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Naphthalimide-Dyes Bearing Phosphine and Phosphorylamide Moieties: Synthesis and Optical Properties

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Dedicated to Prof. Maurizio Prato on the occasion of his 70th birthday.

1,8-Naphthalimides (NIs) represent a class of organic dyes with interesting optical properties that has been extensively explored in the last decades in lighting devices, chemosensors, optical probes or medicinal chemistry. However, despite their remarkable potential, reports on organometallic dyes bearing NIs are scarce and virtually inexistent regarding palladium(II) complexes. Herein, we report the synthesis of NIs bearing phosphine and amine chelating moieties and the characterization of their optical properties both as single molecules and when complexed on Pd(II) ions. It is shown that the introduction of phosphine moieties in the naphthalimide core results in a marked increase in non-radiative processes, leading to a significant reduction of the emission efficiency and lifetime of these dyes, compared to amine-bearing counterparts. The complexation to Pd(II) sequesters the electronic contribution of chelating moieties, with complexes assuming an optical behavior similar to that of unsubstituted 1,8-naphthalimide. The complexation significantly increases the acidity of chelating secondary amines, giving rise to an unexpected intramolecular reaction that results in the formation of a novel 1,8-naphthalimide dye bearing a cyclic phosphorylamide moiety. The new dye exhibits good emission quantum yield, long fluorescence lifetime and sensitivity to basic media, evidencing potential for application in optical imaging and sensing scenarios.

Introduction

The naphthalimide dye continues to attract considerable interest due to its tunable photophysical properties and synthetic versatility that provides for an easy access to structural diversity and tailored properties.[1] In particular, 4-substituted-1,8-naphthalimide is a very versatile platform because the optical and fluorescence behavior of the dye can be easily modified by introducing different electron-donating or electron-withdrawing moieties at the C-4 position.[2] For instance, a nitro group in the 4-position induces a broad absorption band centered at around 360 nm but it is largely non-fluorescent, while the introduction of an electron-donating amino group generates an intramolecular charge transfer (ICT) excited state and leads to a large bathochromic shift in the absorption and emission spectra and a strong emission intensity.[3] These peculiar properties have stimulated the preparation of a very large array of naphthalimide derivatives bearing different substituents which have been exploited in several different applications ranging from classical cation[4] and anion[5] sensing, to the detection of biomolecules[6] and enzymes,[7] to fluorescent cellular imaging agents,[8] to DNA intercalators and anticancer agents,[9] to the preparation of optoelectronic polymers[10] and materials,[11] just to mention a few. Nevertheless, despite the large number of derivatives synthesized in which different heteroatoms like nitrogen, sulfur, oxygen, have been introduced in the 4-position of the naphthalimide core, the preparation and the study of the optical properties of naphthalimides functionalized with phosphorus substituents has not been investigated so far.

This lack of interest in phosphorus-functionalized naphthalimides is rather surprising because, in principle, they may represent interesting ligands for late transition metals, such as Pd(II) and Pt(II), which in turn find important application not only in the homogeneous catalysis of highly relevant reactions such as, for example, metal-catalyzed cross-coupling reactions[12] and catalytic asymmetric hydrogenation,[13] but also

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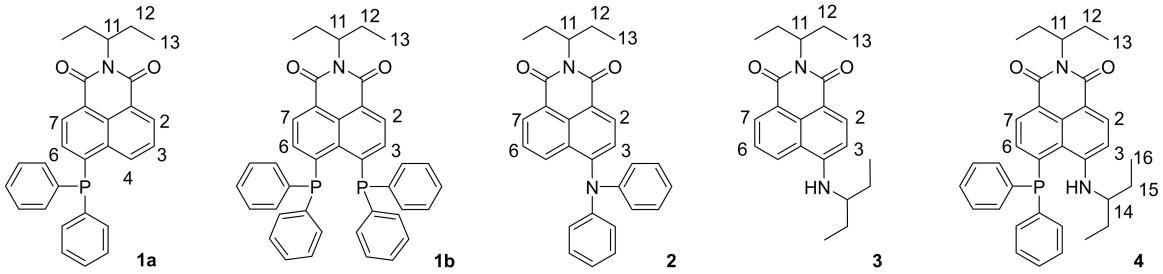
as structural building blocks for the self-assembling of complex supramolecular structures[14] in a controlled and predictable manner following the so-called metal-mediated directional-bonding approach.[15] In this context, the availability of building blocks bearing an optical and electrochemical active component is of evident interest. Furthermore, we have demonstrated that diphosphine Pd(II) complexes act as efficient synthetic ionophores being able to efficiently promote the transport of anions across a phospholipid membrane.[16] In this field, the possibility to track the ionophore inside cells is extremely relevant in order to investigate its localization in the different cellular compartments and the conjugation of the ionophore with a fluorescent tag is one of the most successful strategies.[17]

Due to the potential interest of phosphorus-functionalized naphthalimides we have undertaken a systematic study of the photophysical properties of mono- and disubsituted diphenylphosphino naphthalimides and of phosphino/amino mixed derivatives preparing the compounds shown in Scheme 1. Moreover, the Pd(II) complexes of the bidentate ligands **1** and **4** were prepared and characterized. The Pd(II) complex of compound **4** revealed an unexpected reactivity and spontaneously evolved to a cyclic phosphorylamide derivative that was in turn fully characterized.

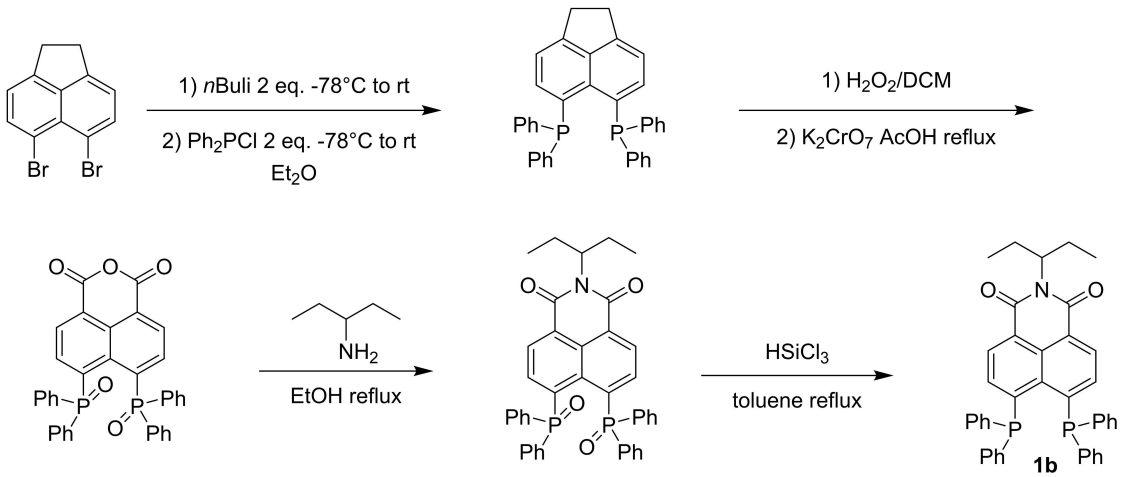
Results and Discussion

Synthesis of phosphorus functionalized naphthalimides and of their metal complexes

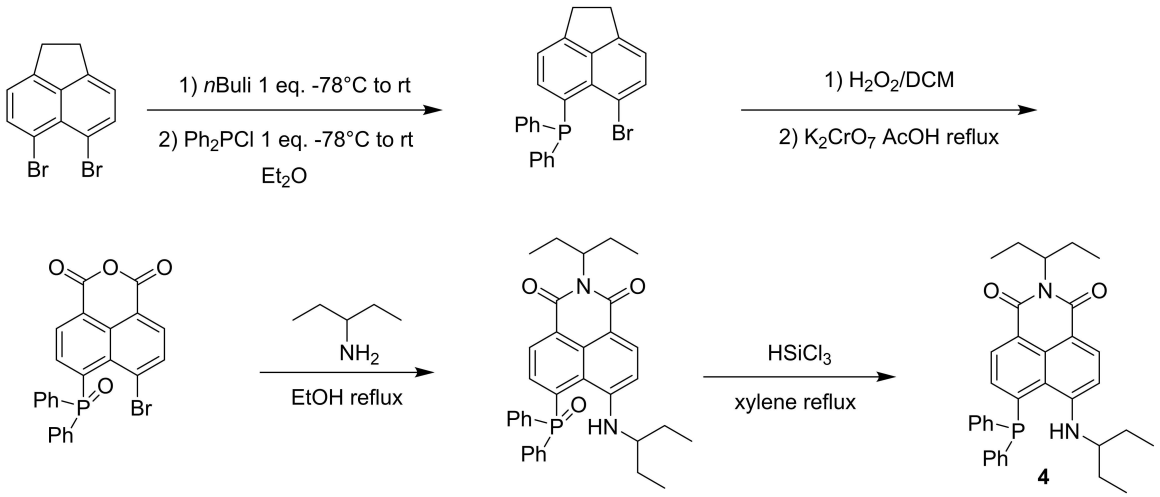
In the design of the naphthalimide derivatives we chose phenyl-substituted phosphine because aromatic phosphines are usually more stable toward oxidation with respect to their alkyl analogues, and the branched 1-ethylpropylamine for the formation of the imide moiety and for the substitution of the aromatic moiety in order to avoid possible stacking interactions and to improve the solubility of the molecules. The preparation of naphthalene mono- and bis-phosphine derivatives usually involves halogen-lithium exchange of bromonaphthalene precursors followed by a P–C coupling reaction with the desired chlorophosphine.[18] In particular, naphthalimides **1 a** and **1 b** can be readily obtained starting from 5,6-dibromoacenaphthene as shown in Scheme 2 for the preparation of **1 b**. The synthetic pathway starts with the reaction of 5,6-dibromoacenaphthene with 2 equivalents of *n*-BuLi to give the bis-lithium derivative which was reacted with chlorodiphenylphosphine leading to 5,6-diphenylphosphinoacenaphthene in high yield (90 %).[16c] The phosphine moieties and the upper ethane bridge were then oxidized in two consecutive steps to give 4,5-diphenylphosphinoxide naphthalic anhydride. The anhydride was first transformed into imide by reaction with 1-ethylpropylamine and then the phosphine oxide was reduced with



Scheme 1. Structures of the naphthalimides derivatives investigated in this work with their numbering scheme.



Scheme 2. Synthesis of the diphosphine naphthalimide **1 b**.



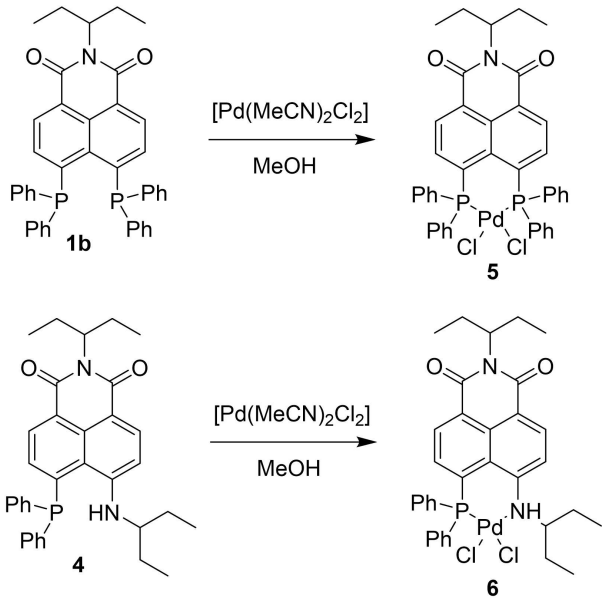
Scheme 3. Synthesis of the mixed phosphine/amine naphthalimide **4**.

$HSiCl_3$ to give the target product **1 b** in 12% overall yield. Attempts to introduce the two phosphine groups in the last step of the synthesis, in order to avoid the final reduction steps, failed due to the lability of the imide functional group toward the organolithium reagent. Compound **1 a** was obtained in 17% overall yield starting from 5-bromo-acenaphthene and following the same synthetic scheme. Both derivatives are stable in the solid state. However, while **1 a** is also reasonably stable in solution, **1 b** is slowly oxidized back to the respective phosphine oxide.

The synthetic pathway of Scheme 2 can be easily adapted for the preparation of the phosphino/amino mixed derivative **4** as shown in Scheme 3. The dibromo-acenaphthene was mono-substituted with one phosphine and, after oxidation and formation of the imide, the amino group was introduced by a S_NAr reaction with 1-ethyl-propylamine. The phosphine oxide/amine ligand was obtained with an overall yield of 49%. Due to the electron donation of the adjacent amine, the reduction of the phosphine oxide was more difficult and required the use of the higher boiling xylene instead of toluene as solvent. In any case the target phosphine **4** was obtained after 24 h reflux, and with full conversion.

4-Aminosubstituted 1,8-naphthalimides **2**[19] and **3** were prepared for comparison purpose using Buchwald-Hartwig amination of 4-bromo-N-(1-ethyl-propyl)-naphthalimide with the proper amine under the Pd-BINAP catalysis.

Pd(II) complexes of the bidentate ligands **1 b** and **4** were readily prepared by reaction in methanol with $[Pd(MeCN)_2Cl_2]$ leading to the precipitation of the pure complexes in 75% and 83% yield, respectively (Scheme 4). All the prepared compounds and complexes were characterized by ESI-MS and by ^1H, ^{13}C and ^{31}P NMR spectroscopy.



Scheme 4. Synthesis of the Pd(II) complexes **5** and **6**.

Optical properties of the naphthalimide derivatives 1–4

To assess the effects of amine and phosphine substituents on the optical properties of the prepared naphthalimide derivatives, absorption and emission data were collected in organic solvents of varying polarity (methylcyclohexane (MCH), toluene (Tol), dichloromethane (DCM) and acetonitrile (AcN)), and compared. Figures 1 and S1 (Supporting Information) and Table 1 summarize the results obtained for compounds **1 a–4** regarding the absorption and emission maxima, fluorescence quantum yield and lifetime, and corresponding radiative and non-radiative rate constants. All compounds were assessed regarding photostability in the selected conditions and demonstrated to be stable except for **1 b** which in solution shows slow oxidation of the phosphine moieties and was not further investigated.

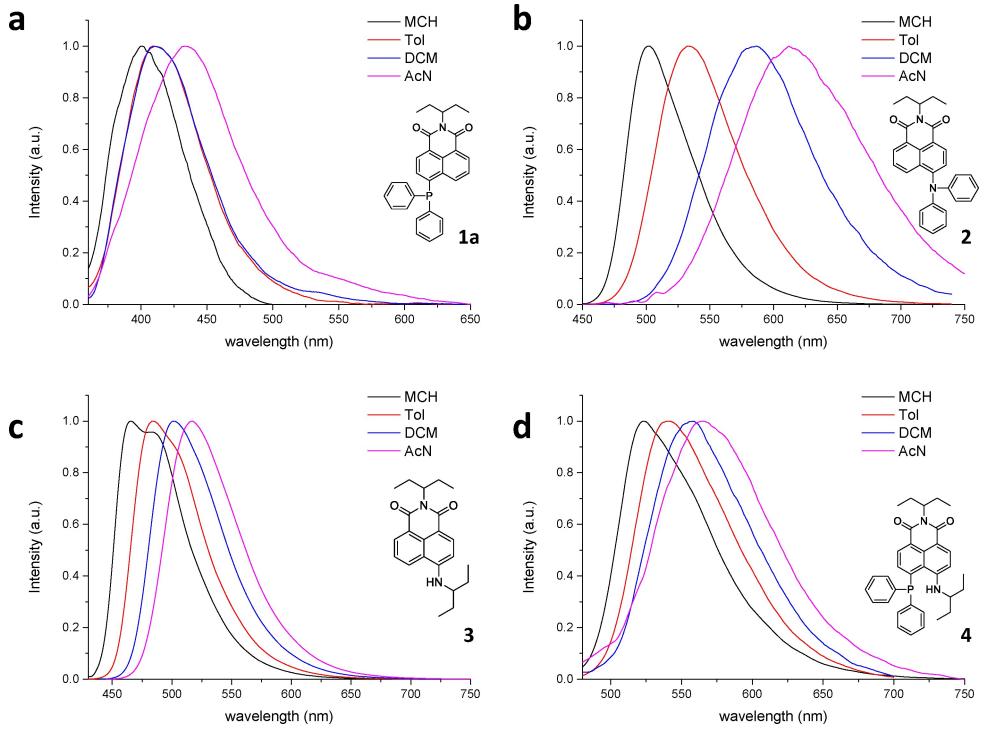


Figure 1. Normalized emission spectra of compound **1a**–**4** in organic solvents. λ_{exc} = 350 nm (a); 440 nm (b); 420 nm (c); 455 nm (d).

Table 1. Absorption (λ_{abs}) and emission (λ_{em}) maxima wavelength, fluorescence lifetime (τ_F) and quantum yield (Φ_F) and radiative (k_r) and non-radiative rate constants (k_{nr}) for compounds **1a**–**4** in different solvents.

Compound	Solvent	λ_{abs} [nm]	λ_{em} [nm]	τ_F [ns]	Φ_F[a]	k_r [ns^{-1}]	k_{nr} [ns^{-1}]
1a	MCH	369	400	3.67	0.004	0.001	0.271
	Tol	374	410	4.83	0.002	< 0.001	0.207
	DCM	373	411	6.46	0.001	< 0.001	0.155
	AcN	370	435	7.48	0.001	< 0.001	0.134
2	MCH	441	502	10.60	0.790	0.075	0.020
	Tol	449	533	12.20	0.450	0.037	0.045
	DCM	453	586	9.90	0.140	0.014	0.087
	AcN	447	612	1.50	0.010	0.007	0.660
3	MCH	416	466	8.20	0.990	0.121	0.001
	Tol	424	484	8.50	0.950	0.112	0.006
	DCM	432	501	10.50	0.900	0.086	0.010
	AcN	436	517	10.20	0.760	0.075	0.024
4	MCH	451	523	4.60	0.015	0.003	0.214
	Tol	457	533	4.90	0.012	0.002	0.202
	DCM	464	542	7.60	0.005	0.001	0.131
	AcN	460	550	6.60	0.002	< 0.001	0.151

[a] Determined by the comparative method, as described in the Experimental Section.

Compound **1a**, bearing a diphenylphosphine substituent, exhibits an absorption spectrum dominated by a band centred at ca. 360 nm with residual vibronic resolution, which does not vary significantly with the solvent. Regarding the emission properties, **1a** exhibits low photoluminescence quantum yield (PLQY, < 0.01) and an emission band with maximum between 400–435 nm depending on solvent polarity, lacking vibronic resolution. Despite the solvatofluorochromic behaviour, the changes in emission maximum and Stokes Shift do not correlate significantly with solvent polarity (Supporting Information, Figure S2a). Conversely, the amine analogue, **2**, shows remarkably different optical properties. The absorption spectrum

exhibits a longest wavelength transition at ca. 450 nm that lacks vibronic resolution and with maximum shifting depending on solvent polarity. **2** also exhibits very strong solvatofluorochromism, with the emission maximum shifting to longer wavelengths with increasing solvent polarity (λ_{em} = 502 nm in MCH; 612 nm in AcN). This behaviour is accompanied by a marked decrease in PLQY and emission lifetime with increasing solvent polarity (lowering from 0.79 in MCH to ca. 0.010 in AcN, and 10.60 ns in MCH to 1.50 ns in AcN, respectively), evidencing the effects of the energy gap law on the non-radiative rate constant (30-fold increase). The change in emission maxima and Stokes shift is highly correlated with solvent polarity (Supporting Information, Figure S2b), suggesting that the $S_1 \rightarrow S_0$ has a strong charge transfer (CT) character with a significant dipole moment difference between the two states. Replacing the diphenylamine moiety with a less electron-donating isopentylamine group, in compound **3**, decreases the solvatochromic behaviour of the naphthalimide dye. In this case, both the absorption and emission spectra exhibit bands with vibronic resolution in low polarity solvents (MCH and toluene), which are not present in higher polarity solvents. This apparent change in transition character with solvent polarity is further evidenced by the difference in the luminescence lifetime and radiative rate constants in both sets of solvents (Table 1). Compared to **2**, compound **3** exhibits significantly less sensitivity to solvent polarity in terms of emission maxima and Stokes shift (Supporting Information, Figure S2c), retaining high PLQY even in acetonitrile. Compound **4**, bearing both diphenylphosphine and isopentylamine moieties, combines optical properties of its counterparts. While it shows similar solvatochromic behaviour to **3**, with a decrease in emission maximum energy and increase in Stokes shift with increasing solvent polarity (Supporting Information, Figure S2d), the PLQY is considerably lower, closer to the values of **1 a**.

Overall, these results show that the introduction of a phosphine moiety in the naphthalimide core leads to a significant decrease in PLQY, mainly due to the increase in non-radiative rate constants, with **1 a** and **4** exhibiting k_{nr} values between one and two orders of magnitude higher than **2** and **3**. Furthermore, the phosphine moiety appears to be responsible for a distinct behaviour of compounds **1 a** and **4**, which exhibit decreasing k_{nr} values with increasing solvent polarity, whereas **2** and **3** follow the more common opposite effect. The k_{nr} values for **1 a** are particularly correlated with solvent viscosity (Supporting Information, Figure S3), suggesting that an interplay between states involving rotation of the diphenylphosphine moiety gives rise to this behaviour.

Optical properties of the Pd(II) complexes 5–6 and reactivity of complex 6

On the ground of the results obtained with derivatives **1 a** and **4**, it was hypothesized that the complexation through phosphine moieties would give rise to significant changes in the optical properties of phosphinated naphthalimide dyes. Both complexes exhibited similar absorption spectra that resemble those of non-substituted naphthalimide dyes, with a lowest energy transition band centred at ca. 350 nm (Figure 2) with residual vibronic resolution, which is attributed to a ligand-centred transition (LCT).[20] It is worth noting that the spectrum of **6** lacks the characteristic CT band at ca. 450 nm (present in the spectra of **4**), suggesting that complexation decreases the electronic contribution of the chelating amine moiety. Neither complex exhibits measurable emission in solution.

However, upon storage of solutions of **6** in soda-lime glass labware, the development of an emissive species was detected, which absorbed at ca. 450 nm, as determined by the excitation spectrum (Figure S4a). This was accompanied by changes in the absorption spectrum, which are depicted in Figure S4b. Upon contact with glass, an initial absorption band centred at ca. 620 nm appeared, with concomitant decrease in the LCT band absorbance. After 24 h, the band at 620 nm was no longer detected, giving rise to a new band at ca. 450 nm, which corresponds to the emissive species absorption maximum. These changes did not occur upon usage of plastic, quartz or boron-silicate glass material, suggesting that the basic surface of soda-lime glass played a critical role in the evolution of **6** into an emissive species. Therefore, solutions of **6** in acetonitrile were treated with NaOH (0.1 equiv. and 1.0 equiv.), and the resulting spectral changes were monitored (Figure 3). It is

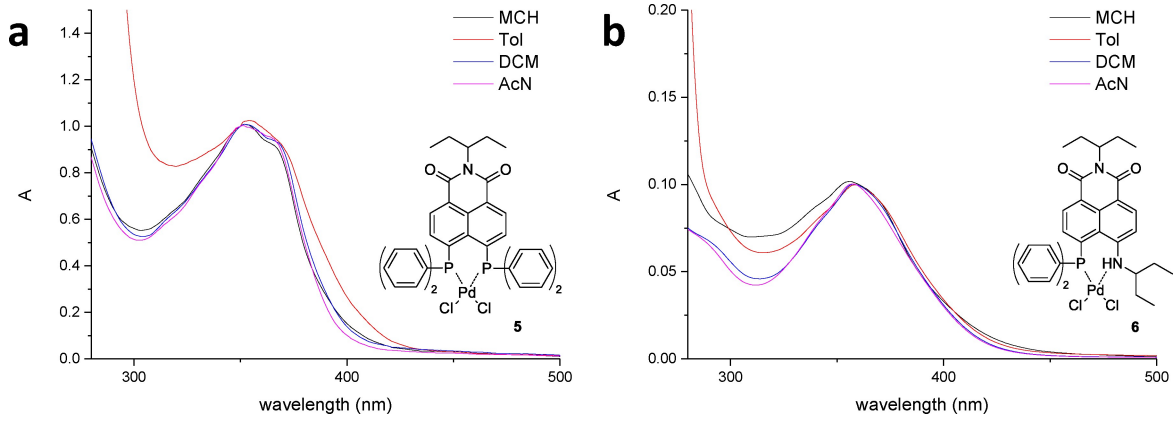


Figure 2. Absorption spectra of complexes **5** and **6** in organic solvents.

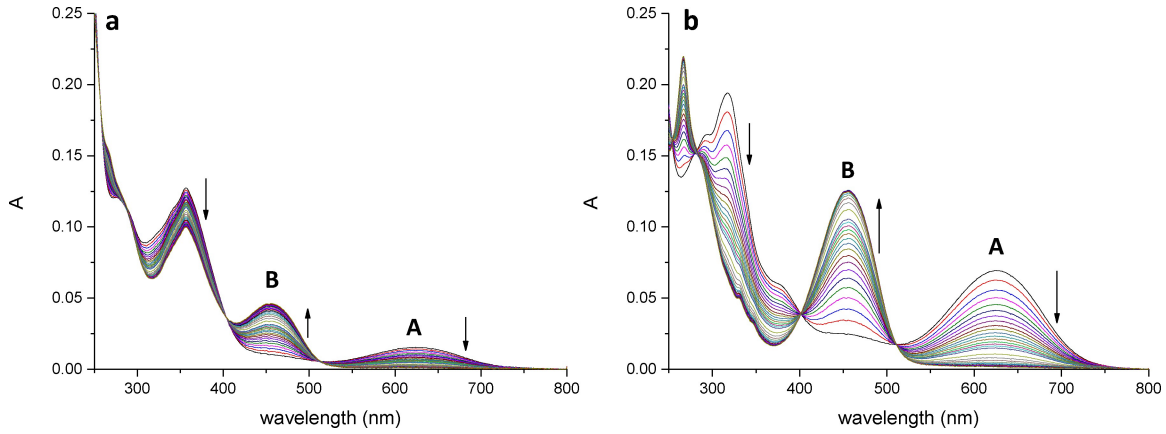
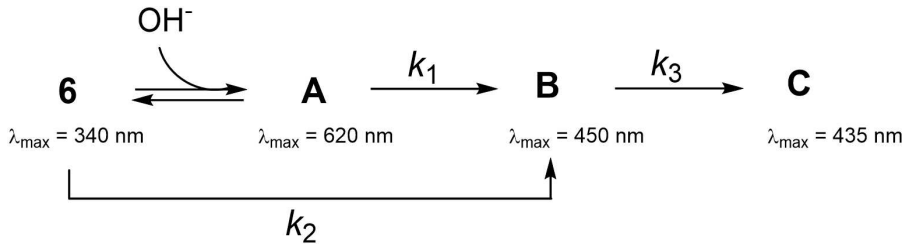


Figure 3. Spectral changes in the absorption spectra of AcN solutions of **6** upon addition of 0.1 equiv. (a) and 1.0 equiv. (b) of NaOH, as a function of time. Equilibration time = 20 h.

shown that, upon addition of 0.1 equiv. of NaOH, there is a decrease in the absorbance of the LCT band of **6**, which is accompanied by a proportional increase in the absorption at 620 nm (corresponding to species **A**, Scheme 5), which in turn gradually disappeared over time to give rise to a new absorbance band centred at ca. 450 nm (corresponding to the emissive species, **B**, Scheme 5). Both absorption bands (350 nm and 620 nm) gradually disappeared over time, suggesting that **6** and **A** are in fast equilibrium, and gave rise to a new absorbance band centred at ca. 450 nm (corresponding to the emissive species, **B**). At 1.0 equiv. of added NaOH, complex **6** is completely converted to **A** in the initial spectrum, which in turn disappears to give rise to **B**. Following the kinetic traces of this spectral transformations (Figure S5), it is evident that the amount of added base influences the rate at which the system evolves. At 0.1 equiv., both the consumption of **6** and the formation of **B** follow a biexponential kinetic law with one fast ($k_1 \approx 6.5 \times 10^{-3}$ min^{-1}) and one slow ($k_2 \approx 9.5 \times 10^{-4}$ min^{-1}) component, while the disappearance of **A** follows a simple single-order kinetics with a rate constant matching the fast component (k_1). At 1.0 equiv., both the disappearance of **A** and the formation of **B** follow a single-order kinetics at the same rate constant, which matches k_1. These results suggest that **6** reacts with NaOH in a very fast step to give rise to **A**, which in turn evolves to **B** with a single-order reaction kinetics. However, at a partial consumption of **6** (0.1 equiv. of NaOH added), an additional slower step takes place (k_2), which is observed as an apparent direct conversion from **6** to **B** that may involve formation of **B** promoted by water, although other possible mechanisms may be at play.

Further monitoring the samples for a period of 96 h shows that **B** is not the thermodynamically stable species, as the absorption spectrum continues changing, with a reduction in absorbance and a shift of the absorption maximum to ca. 435 nm (Figure 4a). These changes are accompanied by a small shift in the emission spectrum and a significant increase in the emission lifetime (Figure 4b–c), suggesting that a new species (**C**) is formed.

With these results into account, we propose the kinetic network represented in Scheme 5, which is triggered by the fast reaction between **6** and NaOH. To determine the structure of the species involved in this network, data from high-resolution mass spectrometry and ^{1}H-, ^{13}C- and ^{31}P NMR spectroscopy were collected. Figure 5 depicts the transformations in the ^{1}H NMR spectra upon addition of 1.0 equiv. of NaOD to a CD_3CN solution of **6**. The spectrum acquired immediately after addition of base shows essentially the same proton signals, with exception to the disappearance of the doublet at ca. 6.8 ppm, which corresponds to the chelating secondary amine proton. Furthermore, the multiplicity of the signal corresponding to the proton of the adjacent carbon at ca. 2.7 ppm is also reduced (Figure S7). This suggests that the initial step is a fast deprotonation of the secondary amine moiety, which is made acidic due to the complexation with Pd(II), giving rise to species **A** detected by UV-Vis spectroscopy. In the first 2 h, new broad signals appear in the low-field region of the spectrum, which



Scheme 5. Proposed kinetic network triggered by the addition of NaOH to solutions of **6**.

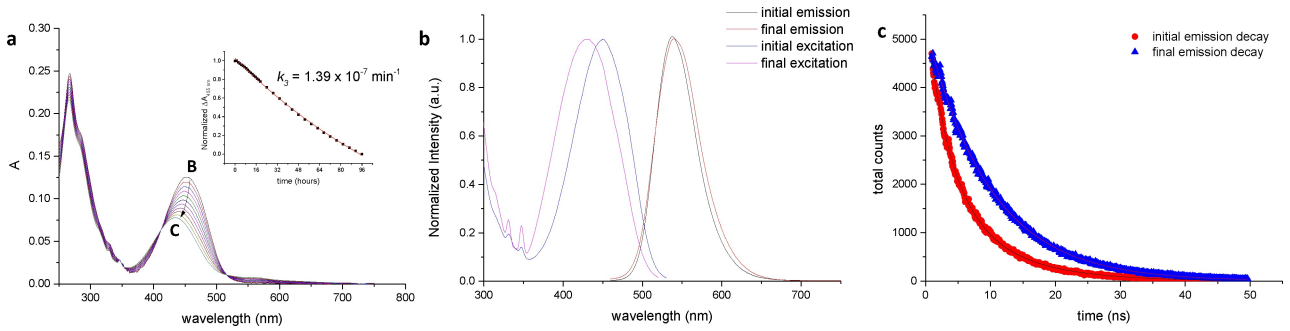


Figure 4. Optical changes in the absorption spectra (a), emission and excitation spectra (b), and fluorescence lifetime (c) of an AcN solution of **6** upon addition of 1.0 equiv. of NaOH, as a function of time. Inset shows the kinetic trace followed at λ_{abs} = 455 nm. Time range = 20–96 h.

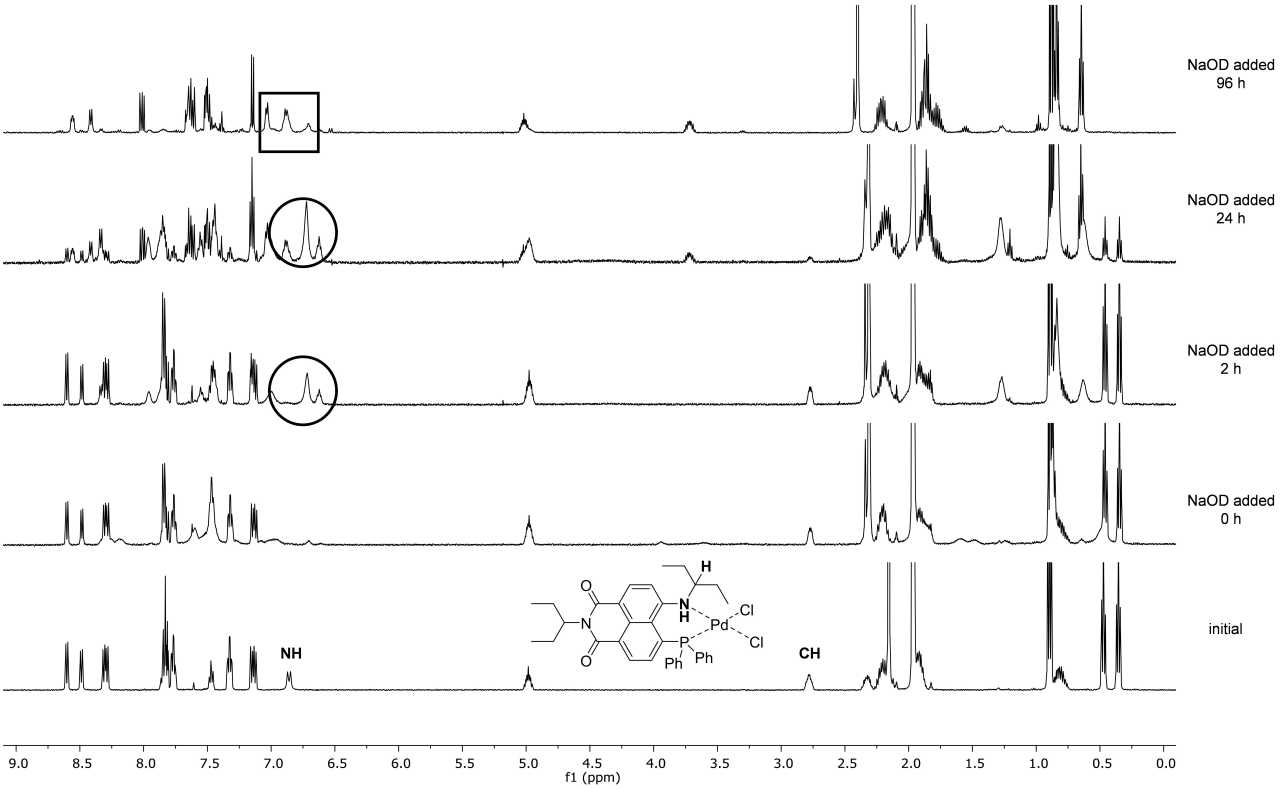


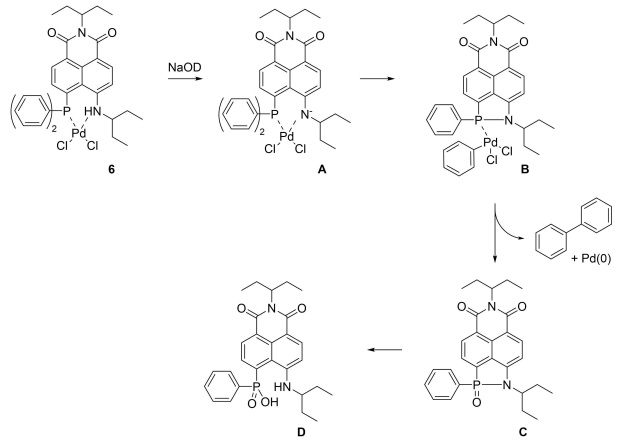
Figure 5. ^{1}H NMR spectra in CD_3CN of complex **6** in the absence and at different reaction times after the addition of 1.0 equiv. of NaOD.

are attributed to the formation of species **B** (see for example the signals circled in Figure 5 which by integration correspond to one phenyl moiety). At ca. 24 h after the addition of NaOD, only residual peaks corresponding to **A** are visible. The aromatic region of the spectra is rather complex showing in addition to the broad peaks previously detected a set of new broad peaks and a set of sharp signals. This last set of signals becomes prevalent after 96 h (Figure 5 and Figure S8), which is consistent with the formation of species **C** after the formation of **B**. This transformation is accompanied by a simplification of the downfield region of the NMR spectrum which is now dominated by the set of sharp peaks but it is worth noting that a set of broad peaks, that by integration corresponds to one phenyl moiety, is still present at around 7 ppm (squared in Figure 5).

Under these conditions the system kept evolving and Figure S8 shows the ^{1}H NMR spectra acquired after 18 and 32 days from the addition of NaOD. It is evidenced that the broad signals observed at ca. 7.0 ppm disappear after 18 days, giving rise to a set of sharp peaks at 7.7, 7.5 and 7.4 ppm, which were attributed to the formation of biphenyl (see below). In addition to these signals, a new set of sharp peaks appear at 8.7, 8.5, 8.2 and 6.5 ppm, corresponding to a new species (**D**). The spectrum after 32 days shows that the slow evolution of **C** to **D** is still going on while the peaks of biphenyl have not changed suggesting that the transformation of **C** to **D** is independent from the process of biphenyl formation. To speed up the transformation of **C** to **D** an additional amount (2.0 equiv.) of NaOD was added. After further 28 days a clear spectrum of the final species (**D**) and biphenyl was acquired

(Figure S9a), evidencing the full consumption of species **C**. Addition of water to the reaction mixture and extraction with DCM first from basic and then from acidic pH allowed isolation of biphenyl and **D**, respectively (Figure S9b,c). The identity of biphenyl was confirmed by comparison with an authentic sample (Figure S9d).

With these results in mind, **C** and **D** were fully characterized by mono and bidimensional NMR and HR-MS (Figure S10–S29) allowing to assign all the resonances in the NMR spectra and to propose the structures reported in Figure S10 and Scheme 6. It is evident that both **C** and **D** bear one phenyl ring attached to the phosphorus atom (consistent with the formation of biphenyl) and are no longer complexed with Pd(II) metal centre. This latter observation was further confirmed through optical spectroscopy through a displacement assay using triphenylphosphine (TPP). Whereas adding TPP to a solution of complex **6** resulted in significant changes in the absorption spectrum due to the displacement of ligand **4**, no changes in absorption and emission spectra or emission lifetime were observed upon addition of TPP to a solution of **C** (Figure S6a). It is also worth noting that, while **C** exhibits diastereotopic methyl groups (similarly to complex **6**), this does not occur in **D** (Figure S12)



Scheme 6. Proposed mechanism for the base promoted transformation of complex **6** to cyclic phosphorylamide **C** and phosphinic acid **D**.

suggesting free pyramidal inversion of the secondary nitrogen which, on the contrary, is hampered in **6** and **C** by chelation to Pd(II) and by the ring closure, respectively. With these results into account, we propose the mechanism in Scheme 6 for the transformation of **6** upon addition of base, in which **C** corresponds to a phosphorylamide-bearing naphthalimide dye, and **D** to a phosphinic acid hydrolysis product. After deprotonation of **6**, **A** evolves to **B** by nucleophilic attack of the nitrogen on the phosphorus and simultaneous transfer of a phenyl on Pd.[21] Complex **B** decomposes forming **C** and releasing a Pd-phenyl complex which, in turn, decomposes by reductive elimination with a second Pd-phenyl fragment forming biphenyl and Pd(0). As a matter of fact, formation of palladium black is observed during the reaction in the NMR tube. Eventually, **C** evolves to **D** by a simple base promoted hydrolysis of the cyclic phosphorylamide. Figure S30 reports a comparison of the absorption spectra off all the species involved in the observed reactivity.

Compared to the analogues **1a**–**4**, **C** shows distinct behaviour, evidencing the effect of the phosphoryl amide moiety. The absorption spectrum (Figure 6a) exhibits a longest wavelength transition lacking vibronic resolution, even in non-polar MCH, and without significant maximum shift with increasing solvent polarity. The emission spectra (Figure 6b) show a broad band without vibronic resolution that does not shift considerably with solvent polarity, especially when compared to amine-bearing analogues **2**–**4**. The relatively small Stokes shift dependence with polarity (Figure S6b) indicates that the dipole moment variation upon excitation is smaller for **C** than for the amine analogues, suggesting that the phosphoryl amide moiety confers considerable dipole moment to the ground state. Regarding the emission kinetics, **C** evidences a remarkably long fluorescence lifetime (15.5 ns in MCH) and k_r values that do not change with increasing solvent polarity (Table 2).

As demonstrated by NMR experiments (Figure S8), the phosphoryl amide moiety also makes **C** labile in basic media. The hydrolysis of this group gives rise to the phosphinic acid derivative **D**, which displays distinct optical properties. Both its absorption and emission spectra are shifted to lower energies

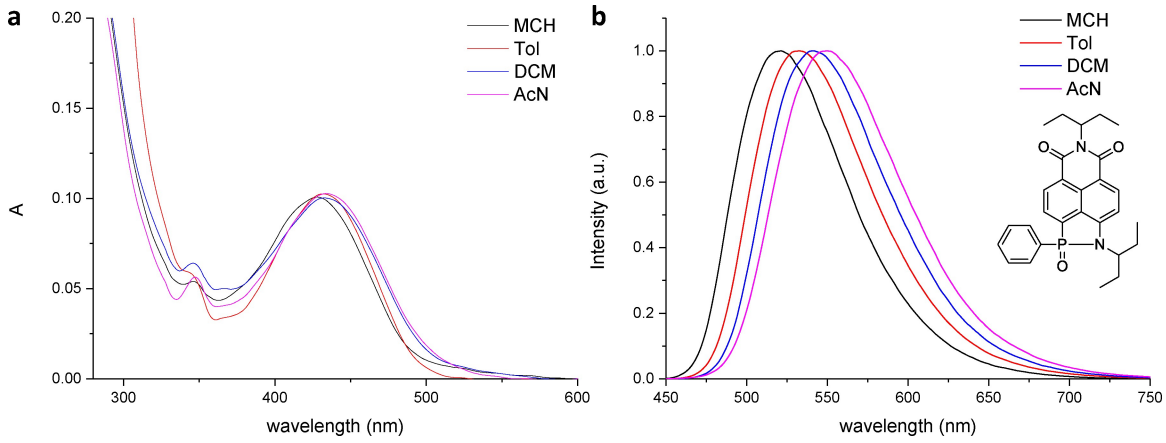


Figure 6. Absorption (a) and emission (b) spectra of isolated compound **C** in organic solvents. $\lambda_{exc} = 420$ nm.

Table 2. Absorption (λ_{abs}) and emission (λ_{em}) maxima wavelength, fluorescence lifetime (τ_F) and quantum yield (Φ_F) and radiative (k_r) and non-radiative rate constants (k_{nr}) for compounds C and D in different solvents.

Compound	Solvent	λ_{abs} [nm]	λ_{em} [nm]	τ_F [ns]	Φ_F[a]	k_r [ns^{-1}]	k_{nr} [ns^{-1}]
C	MCH	428	521	15.5	0.40	0.026	0.039
	Tol	432	533	14.4	0.40	0.028	0.042
	DCM	433	542	13.2	0.36	0.027	0.048
	AcN	433	550	11.2	0.31	0.028	0.062
D	MCH	insoluble					
	Tol	471	565	2.5	0.33	0.132	0.268
	DCM	476	575	2.7	0.21	0.078	0.293
	AcN	474	570	3.5	0.16	0.045	0.240

[a] Determined by the comparative method, as described in the Experimental Section.

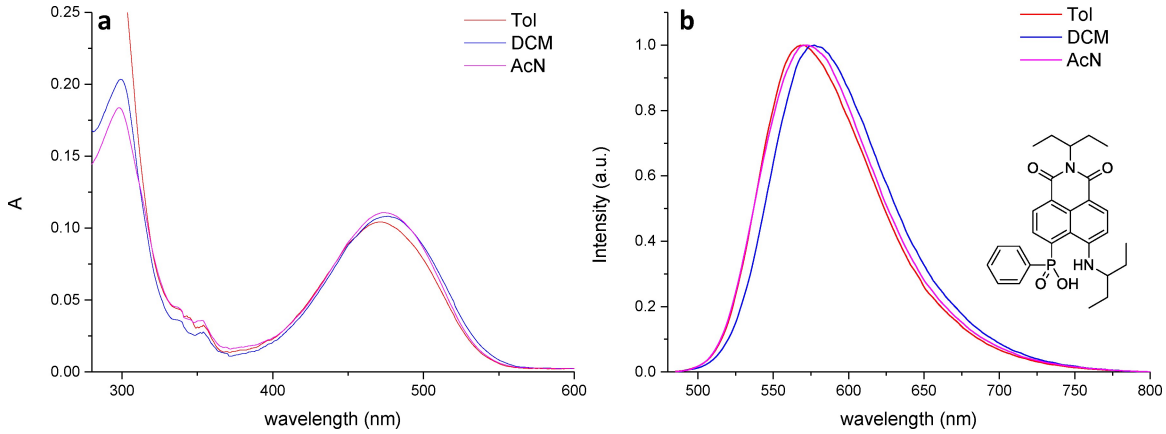


Figure 7. Absorption (a) and emission (b) spectra of isolated compound **D** in organic solvents. $\lambda_{exc} = 450$ nm.

(λ_{abs} ca. 475 nm and λ_{em} ca. 575 nm, for the longest wavelength transition, Figure 7), dominated by broad bands lacking vibronic resolution, and with position practically independent of solvent polarity, suggesting that the molecule is considerably polar even in the ground state. Furthermore, the emissive properties of the dye are considerably affected upon hydrolysis, with **D** exhibiting remarkably lower PLQY and shorter emission lifetime than **C** in organic solvents (Table 2).

Conclusions

We reported the preparation of mono- and di-phosphinated 1,8-naphthalimide dyes, phosphino/amino mixed derivatives and their corresponding Pd(II) complexes. We assessed the effects of phosphination in the optical properties of these compounds through absorption and emission spectroscopy, showing that the electron-donating character of phosphorus-based groups is significantly lower than the nitrogen-bearing counterparts and does not give rise to the characteristic CT transitions that typically endow 1,8-naphthalimide dyes with remarkable optical properties. In addition, the presence of phosphine moiety leads to a marked increase in non-radiative rate constants and consequently to unusually low PLQY values for this class of compounds. The obtained Pd(II) complexes did not show luminescence in solution. However, the compound with the phosphino/amino bidentate ligand (complex **6**) exhibited sensitivity to traces of basic species, resulting in the formation of an emissive dye. Through NMR and optical spectroscopy and mass spectrometry data, we demonstrated that a novel 1,8-naphthalimide dye bearing a cyclic phosphoryl amide moiety was formed due to the deprotonation of the highly acidic secondary amine moiety in complex **6**. This dye exhibited a remarkably long emission lifetime (up to 15 ns in apolar solvents), showing potential interest for application in fluorescence imaging. Furthermore, this work demonstrates that the preparation of phosphoryl amide moieties, which have interest in medicinal chemistry, organic synthesis and lubricant industry, can be addressed through Pd(II) catalyzed reactions using mildly basic conditions without the need to employ rare-earth metal catalysts or corrosive phosphoryl halides, paving the way for the emergence of a new class of luminescent dyes.

Experimental Section

The reagents and solvents have been purchased from Sigma-Aldrich or Alfa Aesar and used without further purification. Column

chromatography was performed on silica gel 60 (Merck, 230–400 mesh ASTM), eluting with solvents mixtures as specified below. The reactions were monitored by TLC (silica gel/ UV 254, 0.20 mm, glass or aluminum support). All solvents used for spectroscopy measurements were of spectroscopic grade and used as acquired without further purification. Unless otherwise stated, all experiments were carried out at 20 °C. UV-Vis spectra were recorded on an Agilent Cary 60 spectrometer or a Shimadzu UV-3600 double beam spectrophotometer in a quartz cuvette (1 cm optic path length). Fluorescence emission spectra and kinetics were recorded on a Jobin Yvon Fluorolog spectrofluorimeter in a quartz cuvette (1 cm optic path length). Fluorescence decays were recorded in a Horiba DeltaFlex system using a BDS-405-SM-FBE ps diode laser, with 500 ps pulse width and a Picosecond Photon Detector (PPD-900). Impulses were recorded with a Ludox scattering suspension to define the instrument response function (IRF). Fluorescence decays were measured using time-correlated single-photon counting (TC-SPC) mode and were IRF-deconvoluted and fitted with exponential decay equation using EZTime software. Fluorescence Quantum Yields were determined by the comparative method using Quinine Sulfate in aq. H_2SO_4 0.05 M ($\Phi_F = 0.546$), Coumarin 1 in EtOH ($\Phi_F = 0.64$) or Fluorescein in basic EtOH ($\Phi_F = 0.97$), depending on the absorption and emission spectral range of studied dyes.[22] Rate constants were calculated using Equations (1) and (2), where Φ_F is the fluorescence quantum yield and τ_F is the fluorescence lifetime, in nanoseconds.

$$k_r = \frac{\Phi_F}{\tau_F} \quad (1)$$

$$k_{nr} = \frac{1 - \Phi_F}{\tau_F} \quad (2)$$

The concentration of all samples was adjusted for $A < 0.1$ at the longest wavelength transition, thus discarding reabsorption interferences. Mass spectra have been acquired using a Bruker Esquire 4000 ESI-MS instrument or a Bruker micrOTOF–Q for HRMS by Dr. Fabio Hollan. Only molecular ions and major peaks are reported. Infrared spectra (IR) were measured on a Jasco FT/IR-200 instrument. NMR spectra were recorded on a Varian 500 MHz (125 MHz for carbon and 202 MHz for phosphorous) or a Varian 400 MHz (101 MHz for carbon and 162 MHz for phosphorous). Chemical shifts are reported as parts per million (ppm) relative to the solvent residual signal as internal reference. Coupling constants (J) are quoted in Hertz (Hz). The s, d, t, q, quint, sex, m, and bs signal notations indicate respectively: singlet, doublet, triplet, quartet, quintet, sextet, multiplet and broad signal. 5-Bromo-acenaphthene,[23] 5,6-dibromo-acenaphtene,[24] 5,6-bis(diphenylphosphino)acenaphthene and 5,6-bis(diphenylphosphinoxide)acenaphthene,[16c] 5-bromo-6-diphenylphosphinoxide-acenaphthene[25] were synthesized according to published literature.

Synthesis of 4-diphenylphosphino-1,8-naphthalic-N-(1-ethylpropyl)-imide (1 a)

5-diphenylphosphinoxide-acenaphthene: 4.66 g of 5-bromo-acenaphthene (19.9 mmol, 1 equiv.) were suspended in 50 mL of dry Et_2O under Ar atmosphere. The suspension was cooled at −78 °C and 1 equiv. of *n*BuLi (pentane solution 1.7 M) was added slowly. The suspension was stirred at −78 °C for 10 min and then it was brought to room temperature using a water bath. The reaction was monitored using TLC (EP) and, after the complete disappearing of the starting material, 4.41 mL of chlorodiphenylphosphine (d = 1.23 g/mL, 24.6 mmol, 1.23 equiv.) were added at −78 °C. The solution was warmed up to ambient temperature and a copious amount of pale yellow precipitate was formed. After 2 h the precipitate was filtered through a glass sintered filter, washed with 10 mL of cold Et_2O and the solution was discarded. The precipitate was then dissolved with DCM and some LiCl was left on the filter. The solvent was then removed under vacuum yielding 5.50 g of crude. The crude 5-diphenylphosphino-acenaphthene thus obtained was dissolved in 50 mL of DCM and 20 mL of H_2O_2 30% were carefully added using an ice bath to cool the reaction. After 10 min, the two phases were added to a separatory funnel. The water was discarded and the organic phase was washed with brine (1 × 30 mL). The DCM was then dried with Na_2SO_4, filtered and the solvent removed under vacuum, yielding 4.50 g (12.7 mmol, yield 64%) of pure product.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.02 (d, J = 8.3 Hz, 1H), 7.80–7.63 (m, 5H), 7.61–7.26 (m, 8H), 7.22 (d, J = 7.0 Hz, 1H), 3.43 (s, 4H);^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.4, 152.3, 146.5, 139.5, 139.4, 135.7, 135.6, 133.3, 132.3, 132.1, 132.0, 131.9, 131.8, 131.4, 131.3, 131.2, 129.2, 128.6, 128.5, 128.2, 128.1, 124.1, 123.1, 122.8, 122.7, 120.3, 118.2, 118.1, 77.4, 77.1, 76.7, 30.4, 30.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 31.6; ESI-MS (m/z) calculated for $C_{24}H_{20}OP^+$: 355.1 $[M+H]^+$, found 355.2.

4-diphenylphosphinoxide-1,8-naphthalic anhydride: 4.50 g of 5-diphenylphosphinoxide-acenaphthene (12.7 mmol, 1 equiv.) and 12 g of sodium dichromate (46 mmol, 3.6 equiv.) were heated at 80 °C in 70 mL of glacial acetic acid for 2 h. The reaction mixture was diluted with water and added to 300 mL of NaOH 5%. The suspension was filtered to remove the insoluble part and the solution was acidified with sulfuric acid to pH 1. A copious amount of pale green precipitate was formed and the suspension was filtered on a paper filter. The solid was dried in the oven, yielding 4.10 g of product (10.3 mmol, yield 81%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.26 (s, 1H), 8.67 (s, 1H), 8.54 (s, 1H), 7.68 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.9, 159.8, 138.7, 137.7, 135.4, 135.3, 133.8, 133.6, 133.5, 132.8, 132.7, 132.6, 132.0, 131.9, 131.4, 131.2, 131.1, 130.6, 130.5, 130.4, 129.1, 129.0, 128.6, 122.1, 119.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 31.5; ESI-MS (m/z) calculated for $C_{24}H_{16}O_4P^+$: 399.1 $[M+H]^+$, found 399.1.

4-diphenylphosphinoxide-1,8-naphthalic-N-(1-ethylpropyl)-imide: 3.60 g of 4-diphenylphosphinoxide-1,8-naphthalic anhydride (9.04 mmol, 1 eq,) were suspended in 50 mL of EtOH absolute. To the suspension 2.1 mL of 1-ethylpropylamine (d = 0.748 g/mL, 18 mmol, 2 equiv.) were added and the mixture was refluxed overnight. The solvent was removed under vacuum and the product was purified by flash column chromatography (EP : AcOEt 50 : 50 to 20 : 80) yielding 1.60 g of pure product (3.42 mmol, yield 38%) as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.08 (d, J = 8.6 Hz, 1H), 8.60 (d, J = 7.2 Hz, 1H), 8.48 (d, J = 7.1 Hz, 1H), 7.78–7.67 (m, 5H), 7.63 (m, 2H), 7.54 (m, 5H), 5.12–4.94 (m, 1H), 2.31–2.15 (m, 2H), 2.01–1.85 (m, 2H), 0.91 (t, J = 7.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 136.3, 135.4, 133.6, 133.5, 133.4, 132.6, 132.5, 132.4, 132.3, 132.1, 132.0, 131.9, 131.1, 128.9, 128.8, 128.7, 128.1, 57.7, 24.9, 11.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 31.5; ESI-MS (m/z) calculated for $C_{29}H_{27}NO_3P^+$: 468.2 $[M+H]^+$, found 468.2.

4-diphenylphosphino-1,8-naphthalic-N-(1-ethylpropyl)-imide (1 a): 400 mg of 4-diphenylphosphinoxide-1,8-naphthalic-N-(1-ethylpropyl)-imide (0.85 mmol, 1 equiv.) were dissolved in 8 mL of dry toluene under Ar atmosphere. An excess of trichlorosilane (10 equiv.) was added and the solution was refluxed in a closed vessel for 24 h. The solution was diluted with 200 mL of degassed NaOH 5% directly in a separatory funnel. The water phase was extracted with degassed Et_2O (3 × 30 mL). The organic phase was then dried with Na_2SO_4, filtered and the solvent removed under

vacuum. The crude was purified using flash chromatography (EP:AcOEt 97:3) affording 339 mg of product (0.75 mmol, yield 88%) as a bright yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (dd, J_{H-H} = 8.5, 7.3 Hz, 1H, H^2), 8.59 (d, J = 7.3 Hz, 1H, H^7), 8.43 (d, J = 7.5 Hz, 1H, H^4), 7.69 (dd, J = 8.5, 7.3 Hz, 1H, H^3), 7.47–7.30 (m, Ph), 5.12–5.00 (m, 1H, CH^{11}), 2.34–2.17 (m, 2H, CH_2^{12}), 2.02–1.83 (m, 2H, CH_2^{12}), 0.92 (t, J = 7.5 Hz, 6H, CH_3^{13}); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 143.9, 143.6, 134.7, 134.7, 134.4, 134.2, 133.5, 133.3, 132.1, 132.1, 131.8, 129.5, 129.0, 128.9, 128.3, 128.2, 128.2, 127.0, 126.9, 125.3, 57.4, 25.0, 11.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ: −12.9; ESI-MS (m/z): calculated for $C_{29}H_{27}NO_2P^+$: 452.2 $[M+H]^+$, found 452.2; HRMS (ESI) calculated for $C_{29}H_{27}NO_2P^+$: 452.1774 $[M+H]^+$, found 452.1778.

Synthesis of 4,5-bis(diphenylphosphino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (1 b)

4,5-bis(diphenylphosphinoxide)-1,8-naphthalic anhydride: 1.61 g of 5,6-bis-diphenylphosphinoxide-1,2-dihydroacenapthylene (2.91 mmol, 1 equiv.) and 3.7 g of sodium dichromate (14 mmol, 4.8 equiv.) were heated at 80 °C in 25 mL of glacial acetic acid for 2 h. The reaction mixture was diluted with water and added to 200 mL of NaOH 5%. The suspension was filtered in order to remove the insoluble part and the solution was acidified with sulfuric acid to pH 1. A copious amount of pale green precipitate was formed and the suspension was filtered on a paper filter. The solid was dried in the oven, yielding 0.794 g of product (1.33 mmol, yield 46%). The ^{13}C NMR was not recorded due to the low solubility of the compound.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (d, J = 7.5 Hz, 2H), 8.00 (dd, J_{H-H} = 7.5 Hz, J_{H-P} = 15.1 Hz, 2H) 7.54–7.39 (m, 20H); ^{31}P NMR (162 MHz, $CDCl_3$) δ: 30.4; ESI-MS (m/z) calculated for $C_{36}H_{25}O_5P_2^+$: 599.1 $[M+H]^+$, found 599.2.

4,5-bis(diphenylphosphinoxide)-1,8-naphthalic-N-(1-ethylpropyl)-imide: 4.032 g of 4,5-bis(diphenylphosphinoxide)-1,8-naphthalic anhydride (6.74 mmol, 1 eq,) were suspended in 40 mL of EtOH absolute. To the suspension 1.60 mL of 1-ethylpropylamine (d = 0.748 g/mL, 13.7 mmol, 2.0 equiv.) were added and the mixture was refluxed overnight. The solvent was removed under vacuum and the product was purified by flash column chromatography (EP:AcOEt 50:50 to 20:80) yielding 1.943 g of pure product (2.91 mmol, yield 43%) as pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (d, J = 7.4 Hz, 2H), 7.93 (dd, J_{H-H} = 7.4 Hz, J_{H-P} = 15.7 Hz, 2H), 7.52 (m, 8H), 7.44 (m, 4H), 7.36 (m, 8H), 4.99 (m, 1H), 2.28–2.13 (m, 2H), 1.99–1.85 (m, 2H), 0.91 (t, J = 7.5 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.6, 137.6, 137.4, 137.3, 136.2, 131.6, 131.5, 131.2, 128.2, 128.1, 58.1, 25.1, 11.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 30.6; ESI-MS (m/z) calculated for $C_{41}H_{36}NO_4P_2^+$: 668.2 $[M+H]^+$, found 668.3.

4,5-bis(diphenylphosphino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (1 b): 500 mg of 4,5-bis(diphenylphosphinoxide)-1,8-naphthalic-N-(1-ethylpropyl)-imide (0.75 mmol, 1 equiv.) were dissolved in 8 mL of dry toluene under Ar atmosphere. An excess of trichlorosilane (10 equiv.) was added and the solution was refluxed in a closed vessel for 24 h. The solution was diluted with 200 mL of degassed NaOH 5% directly in a separatory funnel. The water phase was extracted with degassed Et_2O (3×30 mL). The organic phase was then dried with Na_2SO_4, filtered and the solvent removed under vacuum. The red oil was purified using flash chromatography (EP:AcOEt 97:3) affording 350 mg of product (0.55 mmol, yield 73%) as a red solid. In solution the compound shows slow oxidation of the phosphine moieties back to the diphenylphosphinoxide derivative.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (d, J = 7.7 Hz, 2H, $H^{2,7}$), 7.61 (d, J = 7.7 Hz, 2H, $H^{3,6}$), 7.33 (m, Ph), 7.19 (m, 8H, Ph), 5.01 (m, 1H, CH^{11}), 2.24 (m, 2H, CH_2^{12}), 1.91 (m, 2H, CH_2^{12}), 0.91 (t, J = 7.5 Hz, 6H, CH_3^{13}); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 138.3, 137.4, 134.3, 134.2, 133.9, 133.8, 133.7, 131.5, 131.4, 131.1, 129.1, 128.9, 128.5, 128.1, 128.0, 57.4, 24.9, 11.31; ^{31}P NMR (162 MHz, $CDCl_3$) δ: −13.3; ESI-MS (m/z) calculated for $C_{41}H_{36}NO_2P_2^+$: 636.2 $[M+H]^+$, found 636.2; HRMS (ESI) (m/z) calculated for $C_{41}H_{36}NO_2P_2^+$: 636.2216 $[M+H]^+$, found 636.2214.

Synthesis of 4-(diphenylphosphino)-5-(1-ethypropylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (4)

4-bromo-5-(diphenylphosphinoxide)-1,8-naphthalic anhydride: 0.875 g of 5-bromo-6-diphenylphosphinoxide-acenaphthene (2.02 mmol, 1 equiv.) and 1.6 g of sodium dichromate (6.1 mmol, 3 equiv.) were heated at 80 °C in 25 mL of glacial acetic acid for 2 h. The reaction mixture was diluted with water and added to 200 mL of NaOH 5%. The suspension was filtered to remove the insoluble part and the solution was acidified with sulfuric acid to pH 1. A copious amount of pale green precipitate was formed and the suspension was filtered on a paper filter. The solid was dried in the oven, yielding 0.850 g of product (1.78 mmol, yield 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (s, 2H), 8.26 (s, 1H), 7.71 (m, 11H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 159.4, 159.2, 139.0, 138.5, 138.4, 138.2, 136.4, 135.1, 134.0, 133.5, 133.5, 133.4, 132.8, 132.7, 132.3, 132.2, 131.6, 131.5, 131.4, 130.9, 130.8, 128.9, 128.8, 122.6, 118.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 35.2; ESI-MS (m/z) calculated for $C_{24}H_{15}BrO_4P^+$: 477.0 $[M+H]^+$, found477.1.

4-diphenylphosphinoxide-5-(1-ethypropylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide: 400 mg of 4-bromo-5-(diphenylphosphinoxide)-1,8-naphthalic anhydride (0.838 mmol, 1 eq,) were suspended in 15 mL of EtOH absolute. To the suspension 0.30 mL of 1-ethylpropylamine (d = 0.748 g/mL, 2.6 mmol, 3 equiv.) were added and the mixture was refluxed overnight. The solvent was removed under vacuum and the product was purified by flash column chromatography (EP:AcOEt to 80:20) yielding 287 mg of pure product (0.520 mmol, yield 62%) as bright red orange solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.71 (d, J = 5.4 Hz, 1H), 8.44 (d, J = 8.7 Hz, 1H), 8.37 (d, J = 7.5 Hz, 1H), 7.64–7.41 (m, 10H), 7.30 (dd, J_{H-H} = 8.0 Hz, J_{H-P} = 17.6 Hz, 1H), 6.62 (d, J = 8.9 Hz, 1H), 5.04 (m, 1H), 3.23 (m, 1H), 2.36–2.15 (m, 2H), 2.00–1.82 (m, 2H), 1.49–1.20 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H), 0.79 (t, J = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 151.7, 133.2, 132.8, 132.7, 132.6, 132.5, 132.4, 132.3, 132.2, 132.1, 131.9, 131.8, 131.0, 128.9, 128.8, 123.2, 123.1, 106.6, 57.0, 25.8, 25.0, 11.3, 10.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 43.1; ESI-MS (m/z) calculated for $C_{34}H_{38}N_2O_3P^+$: 553.3 $[M+H]^+$, found 553.3.

4-(diphenylphosphino)-5-(1-ethypropylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (4): 400 mg of 4-diphenylphosphinoxide-5-(1-ethypropylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (0.72 mmol, 1 equiv.) were dissolved in 8 mL of dry toluene under Ar atmosphere. An excess of trichlorosilane (10 equiv.) was added and the solution was refluxed in a closed vessel for 24 h. The solution was diluted with 200 mL of degassed NaOH 5% directly in a separatory funnel. The water phase was extracted with degassed Et_2O (3×30 mL). The organic phase was then dried with Na_2SO_4, filtered and the solvent removed under vacuum. The crude was purified using flash chromatography (EP:AcOEt 97:3) affording 268 mg of product (0.50 mmol, yield 69%) as an orange yellow solid.

^{1}H NMR (500 MHz, CD_3CN, 298 K) δ = 8.31 (d, 1H, H^2), 8.27 (d, 1H, H^7), 8.10 (dd, 1H, NH), 7.46–7.39 (m, 6H, H^{Ph}, $H^{Ph'}$), 7.26–7.23 (m, 4H, H^{Ph}, $H^{Ph'}$), 7.19 (dd, 1H, H^6), 6.78 (d, 1H, H^3), 4.96 (quint, 1H, H^{11}), 3.56

(quint, 1H, H^{14}), 2.22–2.16 (m, 2H, H^{12}, $H^{12'}$), 1.85–1.79 (m, 2H, H^{12}, $H^{12'}$), 1.61–1.48 (m, 4H, H^{15}, $H^{15'}$), 0.84–0.80 (m, 12H, H^{13}, $H^{13'}$, H^{16}, $H^{16'}$); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 152.3, 134.1, 134.0, 133.9, 132.7, 129.8, 129.5, 129.1, 129.0, 128.1, 126.0, 125.7, 123.1, 106.2, 56.3, 26.0, 25.1, 11.35, 10.2, 10.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ: −4.6; ESI-MS (m/z) calculated for $C_{34}H_{38}N_2O_2P^+$: 537.3 $[M+H]^+$, found 537.4; HRMS (ESI) (m/z) calculated for $C_{34}H_{38}N_2O_2P^+$: 537.2665 $[M+H]^+$, found 537.2663.

Synthesis of 4-(diphenylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (2) and 4-(1-ethypropylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (3)

4-bromo-1,8-naphthalic-N-(1-ethylpropyl)-imide: To a suspension of 1.00 g of 4-bromo-1,8-naphthalic anhydride (3.61 mmol, 1 equiv.) in 20 mL of diethyleneglycol, 500 μL of 1-ethylpropylamine (d = 0.748 g/mL, 4.29 mmol, 1.19 equiv.) were added. The suspension was heated at 130 °C for 3 h. After cooling the suspension to room temperature, it was diluted with 250 mL of water. The water phase was extracted with DCM (4×25 mL) and then dried with Na_2SO_4, filtered and the solvent removed under vacuum, affording 1.04 g of pure product (3.00 mmol, yield 83 %).

ESI-MS (m/z): 368.0 $[M+Na]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (d, J = 7.3 Hz, 1H), 8.52 (dd, J = 8.5 Hz, J = 1.1 Hz, 1H), 8.37 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 7.9 Hz, 1H), 7.82 (dd, J = 8.5 Hz, J = 7.3 Hz, 1H), 5.00 (tt, J = 9.6 Hz, J = 5.9 Hz, 1H), 2.21 (m, 2H), 1.89 (m, 2H), 0.87 (t, J = 7.5 Hz, 7H); ^{13}C NMR (101 MHz, $CDCl_3$): 132.8, 131.0, 130.4, 129.8, 129.1, 128.0, 57.6, 57.5, 24.9, 11.2; ESI-MS (m/z) calculated for $C_{17}H_{16}BrNO_2Na^+$: 368.0 $[M+Na]^+$, found 368.0.

4-(diphenylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (2)

53 mg of diphenylamine (0.31 mmol, 1.2 equiv.), 90 mg of 4-bromo-1,8-naphthalic-N-(1-ethylpropyl)-imide (0.26 mmol, 1 equiv.), 8 mg of $Pd(dba)_2$ (5 mol %), 8 mg of BINAP (5 mol %) and 254 mg of cesium carbonate (3 equiv.) were added to 10 mL of degassed dry toluene under Ar atmosphere. The suspension was heated at reflux temperature for 4 h. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography eluting CH_2Cl_2/hexane (1/1) to afford 74 mg of compound **2** (0.169 mmol, yield 65 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.51 (d,d J = 7.3 Hz, 2H, $H^{2,7}$), 8.15 (d, J = 8.5 Hz, 1H, H^5), 7.48 (dd, J_1 = 8.5 Hz, J_2 = 7.3 Hz, 1H, H^6), 7.38 (d, J = 8.0 Hz, 1H, H^3), 7.26 (m, Ph, N*H*), 7.09–7.01 (m, 6H, Ph), 5.04 (tt, J_1 = 9.4 Hz, J_2 = 6.0 Hz, 1H, CH^{11}), 2.24 (m, 2H, CH_2^{12}), 1.93 (m, 2H, CH_2^{12}), 0.91 (t, J = 7.5 Hz, 6H, CH_3^{13}); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.0; 150.7, 148.7, 132.2, 131.3, 130.8, 130.4, 129.6, 127.9, 126.5, 125.6, 124.0, 123.8, 119.7, 57.7, 25.3, 11.3; ESI-MS (m/z) calculated for $C_{29}H_{26}N_2O_2Na^+$: 457.2 $[M+Na]^+$, found 457.2; HRMS (ESI) (m/z) calculated for $C_{29}H_{27}N_2O_2^+$: 435.2067 $[M+H]^+$, found 435.2068.

4-(1-ethypropylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (3)

54 mg of 1-ethylpropylamine (0.62 mmol, 1.2 equiv.), 180 mg of 4-bromo-1,8-naphthalic-N-(1-ethylpropyl)-imide (0.52 mmol, 1 equiv.), 16 mg of $Pd(dba)_2$ (5 mol %), 16 mg of BINAP (5 mol %) and 508 mg of cesium carbonate (3 equiv.) were added to 15 mL of degassed dry toluene under Ar atmosphere. The suspension was heated at reflux temperature for 4 h. After removal of the solvent in vacuo, the residue was separated by silica gel column chromatography eluting CH_2Cl_2/hexane (8/2) to afford 154 mg of compound **3** (0.44 mmol, yield 84 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.55 (d, J = 7.3 Hz, 1H, H^7), 8.42 (d, J = 8.4 Hz, 1H, H^2), 8.07 (d, J = 8.5 Hz, 1H, H^5), 7.60 (dd, J_1 = 8.5 Hz, J_2 = 7.3 Hz, 1H, H^6), 6.73 (d, J = 8.4 Hz, 1H, H^3), 5.09-4.97 (m, 2H, H^{11}, N*H*), 3.62 (quint, J = 7.1 Hz, 1H,), 2.24 (m, 2H, H^{14}), 1.87 (m, 2H, H^{12}), 1.77 (m, 2H, H^{12}), 1.66 (m, 2H, H^{15}), 1.01 (t, J = 7.5 Hz, 6H, H^{16}), 0.88 (t, J = 7.5 Hz, 6H, H^{13}); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 166.1, 149.3, 134.3, 130.1, 129.2, 126.4, 125.9, 123.6, 120.5, 112.2, 107.6, 57.4, 55.3, 27.2, 26.9, 10.5, 10.2; ESI-MS (m/z) calculated for $C_{22}H_{28}N_2O_2Na^+$: 375.2 $[M+Na]^+$, found 375.2; HRMS (ESI) (m/z) calculated for $C_{22}H_{28}N_2O_2Na^+$: 375.2043 $[M+Na]^+$, found 375.2048.

Synthesis of [Pd(1 b)Cl_2] (5): 150 mg of 4,5-bis(diphenylphosphino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (**5**, 0.236 mmol, 1.2 equiv.) and 51 mg $[Pd(MeCN)_2Cl_2]$ (0.197 mmol, 1 equiv.) were suspended in 5 mL of MeOH. After a few minutes the suspension cleared up and it was left to stir at ambient temperature for 3 h. An abundant precipitate was formed and it was filtered. The precipitate was then washed with Et_2O and dried under vacuum, yielding 120 mg (0.148 mmol, yield 75 %) of pure product [Pd(**1 b**)Cl_2] (**5**).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56 (d, J = 7.8 Hz, 2H, $H^{2,7}$), 7.75 (m, 2H, $H^{3,6}$), 7.40 (m, 12H, Ph), 7.27 (m, Ph), 4.98 (m, 1H, CH^{11}), 2.19 (m, 2H, CH_2^{12}), 1.92 (m, 2H, CH_2^{12}), 0.90 (t, J = 7.4 Hz, 6H, CH_3^{13}); ^{13}C NMR (101 MHz, $CDCl_3$): 138.2, 134.1, 134.1, 134.0, 131.8, 129.9, 128.9, 128.8, 128.7, 128.2, 127.9, 127.6, 58.3, 24.8, 11.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 22.3; ESI-MS (m/z) calculated for $C_{41}H_{35}ClNO_2P_2Pd^+$: 776.1 $[M–Cl]^+$, found 776.1; HRMS (ESI) (m/z) calculated for $C_{41}H_{35}ClNO_2P_2Pd^+$: 776.0866 $[M–Cl]^+$, found 776.0865.

Synthesis of [Pd(4)Cl_2] (6): 150 mg of 4-(diphenylphosphino)-5-(1-ethypropylamino)-1,8-naphthalic-N-(1-ethylpropyl)-imide (**4**, 0.279 mmol, 1.2 equiv.) and 60 mg $[Pd(MeCN_2)Cl_2]$ (0.233 mmol, 1 equiv.) were suspended in 5 mL of MeOH. After a few minutes the suspension cleared up and it was left to stir at ambient temperature for 3 h. An abundant precipitate was formed and it was filtered. The precipitate was then washed with Et_2O and dried under vacuum, yielding mg (0.193 mmol, yield 83 %) of pure [Pd(**4**)Cl_2] (**6**) as green/brown powder.

^{1}H NMR (500 MHz, CD_3CN, 298 K) δ = 8.58 (d, 1H, H^2), 8.46 (d, 1H, H^7), 8.27 (dd, 2H, $H^{o'}$), 7.86-7.70 (m, 5H, H^3, H^6, $H^{p'}$, $H^{m'}$), 7.44 (t, 1H, H^p), 7.30 (t, 2H, H^m), 7.11 (dd, 2H, H^o), 6.83 (d, 1H, NH), 4.95 (quint, 1H, H^{11}), 2.76 (quint, 1H, H^{14}), 2.29 (bs, 1H, H^{15}), 2.16 (bs, 2H, H^{12}, $H^{12'}$), 1.90 (bs, 3H, H^{12}, $H^{12'}$, H^{15}), 0.87 (t, 6H, H^{13}, $H^{13'}$), 0.79 (bs, 2H, $H^{15'}$), 0.45 (t, 3H, $H^{16'}$), 0.33 (t, 3H, H^{16}); ^{13}C NMR (101 MHz, $CDCl_3$): 141.5, 141.4, 137.8, 133.8, 133.7, 133.3, 133.2, 133.0, 131.8, 131.1, 130.5, 130.4, 130.3, 129.9, 129.8, 128.8, 128.6, 128.5, 126.3, 125.9, 125.0, 124.6, 123.5, 67.5, 58.2, 26.7, 24.9, 24.8, 20.4, 11.3, 11.3, 8.8, 5.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ: 29.9; ESI-MS (m/z) calculated for $C_{34}H_{37}ClN_2O_2PPd^+$: 677.1 $[M–Cl]^+$, found 677.1; HRMS (ESI) (m/z) calculated for $C_{34}H_{37}ClN_2O_2PPd^+$: 677.1316 $[M–Cl]^+$, found 677.1318.

Supporting Information

Additional optical spectroscopy data, NMR investigation of the reactivity and NMR and HRMS characterization of compounds **4**, **6**, **C** and **D**.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[1] H.-Q. Dong, T.-B. Wei, X.-Q. Ma, Q.-Y. Yang, Y.-F. Zhang, Y.-J. Sun, B.-B. Shi, H. Yao, Y.-M. Zhang, Q. Lin, *J. Mater. Chem. C* **2020**, *8*, 13501.
[2] D. Gudeika, *Synth. Met.* **2020**, *262*, 116328..
[3] a) M. S. Alexiou, V. Tychopoulos, S. Ghorbanian, J. H. P. Tyman, R. G. Brown, P. I. Brittain, *J. Chem. Soc. Perkin Trans. 2* **1990**, 837; b) D. Srikun, E. W. Miller, D. W. Domaille, C. J. Chang, *J. Am. Chem. Soc.* **2008**, *130*, 4596.
[4] S. O. Aderinto, S. Imhanria, *Chem. Pap.* **2018**, *72*, 1823.
[5] R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Kruger, T. Gunnlaugsson, *Chem. Soc. Rev.* **2010**, *39*, 3936.
[6] H. Yu, Y. Guo, W. Zhu, K. Havener, X. Zheng, *Coord. Chem. Rev.* **2021**, *444*, 214019.
[7] C. Geraghty, C. Wynne, R. B. P. Elmes, *Coord. Chem. Rev.* **2021**, *437*, 213713.
[8] a) S. Banerjee, E. B. Veale, C. M. Phelan, S. A. Murphy, G. M. Tocci, L. J. Gillespie, D. O. Frimannsson, J. M. Kelly, T. Gunnlaugsson, *Chem. Soc. Rev.* **2013**, *42*, 1601; b) A. Saini, K. R. J. Thomas, A. Sachdev, P. Gopinath, *Chem. Asian J.* **2017**, *12*, 2612.
[9] M. D. Tomczyk, K. Z. Walczak, *Eur. J. Med. Chem.* **2018**, *159*, 393.
[10] A. S. Oshchepkov, M. S. Oshchepkov, M. V. Oshchepkova, A. Al-Hamry, O. Kanoun, E. A. Kataev, *Adv. Opt. Mater.* **2021**, *9*, 2001913.
[11] C. B. Nielsen, S. Holliday, H.-Y. Chen, S. J. Cryer, I. McCulloch, *Acc. Chem. Res.* **2015**, *48*, 2803.
[12] S. Luhr, J. Holz, A. Borner, *ChemCatChem* **2011**, *3*, 1708.
[13] R. Noyori, *Angew. Chem. Int. Ed.* **2013**, *52*, 77.
[14] E. Iengo, P. Cavigli, D. Milano, P. Tecilla, *Inorg. Chim. Acta* **2014**, *417*, 59.
[15] R. Chakrabarty, P. S. Mukherjee, P. J. Stang, *Chem. Rev.* **2011**, *111*, 6810.
[16] a) F. De Riccardis, I. Izzo, D. Montesarchio, P. Tecilla, *Acc. Chem. Res.* **2013**, *46*, 2781; b) D. Milano, B. Benedetti, M. Boccalon, A. Brugnara, E. Iengo, P. Tecilla, *Chem. Commun.* **2014**, *50*, 9157; c) M. Tosolini, J. Avó, A. J. Parola, G. Balducci, P. Tecilla, *Eur. J. Inorg. Chem.* **2020**, 3859; d) A. Vidal, M. Tosolini, G. Balducci, P. Tecilla, *Eur. J. Org. Chem.* **2022**, e202201121.
[17] S. N. Berry, V. Soto-Cerrato, E. N. W. Howe, H. J. Clarke, I. Mistry, A. Tavassoli, Y.-T. Chang, R. Pérez-Tomás, P. A. Gale, *Chem. Sci.* **2016**, *7*, 5069.
[18] B. A. Chalmers, P. S. Nejman, A. V. Llewellyn, A. M. Felaar, B. L. Griffiths, E. I. Portman, E.-J. L. Gordon, K. J. H. Fan, J. D. Woollins, M. Bühl, O. L. Malkina, D. B. Cordes, A. M. Z. Slawin, P. Kilian, *Inorg. Chem.* **2018**, *57*, 3387.
[19] K. Tajima, N. Fukui, H. Shinokubo, *Org. Lett.* **2019**, *21*, 9516.
[20] K. Matsubayashi, Y. Kubo, *J. Org. Chem.* **2008**, *73*, 4915.
[21] a) H. Yasuda, N. Maki, J.-C. Choi, M. Abla, T. Sakakura, *J. Organomet. Chem.* **2006**, *691*, 1307; b) D. Duvinage, P. Puylaert, E. K. Wieduwilt, L. A. Malaspina, A. J. Edwards, E. Lork, S. Mebs, E. Hupf, S. Grabowsky, J. Beckmann, *Inorg. Chem.* **2022**, *61*, 8406.
[22] J. Olmsted, *J. Phys. Chem.* **1979**, *83*, 2581.
[23] K. Shoyama, D. Schmidt, M. Mahl, F. Würthner, *Org. Lett.* **2017**, *19*, 5328.
[24] T. Norio, K. Toshiyasu, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3020.
[25] J. Beckmann, T. G. Do, S. Grabowsky, E. Hupf, E. Lork, S. Mebs, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2233.

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