (Figure SI 2) were recorded with an i-phone 3G (apple corporation).

**Steady-state fluorescence:**
Steady-state fluorescence spectra were recorded on a Spex Fluorolog 3 spectrometer, equipped with double grating monochromators in the excitation and emission channels. The excitation light source was a 450 W Xe lamp and the detector a Peltier cooled R636-10 (Hamamatsu) photomultiplier tube. The fluorescence spectra were corrected for the wavelength response of the detection system. The fluorescence of fluorophores in solution was detected in a right angle geometry using solutions with low absorbances (optical density below 0.10 cm). Fluorescence of the immobilized nixantphos coverslips was recorded in a front face set-up.

**Time-resolved fluorescence:**
Time-resolved fluorescence was measured with a time-correlated single-photon counting (TCSPC) setup. This setup consists of a cavity dumped DCM dye laser (Coherent model 700) pumped by a mode-locked Ar⁺ laser (Coherent 486 AS Mode Locker, Coherent Innova 200 laser). The fluorescence was collected through a polarizer at the magic angle (54.7°) with respect to the (vertical) polarization of the laser beam to exclude polarization effects. A microchannel plate (Hamamatsu R3809) was used as the detector. The overall
response function (IRF) was measured from the Rayleigh scattering of colloidal silicon dioxide (LUDOX from DuPont).

The fluorescence decay times were obtained from the fluorescence decays by fitting the data with the convolution of the appropriate number of exponentials and the IRF. The fitting was done by numerical iterative reconvolution with a home written program. The program was implemented in Igor Pro 5 and uses a Levenberg-Marquardt algorithm to minimize $\chi^2$.

**Cleaning of cover slips:**

Borosilicate-glass microscope cover slips (20 × 20 mm, 1.5 µm thick, Willmat) were sonicated for 1 hour in MilliQ water and 1% w/w aqueous Hellmanex solution, rinsed with MilliQ water and sonicated two more times in pure MilliQ water. After blown dry with dry nitrogen, the cover slips were placed in a UV-Ozone cleaner for 4 hrs, sealed and stored.

**Immobilization of $N$-(3-(trimethoxysilyl)propyl) nixantphos 2 on glass coverslips (Method A):**

Into a toluene solution (50 mL) containing $2.5 \times 10^{-5}$ mmol of $N$-(3-trimethoxysilane-$n$-propyl)-4,5-bis(diphenylphosphino)-phenoxazine clean cover slips were immersed. The solution was stirred and heated to reflux temperature for 18 hours. Then $2.5 \times 10^{-5}$ mmol of $n$-propyl(trimethoxy)silane was added and the reaction mixture was refluxed for another 18 hours. After the solution was cooled to room temperature, the solvent was removed with the use of a syringe and the cover slips were washed with toluene (3 × 50 mL). Then the cover slips were sonicated for 15 min with toluene (2 × 50 mL) and with methanol (1 × 50 mL). The cover slips were then washed with $\text{Et}_2\text{O}$ (50 mL), dried under reduced pressure, and stored in a desiccator under argon.

**Immobilization of $N$-(3-(trimethoxysilyl)propyl) nixantphos 2 on glass cover slips (Method B):**

Clean cover slips were immersed in a toluene solution (50 mL) and the solution was stirred and heated to reflux temperature. Then a 1:1 mixture of $2.5 \times 10^{-5}$ mmol of $N$-(3-
trimethoxysilane-\( n \)-propyl)-4,5-bis(diphenylphosphino)-phenoxazine and \( 2.5 \times 10^{-5} \) mmol of \( n \)-propyl(trimethoxy)silane, in 20 mL of toluene, was added dropwise (addition rate: 0.05 mL/min). The mixture was stirred and kept under reflux temperature for 22 hours. After the solution was cooled to room temperature, the solvent was removed with the use of a syringe and the cover slips were washed with toluene (3 \( \times \) 50 mL). Then the cover slips were sonicated for 15 min with toluene (2 \( \times \) 50 mL) and with methanol (1 \( \times \) 50 mL). The cover slips were then washed with \( \text{Et}_2\text{O} \) (50 mL), dried under reduced pressure, and stored in a desiccator under argon.

Immobilization of \( N \)-(3-(trimethoxysilyl)propyl) nixantphos 2 onto silica gel (Method A):
The supporting procedure according to Method A has been carried out following literature procedure.\(^1\)

Synthesis of the Rh-complex and Hydroformylation of 1-octene:
The synthesis of the supported Rh-complex and the hydroformylation procedure were carried out following literature procedure.\(^1\)

ICP-OES analysis:
Silica support:
The silica gel is dissolved in 48% aqueous HF (1 mL \( \times \) 50 mg of silica) and heated until all the volatiles are evaporated. The residue is then dissolved by adding fuming nitric acid (2 mL) and warming up the solution to 90 °C for 1 hour. Hydrogen peroxide (few drops) is then added to the warm sample until the solution become colorless. Water is added to bring the total volume up to 10 mL for analysis.
Rh in the product mixture:
5 mL of product solution are evaporated under vacuum at 80 °C. The residue is dissolved by adding fuming nitric acid and warming up the solution to 90 °C for 1 hour. Hydrogen peroxide (few drops) is added to the warm sample until the solution become colorless. Water is added to bring the total volume up to 10 mL for analysis.

Figure S1 1. Fluorescence decay of nixantphos recorded in toluene solution. Mono exponential fit: $\tau = 1.41$ ns (in green the excitation pulse).
Fluorescence spectra upon 1-photon and 2-photon excitation:

The spectra were recorded in rectangular 1.0 cm quartz cuvettes. Following samples were prepared for measurements:

- nixantphos in toluene, concentration: $1.50 \times 10^{-3}$ M; blank sample pure toluene
- fluorescein in water (pH = 13), concentration: $14.5 \times 10^{-6}$ M; blank sample water (pH = 13).³

Figure SI 2. Photograph of a 0.4 mM nixantphos solution in toluene. 2-Photon absorption is proportional to the square of the light intensity (Emission ~ $I^2$). As a consequence, 2-photon absorption occurs only for very intense light, which, in common application occurs at the focus of a laser beam. The laser (710 nm) was focused inside the cuvette (A) without a filter and (B) with a filter short wave pass filter (LS-650_R Croma).

The excitation source for 2-photon excitation experiments consists of high power Ti:sapphire laser Chameleon (Coherent) and Second Harmonic Generator (APE) for 1-photon excitation measurements. The laser beam is expanded to about 1 cm diameter, passes though long wave pass filter 665LP (Omega Optical) and is focused in a 1 cm quartz cuvette by PlanN (4x, 0.10 NA) objective (Olympus). The emission light from the sample is collected in right angle configuration through short wavelength pass filter LS-650-R (Corion). Fluorescence is focused by an achromatic lens into a spectrograph (SpectraPro 150, Acton Research Corp.) and the spectrum is recorded on a CCD (PhotonMax, Roper Scientific). The average excitation power was measured before the
objective using FieldMax II (*Coherent*) power meter. Background correction for acquired fluorescence spectra was performed using signals recorded for blank samples. There was no correction applied for the spectral response of the CCD.

![Emission spectra](image)

**Figure SI 3.** Emission spectra of a) fluorescein, b) nixantphos upon different excitation wavelengths. Excitation power: 600 mW. Spectra recorded using PhotonMax CCD (accumulation time: 400 ms, gain: 2000). Excitation filter: long wave pass 665LP. Emission filter: short wave pass LS-650-R 807R CC (Corion).

![Emission intensity](image)

**Figure SI 4.** Emission intensity of a) fluorescein at 516 nm and b) nixantphos measured at 423 nm as a function of excitation wavelengths.

The emission intensity of fluorescein as a function of the excitation wavelength is plotted in figure SI 5. One point (at 700 nm) does not fit to the data obtained during two series of
measurements at different samples. Recalculation in GM units was performed using the minimization of the root-mean-square deviation method (excluding the point at 700 nm).

**Figure SI 5.** Emission intensity of fluorescein at 516 nm (our experimental data –red & blue, from ref 3 – green).

**Figure SI 6.** Emission spectra of a) fluorescein (in water pH = 13), b) nixanthphos (in toluene) upon different excitation powers (excitation wavelength 695 nm). Spectra recorded using PhotonMax CCD (accumulation time: 400 ms, a) gain: 2000, b) gain: 3000). Excitation filter: long wave pass 665LP. Emission filter: short wave pass LS-650-R 807R CC (Corion).
The TPE (two-photon fluorescence excitation) cross section was calculated using formula:\textsuperscript{iii}

$$\sigma_{\text{mix}}(\lambda)N_{\text{mix}} = \frac{\phi_{\beta} \sigma_{2,\beta}(\lambda)C_{\beta} \langle P_{\beta}(t) \rangle n_{\beta}}{\phi_{\text{mix}} C_{\text{mix}} \langle P_{\text{mix}}(t) \rangle^2 n_{\text{mix}}} \frac{\langle F_{\text{mix}}(t) \rangle}{\langle F_{\beta}(t) \rangle}$$

where:

- $n_{\text{mix}}$ = Fluorescence quantum yield of nixantphos
- $\sigma_{2,\beta}$ - TPA (two-photon absorption) for fluorescein
- $\phi_{\beta}$ - fluorescence detection efficiency (all differences in accumulation efficiency were recalculated taking into account usage emission filters)
- $\langle P_{\beta}(t) \rangle = \langle P_{\text{mix}}(t) \rangle$ - power was adjusted to be 600 mW for wave dependent experiment
- $C_{\beta}$ - concentration of fluorescein
- $C_{\text{mix}}$ - concentration of nixantphos
- $n_{\text{mix}}$ - refractive index of toluene (1.4969)
- $n_{\beta}$ - refractive index of water (pH~13) (clean water: 1.3330)
- $\langle F_{\text{mix}}(t) \rangle$ - fluorescence emission intensity of nixantphos
- $\langle F_{\beta}(t) \rangle$ - fluorescence emission intensity of fluorescein

**Figure SI 7.** Emission intensity at different excitation powers from figure SI6. Emission intensity of a) fluorescein measured at 516 nm and b) nixantphos measured at 423 nm as a function of excitation power.
Recalculated in GM units:

![Graph showing emission intensity as a function of excitation wavelength.](image)

**Figure SI 8.** Emission measured at 423 nm as a function of excitation wavelengths. Data scaled in GM units (1GM = $10^{-50}$ (cm$^4$/s)/photon).

![Graph showing emission spectra.](image)

**Figure SI 9.** Emission spectra of a) fluorescein, b) nixantphos upon different excitation wavelengths. Excitation power: 600 mW. Spectra recorded using PhotonMax CCD (accumulation time: 400 ms, gain: 2000). Excitation filter: long wave pass 665LP. Emission filter: short wave pass LS-650-R 807R CC (Corion). Data scaled in GM units (1GM = $10^{-50}$ (cm$^4$/s)/photon).

**2-Photon Fluorescence Imaging:**

Fluorescence images were recorded using an inverted light microscope (IX71, Olympus) equipped with an oil immersion, 100x, 1.4 oil objective (UPlanSapo, Olympus), mounted on a piezo scanning stage (Physik Instruments GmbH). Excitation light source
was Ti:Sapphire laser Chameleon ULTRA-II (760 nm, 80 fs, 80 MHz repetition rate). Excitation light was coupled into the adapted confocal unit (Microtime 200, Picoquant GmbH) via polarization maintaining monomode fiberglass (PMC-620-4-NA011-3-XPC-P) and filtered using long wavelength pass filter 665LP (Thorlabs). An appropriate dichroic mirror (675DCSPXR, Semrock) was used to separate the fluorescence from the excitation light. No pinhole was applied for these measurements. Output power from the objective was approximately 20 µW (0.3 fJ/pulse). Scans and lifetime measurements were done with using single photon avalanche diode (SPAD SPCM-AQR-13, Perkin Elmer) connected to the PCI-board for Time-Correlated Single Photon Counting (TimeHarp200, PicoQuant). The emitted light was then passed through a 80/20 beam splitter and sent to the SPAD and CCD camera (PhotonMax, Roper Scientific) respectively. Residual excitation light was filtered from emission light by applying additional short wave pass filter: LS_650_R (Corion) placed in front of SPAD.

Data acquisition and analysis were performed using SymPho Time software. Acquisition resolution for a fluorescence time trace was 39 ps, binning time: 20 ms. Number of pixels per scan area: 120 × 120. Lifetime calculations from fluorescence time traces were done using Maximum Likelihood Estimation method.

Fluorescence images of glass surface covered by nixantphos are shown in figure SI 11.

Figure SI 10. Filter-set used for confocal measurements on nixantphos (2 photon excitation).
Figure SI 11. Fluorescence images of a glass coverslips functionalized by nixantphos, a) inhomogeneous distribution of fluorophore, size of the image: 80 µm × 80 µm, resolution: 150 × 150 px², b) homogeneous distribution of nixantphos, size of the image: 65 µm × 65 µm, resolution: 120 × 120 px²; time per pixel: 0.792 ms, average intensity: 34 cnt/s, average lifetime: 1.373 ns.

Spectra recorded at two different points on the sample (figure SI 12) show practically the same shape and intensity (what also proves homogeneous distribution of the dye).

Figure SI 12. Spectra of nixantphos recorded using CCD camera PhotonMax (Roper Scientific) (integration time: 1 s, gain: 3600).
**Figure SI 13.** Photographs of water drops on clean glass coverslip (left, contact angle 50.3°) and nixantphos immobilized glass coverslip (right, 69.3°)
### Table SI 1. Rh-catalysed hydroformylation of 1-octene

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[a] Catalysis performed under CO/H₂ pressure in a 1/1 mixture in 13 mL toluene as solvent, 1 mL 1-octene as substrate and 1 mL n-decane as internal standard.

[b] Samples were analysed by means of GC analyses.

[c] Turnover frequencies were calculated as (mol product/(mol catalyst))/(hour)⁻¹ at 20-40% conversion, variations in TOF stem from differences in conversion and product distributions.

[d] Data taken from ref 11b.

[e] 1 mL propanol and 12 mL toluene as solvent was used.
