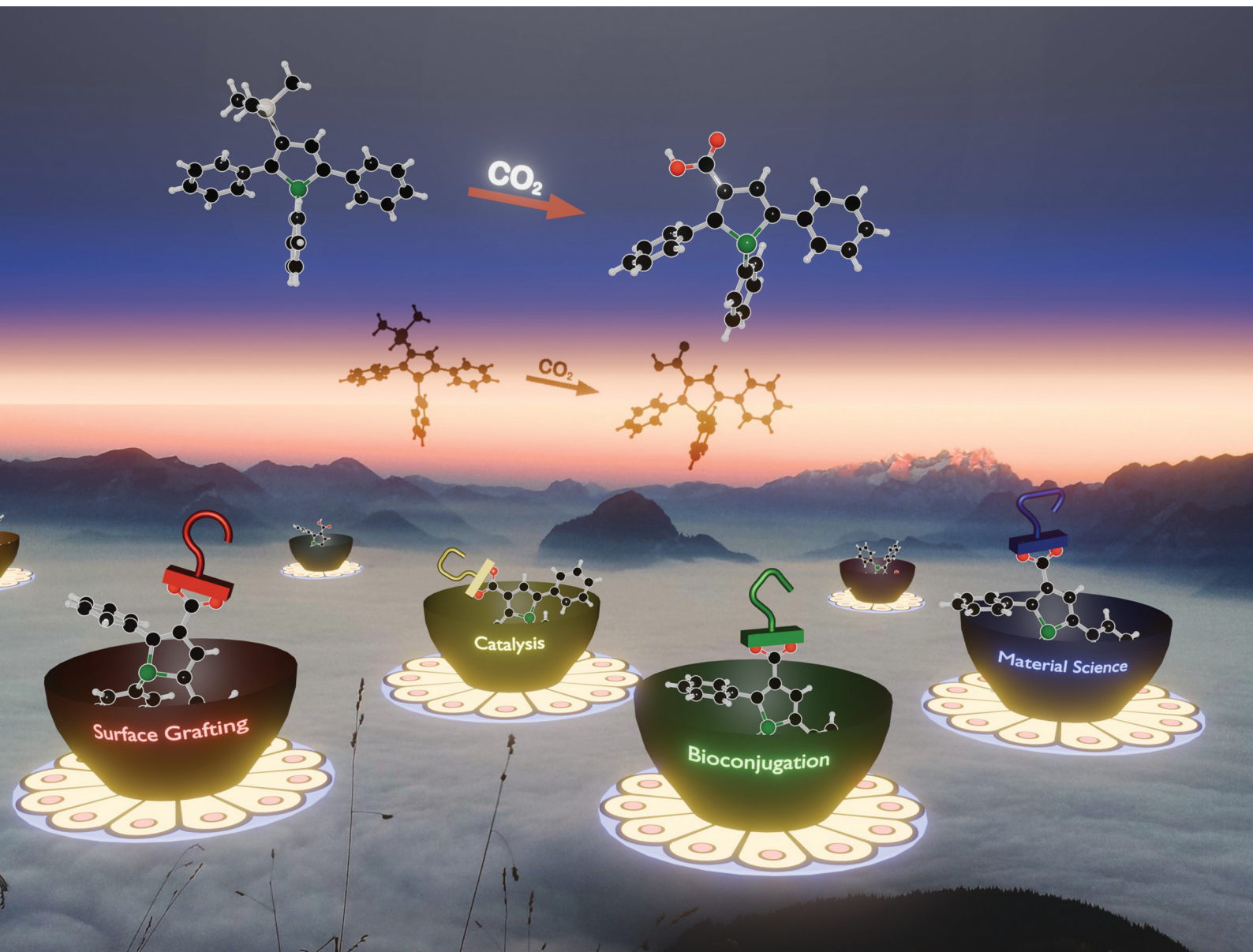


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β -Carboxyphospholes *via* carboxylative desilylation: luminophores with a versatile connectivity attached

 Katharina Eichhorn, Clemens Bruhn and Rudolf Pietschnig *

The synthesis of β -carboxyphospholes has been achieved *via* carboxylative desilylation of their β -TMS-substituted analogues in a CO₂ atmosphere. The title carboxylic acids allow facile transformation into the respective acyl chloride, carboxamide, ester and anhydride, which are compatible with bioconjugation, while the integrity of the phosphole unit is maintained.

Phospholes are highly versatile building blocks with interesting features for application in opto-electronic devices,^{1–4} for grafting on material surfaces,^{5,6} in catalysis^{7–10} and for biomedical applications.^{11–16} By structural modification of the heterocycle, it is possible to tune the electronic and optical properties in order to achieve optimized characteristics for the targeted field of application.^{17–20} However, incorporation of reactive functional groups at the phosphole ring allowing facile modification or bioconjugation is rather limited to date. Previous attempts at incorporating carboxylic groups in the phosphole ring either yielded only unstable products or were limited to α -functionalization.^{21–26} A quite unusually functionalized phosphole derivative has been reported by Goicoechea *et al.*²⁷ Very recently, Imahori *et al.* presented a synthesis towards β -hydroxymethyl phospholes, which they used for a subsequent intramolecular cyclization reaction albeit in moderate yields.²⁸

Here, we present a simple and highly selective synthetic pathway towards β -carboxyphospholes, which provides high potential for flexible modification. Starting from β -trimethyl silyl phosphole **1**, whose synthetic access was described earlier,^{29–31} a desilylation is performed using tetramethylammonium fluoride (TMAF) in dry DMF in a CO₂ atmosphere (Scheme 1). The *in situ* generated, highly reactive carbanion readily reacts with the CO₂ resulting in β -carboxyphosphole **2**. In previously reported carboxylative desilylation reactions, aromatic or heteroaromatic scaffolds have been employed with the heteroatom neighboring the silyl group.^{32–35} While in these latter

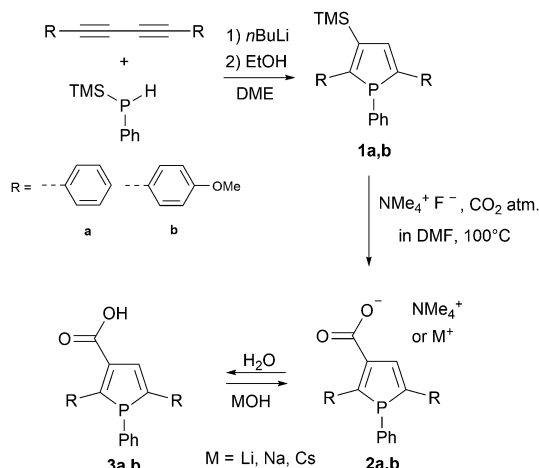
cases CsF as the fluoride source and DMF or DMSO as the solvent provided the best results, these conditions are unsuitable in our case, owing to solubility issues in DMF, and the reactivity of DMSO which leads to bicyclic phospholane oxathiolane systems.³⁶ As an alternative, TMAF shows sufficient solubility in DMF, which increases further upon heating the reaction mixture. Strict exclusion from moisture is necessary to prevent hydrolysis of the carbanionic species formed during desilylation, which would result in the formation of the β -unsubstituted phosphole derivative. Upon carboxylation, the initially formed carboxylate **2** is protonated by treatment with water giving the carboxylic acid **3**.

Carboxylate **2** is well soluble in alcohols, while carboxylic acid **3** shows the best solubility in THF. The ³¹P-NMR shifts together with the ¹³C-NMR shifts of the carboxyl carbon atom are listed in Table 1. Interestingly, the β -trimethylsilyl phospholes **1a** and **1b** and the carboxylic acids **3a** and **3b** respectively show very similar phosphorus shifts, while the signal of the carboxylates **2a** and **2b** is shifted upfield by 11 ppm. The reverse reaction from **3** to **2** is easily achieved by base treatment, *e.g.* with LiOH, NaOH or CsOH, which also allows variation of the counter-cation. In terms of NMR shifts, the counter-cation has only a minor impact in the same solvent (see Table 1). In weakly coordinating CD₂Cl₂ solution, carboxylates **2a-Na** and **2b-Na** show broad ³¹P-NMR resonances at lower field (19.1 ppm (**2a-Na**) and 18.6 ppm (**2b-Na**)), which upon addition of crown ether ([15]crown-5, 1 eq.) become sharp and shift to higher field (10.3 ppm (**2a-Na**) and 9.7 ppm (**2b-Na**)) close to the values observed in methanol solution, consistent with solvent separation in the latter cases.

The molecular structure of carboxylic acid **3a** was investigated *via* single crystal X-ray diffraction (Fig. 1). The sum of angles at the phosphorus atom amounts to 301.04(8)°. The C23–O1 single bond is 1.315(2) Å, and the C23=O2 double bond is 1.229(2) Å, which is in good agreement with standard values for such bonds.³⁷ Neighboring molecules in the crystal lattice interact *via* hydrogen bonding of the carboxyl groups with an O···O distance of 2.6485(18) Å and an estimated O···H distance of 1.8292(12) Å, which classifies it as a moderate and mostly electrostatic hydrogen bond.³⁸

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Scheme 1 Synthesis of β -carboxylate phosphole **2** starting from β -trimethylsilyl phosphole **1** and subsequent protonation to the corresponding carboxylic acid **3** (TMS = trimethylsilyl, Ph = phenyl, Me = methyl, Et = ethyl, DME = dimethoxyethane, DMF = dimethyl formamide).

Table 1 Overview of the ^{31}P -NMR shifts, the ^{13}C -NMR shifts of the C=O carbon atom and the CO stretching frequencies in the IR spectrum (n.d. = not determined)

	^{31}P -NMR [ppm]	^{13}C -NMR C=O [ppm]	IR C=O stretch [cm^{-1}]
1a (CD_2Cl_2)	22.3 ²⁹	—	—
1b (CD_2Cl_2)	21.4 ³⁰	—	—
2a-Li (MeOH- d_4)	11.6	175.8	n.d.
2a-Na (MeOH- d_4)	11.5	175.9	1582.39
2a-Cs (MeOH- d_4)	12.2	175.5	n.d.
2b-Na (MeOH- d_4)	11.1	175.9	n.d.
3a (THF- d_8)	22.7	165.4	1669.89
3b (THF- d_8)	21.4	165.8	n.d.
4 (CD_2Cl_2)	28.2	165.3	1768.58
5 (CD_2Cl_2)	22.5	165.3	1705.38
6 (CD_2Cl_2)	10.2	168.4	1622.30
7 (CD_2Cl_2)	26.2	165.1	1772.56, 1711.35

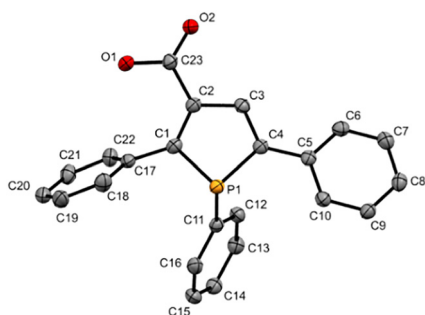
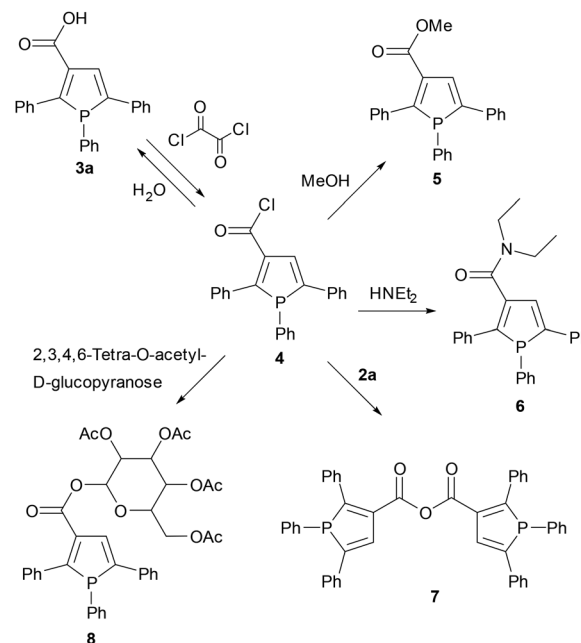


Fig. 1 ORTEP plot of the molecular structure of **3a** in the solid state with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

To explore the reactivity of the β -carboxy phosphole **3a**, we first aimed to obtain the acyl chloride, which is a reactive precursor for many typical modification reactions. However, treatment of **3a** with thionyl chloride only resulted in the



Scheme 2 Synthesis of the acyl chloride **4** by treatment of **3a** with oxalyl chloride and further derivatization towards ester **5**, amide **6**, acid anhydride **7** and sugar ester **8**.

oxidation of the phosphorus atom. A quantitative and fast transformation towards the desired product **4** could be observed with the less oxidative oxalyl chloride (Scheme 2). The reaction progress can be monitored by UV-light irradiation. The solution of **3a** is highly luminescent under UV-light, while the solution of **4** shows no visible fluorescence anymore. The acyl chloride **4** is sensitive towards water, which results in a back reaction to the carboxylic acid **3a**. Treatment with an alcohol or a secondary amine, methanol and diethylamine in our case, selectively yields the corresponding ester **5** or amide **6** (Scheme 2). An acid anhydride **7** can be obtained upon mixing **4** with the carboxylate **2a**. Solutions of **5**, **6** and **7** again show fluorescence under UV-light irradiation.

All derivatives **4–7** could be isolated and fully characterized. The ester **5**, amide **6** and anhydride **7** are stable for purification

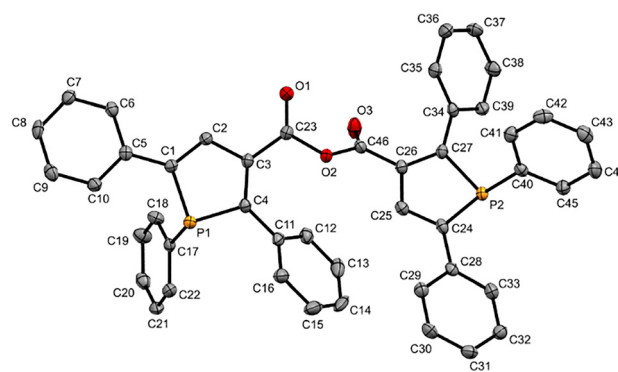


Fig. 2 ORTEP plot of the molecular structure of **7** in the solid state with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.



Table 2 Overview of the maximum absorption wavelength λ_{abs} , extinction coefficient ϵ_{max} , maximum emission wavelength λ_{em} , Stokes shift λ_{S} and quantum yield ϕ of the phospholes **1a-7** in solution (10^{-5} M in dichloromethane) and the solid state

	Solution					Solid			
	λ_{abs} [nm]	$\epsilon_{\text{max}} \times 10^4$ [L mol ⁻¹ cm ⁻¹]	λ_{em} [nm]	λ_{S} [cm ⁻¹]	ϕ	λ_{abs} [nm]	λ_{em} [nm]	λ_{S} [cm ⁻¹]	ϕ
1a ³⁰	362	1.63	473	6483	0.12	375	484	6006	0.82
2a-Na	377	0.98	487	5991	0.08	422	542	5246	0.03
3a	378	1.35	505	6653	0.05	439	532	3982	0.25
4	396	0.81	469	3931	0.03	480 ^a	574	3412	0.15
5	375	1.39	493	6383	0.07	440 ^a	542	4277	0.11
6	373	1.81	467	5396	0.43	425 ^a	512	4278	0.28
7	390	1.99	532	6844	0.01	449	532	3475	0.29

^a λ_{abs} is as excitation wavelength and refers to plateau before the sharp decrease in absorption.

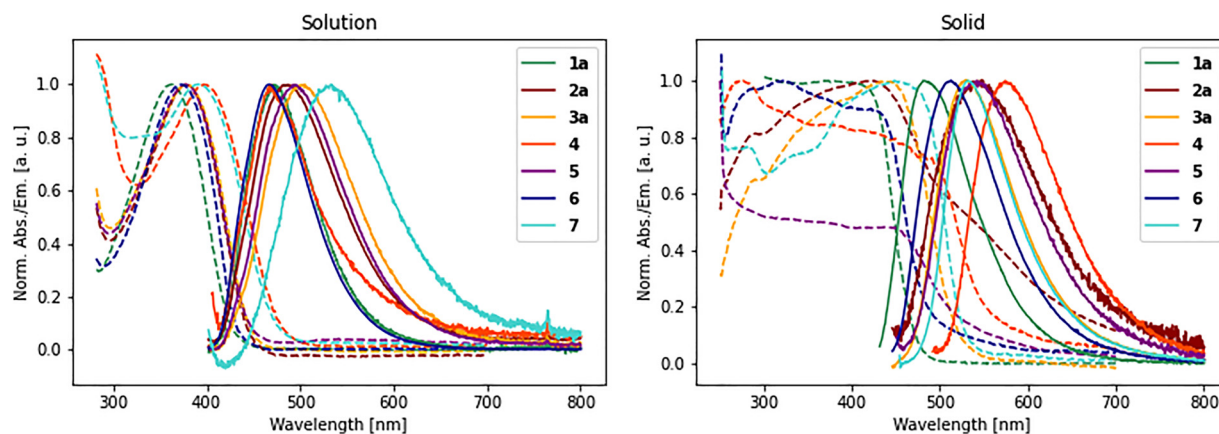


Fig. 3 Normalized absorption (dashed lines) and emission (solid lines) spectra of the herein described phospholes **1a-7** in solution (left, 10^{-5} M in dichloromethane) and in the solid state (right).

via column chromatography. Over time, the phosphorus atom tends to oxidize in air, which can be avoided by storing all compounds under inert conditions. In turn, **3a-O** is obtained easily by oxidation of **3a** with H_2O_2 (cf. SI). Furthermore, we explored the redox properties of **2a-Na** and **3a** via CV and CDPV, which indicates irreversible redox behavior of both compounds (cf. SI). Table 1 summarizes the ³¹P-NMR data together with the ¹³C-NMR shifts and IR-frequencies of the $>\text{C}=\text{O}$ units, featuring no peculiarities.³⁹

The molecular structure of acid anhydride **7** was investigated with single crystal X-ray diffraction (Fig. 2). The two phosphorus atoms are stereogenic centers with opposite absolute configurations at P1 (*R*) and at P2 (*S*), resulting in the *meso* form of the molecule in the crystal (Flack-parameter: 0.03(5)). The sum of angles at P1 amounts to $297.45(12)^\circ$ and that at P2 to $307.74(12)^\circ$. However, it is well-known that owing to aromatic stabilization, the inversion barrier of the phosphorus atom in phospholes is sufficiently low to allow constant inversion in solution,⁴⁰⁻⁴² which is in line with our observation of a single ³¹P-NMR resonance in solution for **7**. The two $\text{C}=\text{O}$ groups are tilted against each other by $54.0(2)^\circ$, and the bond lengths are nearly identical at $1.188(3)$ Å ($\text{C}23=\text{O}1$) and $1.184(3)$ Å ($\text{C}46=\text{O}3$), which again is in good agreement with standard values.³⁷

Furthermore, we investigated the novel phosphole derivatives **2a-7** with respect to their luminescence properties and in comparison with the already reported data of **1a**.³⁰ Table 2 provides an overview of the UV-vis absorption and emission data in solution and the solid state, and the respective spectra are depicted in Fig. 3. Maximum absorption and emission wavelengths of the novel carboxyphospholes are mainly red-shifted in comparison to the β -TMS phosphole **1a**. The acyl chloride **4** shows the most significant red-shift in absorption, both in solution and solid state, and furthermore, in emission in the solid state. Only in solution, the anhydride **7** shows the most red-shifted emission maximum. The quantum yields in solution of the novel compounds are rather limited at 1–12%. The only exception is the amide **6** with a considerable quantum yield of 43%. In the solid state, the overall quantum yields are much better with 3–29%. However, the values are still far below the extraordinary quantum yield of **1a** in the solid state of 82%, which we attributed to aggregation induced emission (AIE) as previously reported for related heterocyclic systems.^{30,43-45} To investigate the impact of the counter-cation on the luminescence properties, we measured the absorption and emission spectra of **2a-Li** and **2a-Cs** but found only minor differences, apart from the very weak emission of **2a-Cs** in solution and its absent emission in the solid state, which can be explained by



heavy atom-induced quenching owing to the cesium cation.^{46–48} Finally, striving for linking a sugar moiety to the carboxy-phosphole scaffold, we attached tetraacetylated glucose *via* esterification to **4** as a proof of concept (Scheme 2). The spectral data of the resulting sugar ester **8** are in the expected range and selective deprotection will be explored in future work (*cf.* SI).⁰

In conclusion, we reported a simple and efficient synthetic route towards β -carboxyphospholes and outlined their reactivity. Transformation into an acid chloride, ester, amide or anhydride is straightforward and allows versatile derivatization of the phosphole core. Moreover, these can be easily tracked with the NMR, IR and UV/vis data provided. All reported compounds show fluorescence in the visible region. In particular, the high reactivity of acyl chloride **4** opens vast flexibility in attaching further functional units or polar moieties such as sugars at the phosphole's β -position, *e.g.* to increase and tune their hydrophilicity or amphiphilicity. This in combination with bioconjugation offers promising perspectives for phospholes in bio-relevant chemistry which is currently ongoing.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: NMR-, HR-MS-, IR-, UV/vis-, CV-, and crystallographic data (CCDC 2481891 and 2481892).⁴⁹ See DOI: <https://doi.org/10.1039/d5cc04850h>.

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