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Efficient metallation in diphenylether – A convenient route to luminescent platinum(II) complexes

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ABSTRACT

The synthesis of luminescent platinum(II) complexes is described. The rapid platination of porphyrins and cyclometallating coumarins was performed in diphenylether using platinum(II) bis(benzonitrile)dichloride and platinum(II) bis(dimethyl sulfoxide)dichloride. Compared to conventional methods, the reaction times are lowered dramatically and yields are significantly improved. For the first time, a NIR-emitting platinum(II) complex with tetraphenyltetrabenzoporphyrin was obtained using a direct route starting from phthalimide and phenylacetic acid.

1. Introduction

Platinum complexes attract much attention of researchers due to their broad applicability in various fields of science and technology. Room temperature luminescence of some platinum(II) complexes is of particular interest. The luminescent complexes are applied increasingly often in OLEDs [1,2], as singlet-oxygen photosensitizers [3–5], labels [6,7], and as indicators for optical sensing of oxygen where complexes with porphyrins proved to be particularly advantageous [8–12]. The platinum(II) porphyrins are also used as transducers in optical bisosensors [13,14]. However, platinum(II) complexes are often difficult to prepare in good yields and metallation is carried out over a long time. For example, cyclometallated platinum(II) complexes are usually prepared by heating potassium tetrachloroplatinate and the appropriate ligand in 2-ethoxyethanol or acetic acid for several days [15–17]. Platination of porphyrins often requires even harsher conditions such as up to 24 h reflux in benzonitrile in a degassed atmosphere [18–21]. Moreover, direct synthesis of some platinum(II) complexes (such as platinum(II) benzoporphyrins) was considered impossible due to steric reasons [22]; thus, rather sophisticated synthetic routs were established [23–25]. It should be noted that red-light excitable platinum(II) benzoporphyrins were shown to be extremely valuable as indicators for optical oxygen sensing [26], dopants in NIR OLEDs [24,27], and luminescent absorbers for organic solar concentrators [28]. These applications require large quantities of the complexes to be produced in an easy manner. However, despite the fact that the platinum(II) benzoporphyrins were reported almost 3 decades ago [29], these promising dyes have been mostly ignored due to synthetic reasons. It was demonstrated that microwave heating can significantly simplify preparation of platinum(II) cyclometallated complexes [30] but it was much less beneficial in case of porphyrins [31]. Here we report a much simpler, rapid and efficient synthesis of platinum(II) complexes with porphyrins and cyclometallated ligands. In addition, a platinum(II) benzoporphyrin complex was obtained for the first time in a single metallation step.

2. Experimental

Phenylacetic acid, phthalimide, zinc acetate, coumarin 6, tetraphenylporphyrin (TPP) triethylamine (TEA), acetylacetone (acac), diphenylether (DPE), aluminium oxide (activated, neutral Brockmann I) and benzonitrile were purchased from Aldrich (www.sigmaaldrich.com). Platinum(II) chloride was from ABCR (www.abcr.de). All other solvents were from Roth (www.carl-roth.de). The silica-gel 60 (0.063–0.200 mm) and TLC SiO_2 plates were from Merck (www.merck.de). Zinc phenylacetate was obtained as

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a white precipitate in an exchange reaction between zinc acetate and phenylacetic acid.

2.1. Synthesis of ZnTPTBP

Phthalimide (4.414 g, 30 mmol), phenylacetic acid (5.45 g, 40 mmol) and zinc phenylacetate (2.52 g, 7.5 mmol) were ground in a mortar and loaded into a 25 mL round-bottom flask. The mixture was melted and stirred for 1 h at 360 °C until the colour turned dark green. The melt was cooled, dissolved in acetone and precipitated with water. The product was dissolved in toluene and purified on Al_2O_3 column. The column was eluted with toluene:hexane (2:1) and then with toluene to remove the yellow and the red fractions, respectively. Finally, CH_2Cl_2 containing 1.5% tetrahydrofuran was used to elute the desired product. The purity of the product was controlled by means of UV–Vis spectroscopy (λ_{max} 467, 611 and 655 nm in dimethylformamide). The last fractions contaminated with zinc *meso*-triphenyltetrabenzoporphyrin and zinc *meso*-diphenyltetrabenzoporphyrin (both absorbing at shorter wavelengths than ZnTPTBP) were discarded. Yield: 1.51 g (23%) of crude product (dark-green crystals).

MS (MALDI): m/z $[M]^+$ calc. 876.2231, found 876.2266. Other peaks: m/z 966.27 (ZnTPTBP–C_7H_7) and 1056.32 (ZnTPTBP–$(C_7H_7)_2$).

UV–Vis ($CHCl_3$): 455, 605 and 652 nm.

2.2. Synthesis of H_2TPTBP

1 g of ZnTPTBP was dissolved in 20 mL of THF and 3 mL of methanesulfonic acid was added. The solution was stirred for 5 min. The product was precipitated with water, washed thoroughly and dried. Yield: 770 mg (83%) of dark-green powder.

MS (MALDI): m/z $[M]^+$ calc. 814.3096, found 814.3061. Other peaks: m/z 904.3566 (H_2TPTBP–C_7H_7) and 994.4035 (H_2TPTBP–$(C_7H_7)_2$).

UV–Vis ($CHCl_3$): 466, 592, 639 and 696 nm.

2.3. Synthesis of PtTPTBP

$PtCl_2$ (130 mg, 0.488 mmol) was dissolved in 1 mL of benzonitrile [ed. Note: incompatible with strong bases, strong acids, strong oxidizing agents, strong reducing agents; air-sensitive; combustible by warming]. The hot solution was added into a 25 mL flask containing 200 mg (0.245 mmol) of H_2TPTBP in 12 g of DPE. The solution was stirred at 190 °C for 50 min. The progress of the reaction was monitored by UV–Vis spectroscopy. The heating was continued until the absorption of the ligand disappeared completely. The solution was cooled, diluted with 20 mL of hexane and brought on a column packed with Al_2O_3 in hexane. The column was washed with hexane, hexane:toluene (50:50) to remove DPE and benzonitrile. The complex was eluted with CH_2Cl_2 and the solvent was removed under reduced pressure. Yield: 185 mg (75%) of dark-green crystals. MS (MALDI): m/z $[M]^+$ calc. 1006.2567, found 1006.2586. Other peaks: m/z 1096.3036 (PtTPTBP–C_7H_7) and 1186.3506 (PtTPTBP–$(C_7H_7)_2$).

Analysis: found C 75.10, H 3.90, N 5.18. Calc. for PtTPTBP: C 71.49, H 3.60, N 5.56; calc. for PtTPTBP–C_7H_7: C 73.28, H 3.85, N 5.10; calc. for PtTPTBP–$(C_7H_7)_2$: C 74.80, H 4.07, N 4.71. UV–Vis ($CHCl_3$): 431, 465, 615 nm.

2.4. Synthesis of PtTPP

The synthesis was performed analogously to the previous procedure. 200 mg (0.325 mmol) of H_2TPP in 9 g of DPE and 174 mg (0.654 mmol) of $PtCl_2$ in 1 mL DPE were used. The product was purified on an Al_2O_3 column subsequently eluted with hexane, hexane:toluene (50:50), toluene, and finally with toluene:CH_2Cl_2 (60:40). An orange fraction was collected to give dark-red crystals after removal of the solvent. Yield: 200 mg (78%).

MS (MALDI): m/z $[M]^+$ calc. 806.1941, found 806.1951.

^{1}H NMR (300 MHz, $CDCl_3$), ppm: 8.26 (d, 8H), 7.91 (t, 4H), 7.85 (t, 8H), 7.21 (m, 8H), 7.08 (m, 8H).

Analysis: found C 65.87, H 3.40, N 6.76; calc. C 65.42, H 3.49, N 6.94.

UV–Vis ($CHCl_3$): 402, 510, 539 nm.

2.5. Synthesis of Pt(C_6)(acac)

$PtCl_2$ (182 mg, 0.684 mmol) was dissolved in 1 mL of benzonitrile by warming at 160 °C for several min. The hot solution was added into a 10 mL flask containing 150 mg (0.428 mmol) of coumarin C_6 dissolved in 6 g of DPE. The solution was stirred at 190 °C for 10 min. The solution was cooled and diluted with 7 mL of acetone. Then, 400 μL of acac and 500 μL of TEA were added and the solution was stirred for 30 min. Finally, 25 mL of hexane were added and the obtained sediment was isolated by centrifugation. It was dissolved in CH_2Cl_2 and chromatographed on silica-gel with mixture of CH_2Cl_2:tetrahydrofuran (7:3). The product was recrystallized from CH_2Cl_2 to give dark orange crystals. Yield: 180 mg (65%).

MS (MALDI): m/z $[MH]^+$ calc. 642.1083, found 642.1126.

^{1}H NMR (300 MHz, $CDCl_3$), ppm: 8.75 (t, 8H), 8.16 (d, 4H), 8.13 (d, 4H), 7.76–7.71 (m, 12H).

Analysis: found C 46.62, H 3.91, N 4.07; calc. C 46.65, H 3.76, N 4.35. UV–Vis ($CHCl_3$): 468, 495 nm.

2.6. Measurements

Absorption spectra were measured at a Cary 50 UV–Vis spectrophotometer (www.lzs-concept.com). Luminescence decay times in case of PtTPTBP were measured with a two-phase lock-in amplifier (SR830, Stanford Research Inc., www.thinksrs.com) equipped with a photomultiplier tube (H5701-02, Hamamatsu, www.sales.hamamatsu.com). The spots on a TLC plate were excited with the light of a 435-nm LED (www.roithner-laser.com) filtered through a BG 12 filter from Schott (www.schott.com). An RG 9 filter was used for the emission. A bifurcated fiber bundle was used to guide the excitation light to the spots and the emission light back to the photomultiplier. The modulation frequency was 5 kHz.

3. Results and discussion

Platinum(II) benzoporphyrins hold much promise for many vital applications. The currently used synthetic procedure [23,24] relies on preparation of cyclohexenoporphyrins, their platination and subsequent aromatization (Fig. 1a). Cyclohexenoporphyrins are synthesized using the Lindsey method from 4,5,6,7-tetrahydroisoindole, a step cannot be upscaled easily since the macrocycle formation occurs only in very dilute solutions. Moreover, rather expensive ethyl isocyanoacetate and 1-nitro-1-cyclohexene are required for preparation of 4,5,6,7-tetrahydroisoindole. On the other hand, a template method [32,33] enables the preparation of zinc *meso*-tetraphenyltetrabenzoporphyrin (ZnTPTBP) in a single step from extremely cheap phthalimide and phenylacetic acid (Fig. 1b). It is known that the use of zinc acetate as a template results in a complex mixture of products including zinc mono-, di- and tri(*meso*-phenyl)tetrabenzoporphyrins apart from ZnTPTBP [34]. This can be tackled by using zinc benzoate as a template [32]. We found zinc phenylacetate to be an excellent template as well; the condensation proceeded smoothly and resulted in only minor

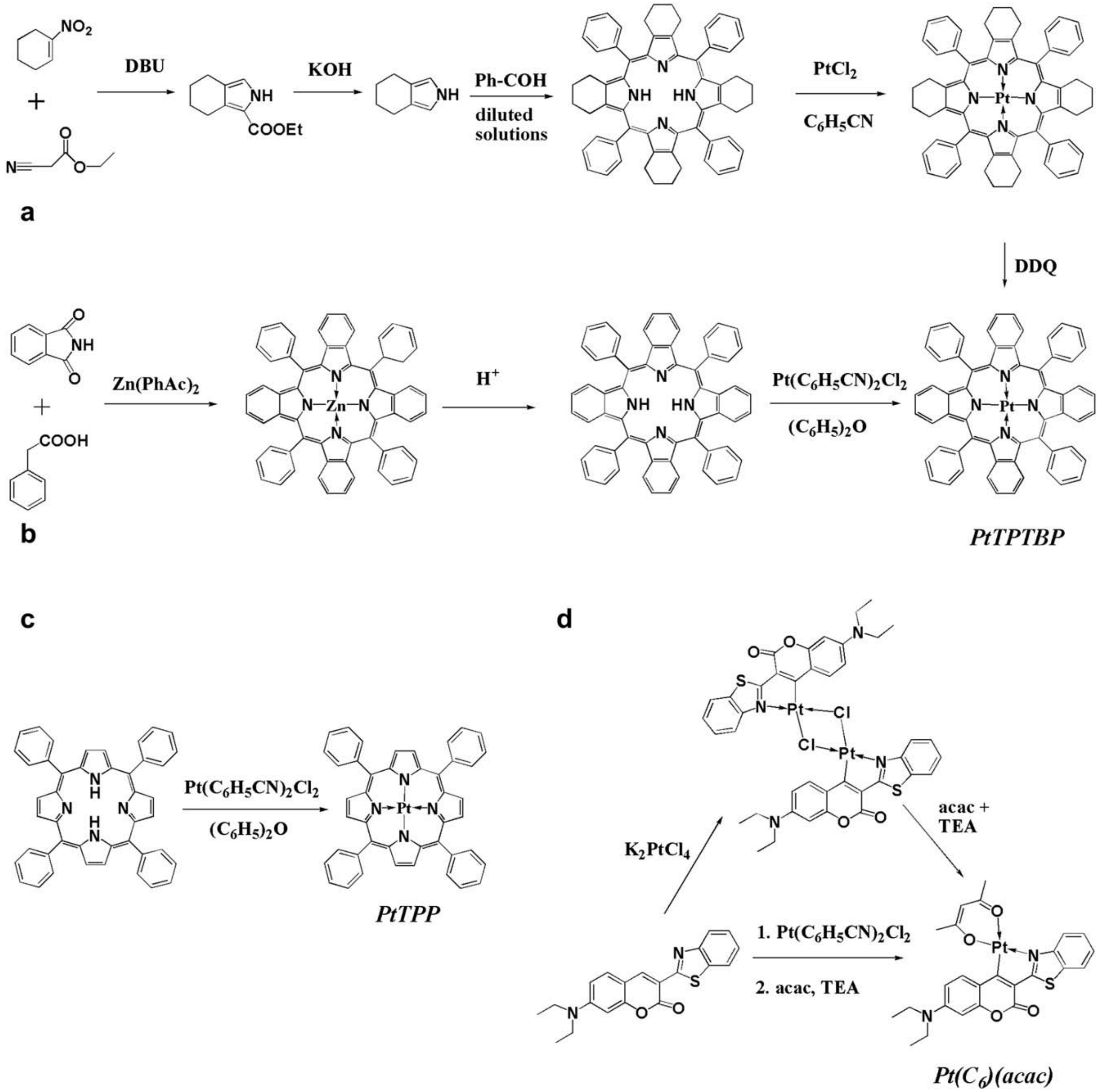

Fig. 1. Synthesis of platinum (II) *meso*-tetraphenyltetrabenzoporphyrin PtTPTBP (a and b), platinum (II) *meso*-tetraphenylporphyrin PtTPP (c) and platinum(II) acetylacetonato-(3-(benzothiazol-2-yl)-7-(diethylamino)-coumarin) Pt(C_6)(acac) (d).

contamination with di- and tri(*meso*-phenyl)tetrabenzoporphyrins which are separated from ZnTPTBP by column chromatography.

Our attempts to platinate the free-base H_2TPTBP (obtained by demetallation of the respective zinc complex) in a conventional manner (prolong boiling with platinum(II) chloride in benzonitrile) were not successful and only trace amounts of PtTPTBP could be obtained. This observation is in good agreement with literature data [22]. It is well known that $PtCl_2$ dissolves in hot benzonitrile to form a square planar complex $Pt(C_6H_5CN)_2Cl_2$. We perceived that a huge excess of coordinating benzonitrile cannot favour the metallation process. However, if benzonitrile is substituted by non-coordinating diphenylether (DPE), the platination requires only tens of minutes at 190 °C (Fig. 2). Notably, most ligand is converted into the complex within first 10 min. Evidently, quantitative conversion is achieved without decomposition of the ligand and/or the complex since several isosbestic points are clearly visible at Fig. 2. Moreover, no inert atmosphere is required and the synthesis is performed under ambient air. DPE was found to be an extremely good solvent for both the ligand and $Pt(C_6H_5CN)_2Cl_2$. Because of its high boiling point DPE cannot be removed under vacuum. However, it can be easily removed directly during purification on an Al_2O_3 column by eluting with hexane and toluene. Alternatively, precipitation of the product with hexane also is possible. The product is isolated in a good yield (75%). It is important that the synthesis can be easily upscaled to obtain the desired product in gram quantities. In a good agreement with the results of Ichimura et al. [32] we also found the benzyl adducts (m/z 966 and 1057) that contaminate ZnTPTBP (m/z 876) (Fig. 3). These adducts are present in the free-base porphyrin H_2TPTBP (m/z 904 and 994) and the respective platinum(II) complex (m/z 1006 for the complex and 1096 and 1186

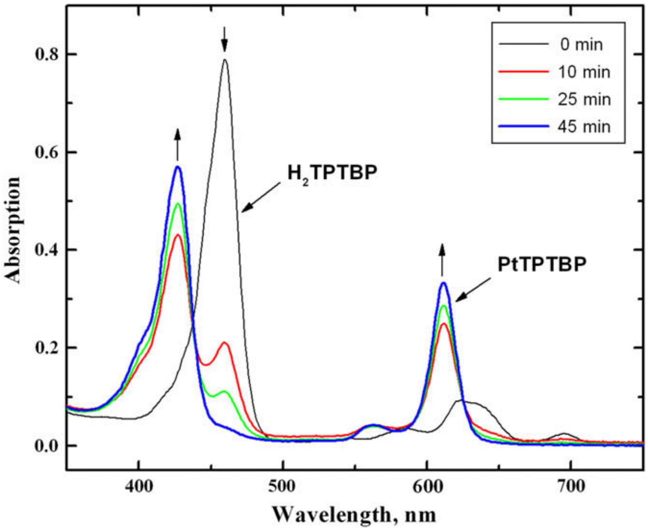

Fig. 2. Progress of the metallation reaction (platination of tetraphenyltetrabenzoporphyrin) monitored by UV–Vis spectroscopy.

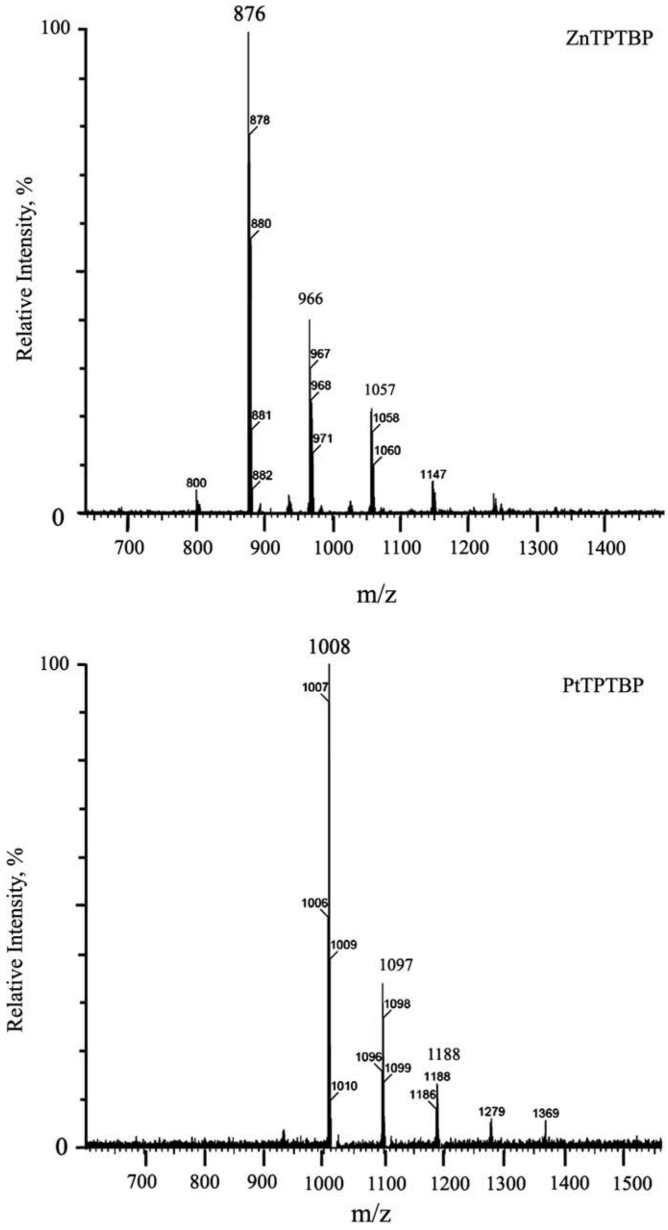

Fig. 3. MALDI-TOF mass spectra of the benzoporphyrin complexes.

for the adducts). The presence of the benzyl adducts also is confirmed by ^{1}H NMR spectroscopy. An additional signal at 3.86 ppm ($CDCl_3$) originating from CH_2 group is observed in the spectrum (~1H per porphyrin molecule).

It is important that photophysical properties of these adducts are identical to the properties of pure PtTPTBP. In fact, the parent compound and the adducts possess the same absorption spectra (as is also the case for ZnTPTBP) [32]. The luminescence decay times (determined for PtTPTBP and for the adducts separated on TLC SiO_2 plates) were found to be identical within the experimental error ($\tau_0 = 58$ μs). If the presence of adducts is highly undesired for some reasons, it is likely to be possible to obtain pure ZnTPTBP (and consequently PtTPTBP) from isoindoline-1,3-diimine [35] since the condensation is performed under much milder conditions.

It was found that the metallation in DPE is also suitable for preparation of platinum(II) complexes with other porphyrins. For example, *meso*-tetraphenylporphyrin (Fig. 1c) can be platinated in less than 1 h to give 78% of complex after purification. Compared to the classical method [22], the reaction times are shortened dramatically while the yields are significantly improved (Table 1).

Cyclometallated platinum(II) complexes are also of great practical interest; thus suitability of the new method for their preparation was investigated (Fig. 1d). A sterically ambitious coumarin 6 was chosen as a ligand because its platinum(II) complex was shown to exhibit bright long-lived room temperature phosphorescence (Q.Y. = 25%) [15]. Excellent absorption in visible (λ_{max} 496 nm, $\varepsilon = 51{,}000$ $M^{-1}cm^{-1}$) make such coumarin complexes particularly suitable for practical applications (e.g. in optical sensors). We found that reaction times can be reduced to several minutes (vs. tens of hours in the conventional procedure). Additionally, one pot synthesis becomes possible since the desired products form almost immediately after addition of triethylamine (TEA) and acetylacetone (acac). No isolation of the chloro-bridged dimer $(PtC\hat{}N)_2Cl_2$ was needed and the yields were dramatically improved (Table 1). Considering cyclometallated complexes, the platination in DPE is particularly promising in case of the bulky ligands such as coumarins. However, the new method may be not fully adequate with small ligands (e.g. phenylpyridine or benzoquinoline) since complexes of the type $Pt(C\hat{}N)_2$ can also be formed.

We also investigated possible modifications of the above procedure. While the platinum(II) complex with acetylacetone ($Pt(acac)_2$) was found to be unsuitable for metallation, $Pt(DMSO)_2Cl_2$ [36] proved to be as efficient as $Pt(C_6H_5CN)_2Cl_2$.

Interestingly, the metallation procedure was found to be nicely suitable for the preparation of palladium(II) benzoporphyrins as well which can also be isolated in a good yield. Thus, prolonged heating in an imidazole melt or dimethylformamide [37] can be avoided.

Table 1
Comparison of the synthetic procedures used for preparation of platinum(II) complexes.

Complex	Conventional methods				This method	
	Time, h[a]	Yield, %[b]	Conditions	Reference	Time, h[a]	Yield, %[b]
PtTPP	48	7	190 °C, C_6H_5CN	[22]	0.83	78
PtTPTBP	10	5	190 °C, C_6H_5CN	[22]	0.83	75
$Pt(C_6)(acac)$	16	10	80 °C, 2 stages	[15]	0.17	65

[a] Reaction times.
[b] Yield after purification steps.

4. Conclusions

An extremely rapid and efficient synthesis of platinum(II) luminescent complexes is described. Diphenylether is found to be most appropriate for metallation since it is a very good solvent for the reactants, is non-coordinating and also enables higher reaction temperatures to be used. Compared to conventional procedures, the reaction times are reduced dramatically and excellent yields are achieved. In particular, the synthesis of the NIR-emitting PtTPTBP can be achieved on a large scale using low cost reagents which offers the potential of using the dye in OLED's and solar concentrators.

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